ORGANOMETALLICS

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Divalent Platinum Complexes of the Carbanion 2-$C_6F_4AsPh_2$: Monodentate or Bidentate Coordination?

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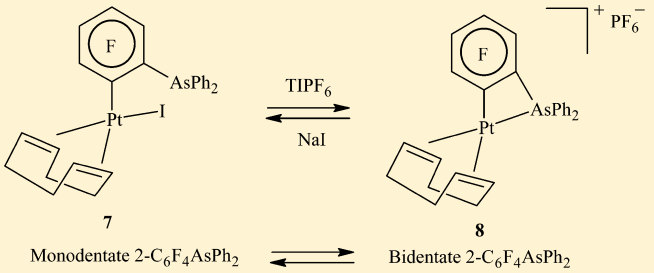
Supporting Information

ABSTRACT: The reaction of [PtI_2(1,5-COD)] with 2-$LiC_6F_4AsPh_2$ affords the planar platinum(II) fluoroaryl complex [PtI(κC-2-$C_6F_4AsPh_2$)(1,5-COD)] (**7**), in which the arsenic atom is not coordinated to the metal atom. Attempts to prepare the bis(chelate) complex [Pt(κ^2As,C-2-$C_6F_4AsPh_2)_2$] analogous to the known phosphorus compound failed. Removal of iodide ion from **7** with $TlPF_6$ gave [Pt(κ^2As,C-2-$C_6F_4AsPh_2$)(1,5-COD)]PF_6 (**8**), in which 2-$C_6F_4AsPh_2$ is now coordinated as a bidentate ligand, giving a four-membered chelate ring. Alternatively, protonolysis (with triflic acid) of the methyl complex [PtMe(κC-2-$C_6F_4AsPh_2$)(1,5-COD)] (**15**), which is obtained from **7** and dimethylzinc, gives the triflate salt **16** of the same chelate cation. The chelate As,C ring in **8** is readily reopened when the complex is treated with pyridine or with halide ions, forming respectively [Pt(py)(κC-2-$C_6F_4AsPh_2$)(1,5-COD)]PF_6 (**9**) and [PtX(κC-2-$C_6F_4AsPh_2$](1,5-COD)] (X = Cl (**10**), Br (**11**), I (**7**)). The appearance of two pairs of olefinic COD resonances in the proton NMR spectra of **7**, **10**, **11**, and **15** may indicate that there is restricted rotation about the Pt−κC-2-$C_6F_4AsPh_2$ bond; the additional signals are not evident in the spectra of **8** or **16**. Complexes **7** and **10** form the 1:1 adducts [PtX(μ-2-$C_6F_4AsPh_2$)(1,5-COD)AuY] (X = Cl, Y = I (**12**); X = Y = I (**13**); X = Y = Cl (**14**)) by attachment of gold(I) halides to their dangling arsenic atoms. In **12** the halides are scrambled between platinum and gold. The X-ray structures of **7**, **8**, **9**, **12**, **15**, and **16** are reported, and possible reasons for the poorer chelating ability of 2-$C_6F_4AsPh_2$ in comparison with that of 2-$C_6H_4PPh_2$ are discussed.



INTRODUCTION

Ortho-metalated complexes containing the bidentate carbanion [2-$C_6H_4PPh_2$]$^-$ are known for most of the transition metals and are usually prepared by C−H bond activation of coordinated PPh_3.[1] Other methods based on transmetalation of 2-$LiC_6H_4PPh_2$ and on oxidative addition of 2-$BrC_6H_4PPh_2$ are also known.[1] The resulting complexes are often mononuclear and contain a four-membered M(κ^2P,C-2-$C_6H_4PPh_2$) chelate ring, although examples are also known where the 2-$C_6H_4PPh_2$ group acts as a bifunctional bridging ligand spanning two metal centers. For example, the reaction of 2-$LiC_6H_4PPh_2$ with [$PtCl_2(SEt_2)_2$] gives the mononuclear bis(chelate) complex *cis*-[Pt(κ^2P,C-2-$C_6H_4PPh_2)_2$] (**1**), which dimerizes in refluxing toluene to give [$Pt_2(\mu$-2-$C_6H_4PPh_2)_2(\kappa^2P,C$-2-$C_6H_4PPh_2)_2$] (**2**), derived by opening of half the available four-membered chelate rings (Scheme 1).

Metal−perfluoroaryl complexes are usually much more stable than their aryl counterparts and show distinctly different chemistry.[2] Although the fluorine-substituted bis(chelate) complex [Pt(κ^2P,C-2-$C_6F_4PPh_2)_2$][3] is prepared similarly to its protio analogue, *cis*-[Pt(κ^2P,C-2-$C_6H_4PPh_2)_2$], the former is isolated as a cis/trans mixture that is converted into the more stable trans isomer on heating and shows no tendency to dimerize. The increased stability conferred by fluorine substitution in the aromatic ring is also evident from the fact that analogous nickel and palladium bis(chelate) complexes *trans*-[M(κ^2P,C-2-$C_6F_4PPh_2)_2$] (M = Ni, Pd) can be prepared,[3] whereas the protio analogues are unknown.

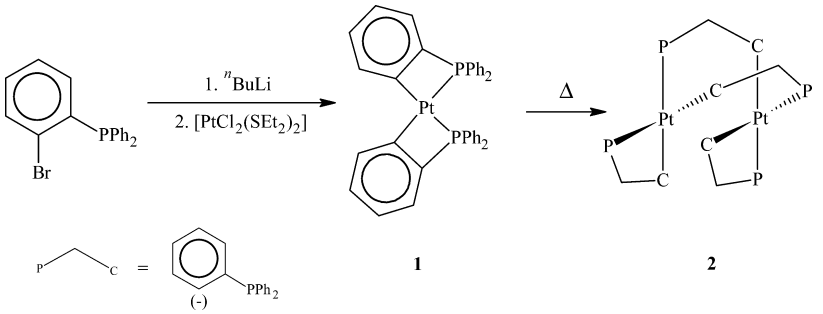
In contrast to the extensive range of ortho-metalated tertiary phosphine species, relatively few examples of ortho-metalated tertiary arsine species have been reported. Early work showed that heating a solution of the iridium(I) complex [IrCl-($AsPh_3)_3$] gave the cyclometalated iridium(III) complex [IrHCl(κ^2As,C-2-$C_6H_4AsPh_2$)($AsPh_3)_2$].[4] More recently, treatment of [AuBr($AsPh_3$)][5] or [$PtCl_2(SEt_2)_2$][6] with LiC_6H_3-5-Me-2-$AsPh_2$ has been reported to give the dinuclear gold(I) complex **3** and a mixture of the dinuclear platinum(II) complexes **4** and **5**, respectively, as shown in Scheme 2.

Compound **4** is analogous to the phosphine compound **2**, whereas the lantern compound **5** has no known phosphine analogue. The two isomeric diplatinum(II) complexes undergo oxidative addition of halogens to give metal−metal-bonded dihalodiplatinum(III) species (Scheme 3), and the photo-

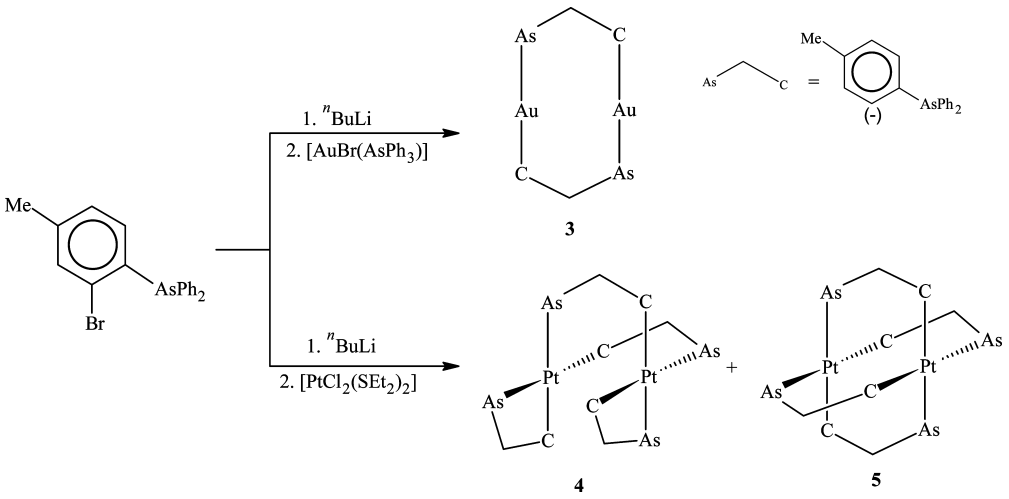
Received: September 30, 2013
Published: December 5, 2013

   dx.doi.org/10.1021/om400961z | *Organometallics* 2013, 32, 7451−7459

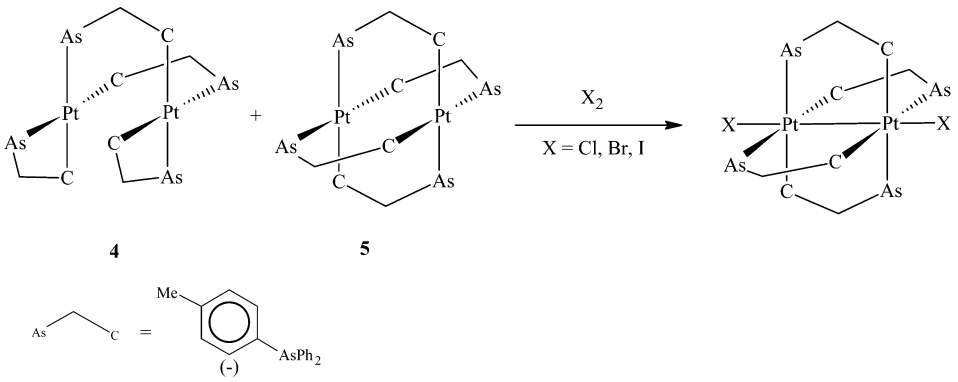
Scheme 1



Scheme 2



Scheme 3



physical properties of the complexes in both oxidation states have been investigated. At room temperature and at 77 K, the parent 5d^8−5d^8 diplatinum(II) dimer **5** exhibits intense green phosphorescence in the range 501−532 nm, whereas the 5d^7−5d^7 dihalodiplatinum(III) complexes are emissive in the near-infrared region.[7]

In view of the different coordination behaviors of [C$_6$H$_3$-5-Me-2-AsPh$_2$]$^-$ and [2-C$_6$H$_4$PPh$_2$]$^-$ toward platinum(II), we were interested in exploring the chemistry and reactivity of platinum(II) complexes containing the carbanion [2-C$_6$F$_4$AsPh$_2$]$^-$ for comparison with those of [2-C$_6$F$_4$PPh$_2$]$^-$. The results are presented herein.

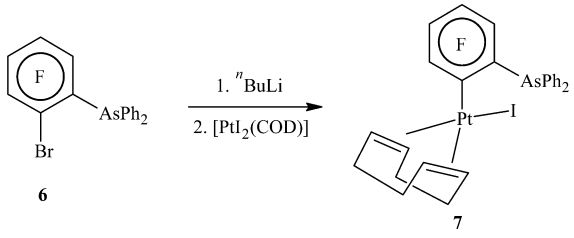
RESULTS

The required ligand precursor, (2-bromotetrafluorophenyl)-diphenylarsine (**6**), was prepared similarly to its phosphine analogue by low-temperature monolithiation of 1,2-dibromotetrafluorobenzene and subsequent treatment with chlorodiphenylarsine.[8] The ESI-mass spectrum of **6** showed a parent ion peak, and the ^{1}H NMR spectrum contained the expected aromatic multiplets. The ^{19}F NMR spectrum consisted of four peaks, each a well-resolved doublet of doublets of doublets arising from F−F coupling, at δ −119.6, −126.2, −151.0, and −153.9. The least shielded resonance at δ −119.6 is assigned to the fluorine atom ortho to the bromine atom. The chemical shifts are similar to those observed for 2-BrC$_6$F$_4$PPh$_2$ but the F−F couplings in the latter are less well resolved owing to superimposed P−F coupling.[9]

dx.doi.org/10.1021/om400961z | *Organometallics* 2013, 32, 7451−7459

As shown in Scheme 4, treatment of 2-Li$C_6F_4AsPh_2$ in ether with [PtI_2(1,5-COD)] in a 1:1 molar ratio at low temperature

Scheme 4



6 **7**

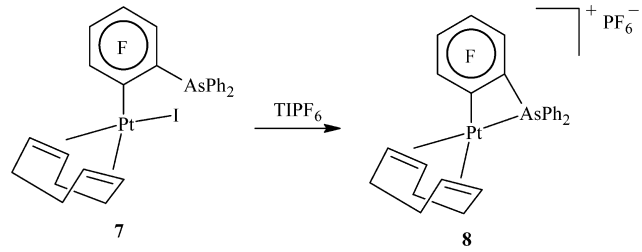
gave [PtI(κC-2-$C_6F_4AsPh_2$)(1,5-COD)] (**7**), which could be isolated as a white powder in ca. 80% yield. Attempts to make the bis(chelate) compound analogous to **1** by use of a 2:1 molar ratio of reactants gave the same product; there was no evidence for the formation of compounds analogous to **1** and **2** (Scheme 1) or **4** and **5** (Scheme 2).

The ESI-mass spectrum of compound **7** showed a peak at m/z 829.9 corresponding to the $[M + Na]^+$ ion. The ^{19}F NMR spectrum showed the expected four multiplets, each flanked by ^{195}Pt satellites (see the Experimental Section). The ^1H NMR spectrum contained four multiplets, accompanied by ^{195}Pt satellites, at δ 4.34 ($^2J_{PtH}$ = 64.3 Hz), 5.08 ($^2J_{PtH}$ = 71.8 Hz), 5.89 ($^2J_{PtH}$ = 43.6 Hz), and 6.09 ($^2J_{PtH}$ = 42.7 Hz), which can be assigned to the olefinic protons of coordinated 1,5-COD, together with four multiplets in the range δ 1.8−2.8 due to the methylene protons of COD. The ^{195}Pt coupling constants of ca. 40 Hz to the less shielded pair of olefinic protons are similar to those trans to the σ-bonded organo group R in compounds of the type [PtRX(1,5-COD)] (R = Me, Ph, C_6F_5; X = halide), while the ^{195}Pt coupling constants of ca. 70 Hz to the more shielded pair are typical of those trans to the halide X.[10] Thus, the perfluoro group and iodide must be coordinated to platinum and, if we assume that the metal atom adopts its usual planar coordination, the arsenic atom must be uncoordinated. These features have been confirmed by the X-ray structure determination of **7** discussed below. The observed inequivalence of all the olefinic protons of COD presumably arises from restricted rotation about the Pt−C(aryl) bond. There are numerous examples of restricted rotation about the metal−carbon bonds in Pt−C_6F_5 complexes,[11−20] and there is evidence for slowed rotation about M−P and M−C bonds in complexes of $(C_6F_5)_3P$.[21−23]

Attempted reactions of 2-Li$C_6F_4AsPh_2$ with other precursors such as [$PtCl_2(SEt_2)_2$], [$PtCl_2$(1,5-COD)], and [$PtCl_2$(NBD)] gave complex mixtures, as shown by ^{19}F NMR spectroscopy, and no tractable products could be isolated.

To achieve coordination of the free arsenic atom to the metal, **7** was treated with $TlPF_6$ to give the salt [Pt(κ^2*As*,*C*-$C_6F_4AsPh_2$)(1,5-COD)]PF_6 (**8**) (Scheme 5), in which the presence of a four-membered As,C chelate ring was confirmed by X-ray crystallography (see below). In addition to aromatic and methylene resonances, the ^1H NMR spectrum of **8** contained a pair of olefinic COD resonances with ^{195}Pt satellites at δ 6.04 ($^2J_{PtH}$ = 43.2 Hz) and 6.58 ($^2J_{PtH}$ = 64.7 Hz). The Pt−H coupling constant for the signal at δ 6.04 suggests that this resonance should be assigned to the olefinic protons trans to the σ-bonded carbon atom of 2-$C_6F_4AsPh_2$; hence, the resonance at δ 6.58 must be due to the olefinic protons trans to $AsPh_2$. Given the inverse correlation of these coupling

Scheme 5



7 **8**

constants with the trans influence of the ligand atom in the trans site, and the fact that As donors are above iodide in the trans-influence series,[24] the observed value of 64.7 Hz seems surprisingly high.

Heating toluene solutions of **8** led to extensive decomposition; there was no evidence for the formation of dinuclear complexes containing bridging $C_6F_4AsPh_2$, in contrast to the behavior of complex **1** containing 2-$C_6H_4PPh_2$ (Scheme 1) or complex **4** containing 5-Me-2-$C_6H_3AsPh_2$ (Scheme 2). The As,C chelate ring in **8** was opened on addition of 1 equiv of pyridine to give [Pt(py)(κC-$C_6F_4AsPh_2$)(1,5-COD)]PF_6 (**9**) (Scheme 6). Under similar conditions, MeCN did not react with **8**. The ^1H NMR spectrum of **9** contained a pair of resonances with ^{195}Pt satellites at δ 5.28 ($^2J_{PtH}$ = 64.1 Hz) and 5.71 ($^2J_{PtH}$ = 38.6 Hz), assigned to the olefinic COD protons trans to pyridine and C(aryl), respectively, in addition to three different pyridine proton signals in the expected region.

The chelate ring in **8** was also opened by the addition of halide ions. Thus, the reaction of **8** with NaI regenerated **7**, and the chloro (**10**) and bromo (**11**) analogues were prepared by use of LiCl and LiBr, respectively (Scheme 6). The chemical shifts and Pt−H coupling constants of the olefinic COD protons in **7**, **10**, and **11** are similar, the Pt−H coupling constants being in the ranges of 39−44 and 64−73 Hz for the protons trans to C(aryl) and halide, respectively.

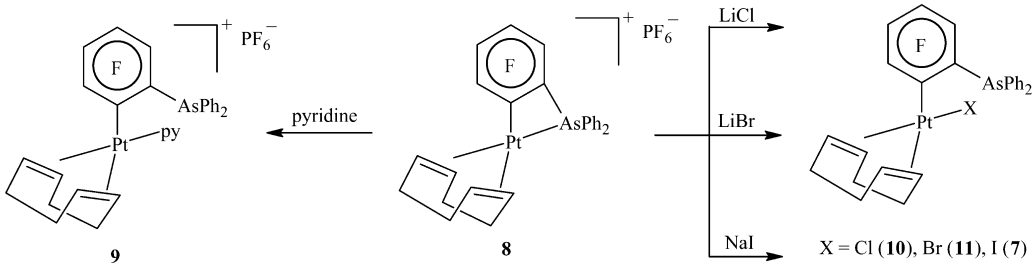
The ^{19}F NMR spectra of **7**, **10**, and **11** differ in the chemical shift of the ortho fluorine atom, which decreases over a range of 2.5 ppm in the order Cl < Br < I.

The free arsenic atom in compound **7** can coordinate to gold(I) to give heterobimetallic species. The solid isolated from the reaction of **7** with [AuCl(tht)] analyzed satisfactorily as a 1:1 adduct (**12**; Scheme 7), but its ^{19}F NMR spectrum showed four sets of four multiplets due to $C_6F_4AsPh_2$ groups, indicative of a mixture, and the ESI-mass spectrum showed $[M + Na]^+$ peaks corresponding to the sodium adducts of [PtX(μ-2-$C_6F_4AsPh_2$)(1,5-COD)AuY] (X = Y = I (**13**), Cl (**14**); X, Y = Cl, I, X ≠ Y (**12**)) arising from halide scrambling. Attempts to separate the mixture by fractional crystallization were unsuccessful, but structure determination of a selected X-ray-quality crystal confirmed the presence of **12**, in which the halide positions are occupied by both chloride and iodide ($\sim^2/_3$ I at gold and $^2/_3$ Cl at platinum). The diiodo complex **13** was prepared by treatment of the mixture with an excess of NaI; its ^{19}F NMR spectrum matched that of one of the components of the mixture. Treatment of [PtCl(κC-2-$C_6F_4AsPh_2$)(1,5-COD)] (**10**) with [AuCl(tht)] gave the corresponding 1:1 dichloro complex, whose ^{19}F NMR spectrum agreed with that of a second component of the original mixture.

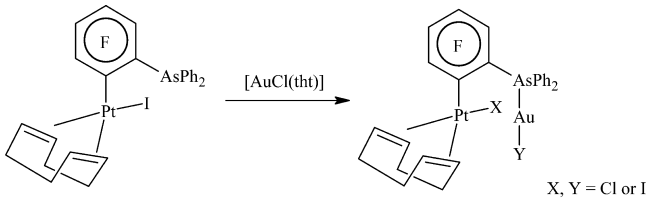
Reaction of complex **7** with dimethylzinc gave the methyl compound [PtMe(κC-2-$C_6F_4AsPh_2$)(1,5-COD)] (**15**; Scheme 8), which was isolated as a white solid in almost quantitative yield. The ^1H NMR spectrum of **15** shows a singlet with

dx.doi.org/10.1021/om400961z | Organometallics 2013, 32, 7451−7459

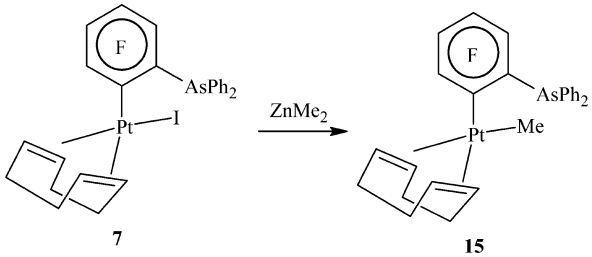
Scheme 6



Scheme 7



Scheme 8



satellites due to Pt–Me at δ 0.78 ($^2J_{PtH}$ = 78.7 Hz), together with multiplet aliphatic COD peaks at δ 2.10–2.76. As with the halo complexes **7**, **10** and **11**, all of the olefinic COD protons are inequivalent and give rise to resonances at δ 4.57 ($^2J_{PtH}$ = 54.1 Hz), 5.06 (with unresolved platinum satellites), and 5.24 ($^2J_{PtH}$ = 43.7 Hz) in a 1:2:1 intensity ratio. The Pt–methyl bond in **15** was selectively cleaved by addition of a stoichiometric amount of triflic acid, generating the cationic complex [Pt(κ^2*As*,*C*-2-$C_6F_4AsPh_2$)(1,5-COD)]OTf (**16**), the ^{1}H and ^{19}F NMR parameters of which are similar to those of the PF_6 salt **8**. As in the case of **8**, attempts to form dimeric species by heating toluene solutions of **16** resulted in decomposition; there was no evidence for ring opening or for the formation of compounds containing bridging 2-$C_6F_4AsPh_2$.

X-ray Crystal Structures. The molecular structures of compounds **7**–**9**, **12**, **15**, and **16** have been confirmed by X-ray crystallography and are shown in Figures 1–5 (except for complex **16**); selected bond distances and angles are summarized in the caption to the relevant figure or in Tables 1–3. For compound **7** we found two modifications (orthorhombic, *Pna*2$_1$, and monoclinic, *P*2$_1$, with one and two independent molecules in the asymmetric unit, respectively). Only the structure of the orthorhombic modification will be discussed in the following as a representative example; the metrical parameters for the monoclinic modification are very similar. In **7** (shown in Figure 1), the platinum atom is coordinated in an approximately square planar array by iodide, COD, and the aromatic carbon atom of 2-$C_6F_4AsPh_2$, while the arsenic atom is not coordinated (d(Pt···As) = 3.264 Å).

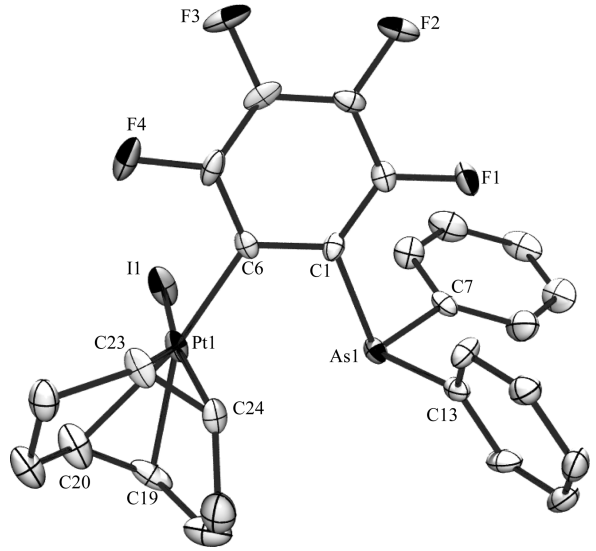


Figure 1. Molecular structure of compound **7**. Ellipsoids are shown at the 50% probability level, and hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) in 7

Pt(1)–I(1)	2.6170(4)	Pt(1)–C(20)	2.309(7)
As(1)–C(1)	1.972(4)	Pt(1)–C(23)	2.147(5)
Pt(1)–C(6)	2.015(4)	Pt(1)–C(24)	2.190(5)
Pt(1)–C(19)	2.249(6)		
Pt(1)–C(6)–C(1)	120.2(3)	C(6)–Pt(1)–C(19)	157.1(2)
C(6)–C(1)–As(1)	115.4(3)	C(6)–Pt(1)–C(20)	167.7(2)
I(1)–Pt(1)–C(24)	167.53(16)	C(6)–Pt(1)–C(23)	92.1(2)
I(1)–Pt(1)–C(23)	155.67(17)	C(6)–Pt(1)–C(24)	92.8(2)
I(1)–Pt(1)–C(19)	94.12(15)	C(23)–Pt(1)–C(24)	36.8(2)
I(1)–Pt(1)–C(20)	95.25(15)	C(20)–Pt(1)–C(19)	34.8(3)

dx.doi.org/10.1021/om400961z | *Organometallics* 2013, 32, 7451–7459

The Pt−I distances in **7** (2.6170(4) Å) and in [PtI_2(1,5-COD)] (2.6094(5) and 2.6130(5) Å) are almost identical.[25] The Pt−C(COD) distances fall into two sets: Pt(1)−C(19) and Pt(1)−C(20) trans to C_6F_4 (2.249(6) Å, 2.309(7) Å) and Pt(1)−C(23) and Pt(1)−C(24) trans to I (2.147(5) Å, 2.190(5) Å), the trend clearly reflecting the higher trans influence of the fluoroaryl ligand relative to that of iodide. The difference within each set arises because the coordinated 1,5-COD adopts its usual twist-boat conformation.

The molecular structure of the cation in **8** is shown in Figure 2. Selected bond distances and angles in **8** and in the corresponding triflate salt **16** are summarized in Table 2.

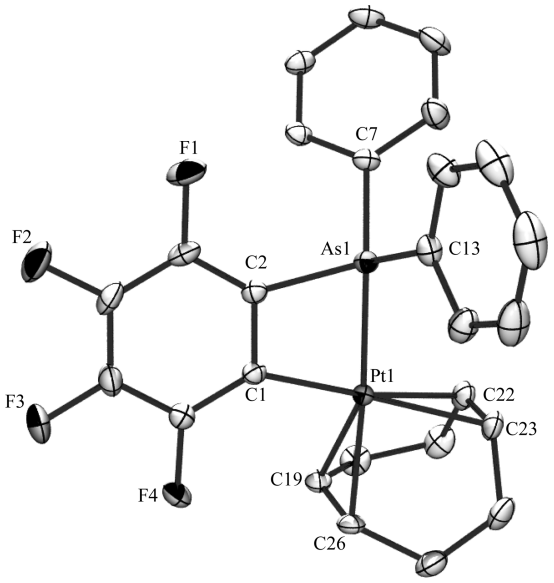


Figure 2. Molecular structure of the cation in **8**. Ellipsoids are shown at the 50% probability level. Hydrogen atoms and the PF_6 counterion have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) in 8 and 16

	8	16
Pt(1)−C(1)	2.033(2)	2.032(4)
Pt(1)−As(1)	2.4308(3)	2.4145(5)
Pt(1)−C(19)	2.220(2)	2.224(4)
Pt(1)−C(22)	2.281(2)	2.258(4)
Pt(1)−C(23)	2.254(2)	2.271(4)
Pt(1)−C(26)	2.231(2)	2.220(4)
As(1)−C(2)	1.910(2)	1.909(4)
C(2)−As(1)−Pt(1)	79.76(7)	79.98(12)
As(1)−Pt(1)−C(1)	70.20(6)	70.29(12)
C(1)−Pt(1)−C(19)	95.61(9)	100.42(16)
C(1)−Pt(1)−C(22)	163.42(9)	160.58(17)
C(1)−Pt(1)−C(23)	160.41(9)	163.43(17)
C(1)−Pt(1)−C(26)	99.63(9)	95.63(17)
As(1)−Pt(1)−C(19)	154.38(6)	163.35(12)
As(1)−Pt(1)−C(22)	106.41(8)	103.52(12)
As(1)−Pt(1)−C(23)	103.87(8)	106.01(13)
As(1)−Pt(1)−C(26)	162.86(7)	154.58(12)

The bond lengths and angles in **8** and **16** are generally comparable, and the angles subtended at platinum by the four-membered rings (70.20(6) and 70.29(12)°, respectively) are similar to those observed in transition-metal complexes containing ortho-metalated PPh_3 and $AsPh_3$.[1] The Pt−C(aryl) bond distances (2.033(2) Å, **8**; 2.032(4) Å. **16**) are slightly longer than that of 2.015(4) Å in **7**. In compounds **8** and **16**, the Pt−C(COD) bond distances trans to carbon (2.2675 (av) and 2.2645 (av) Å, respectively) are longer than those trans to arsenic (2.2255 (av) and 2.2220 (av) Å, respectively).

The molecular structures of the cation of [Pt(py)(κ*C*-2-$C_6F_4AsPh_2$)(1,5-COD)] (**9**) and [PtMe(κ*C*-2-$C_6F_4AsPh_2$)(1,5-COD)] (**15**) are shown in Figures 3 and 4, respectively; selected bond lengths and angles in **9** and **15** are shown in the relevant caption.

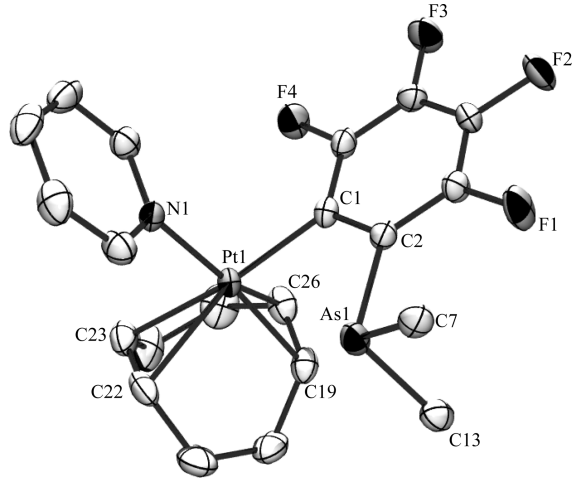


Figure 3. Molecular structure of the cation in **9**. Ellipsoids are shown at the 50% probability level. Hydrogen atoms and the PF_6 counterion have been omitted for clarity. The phenyl rings of the $AsPh_2$ groups only show the ipso carbons. Selected bond lengths (Å) and angles (deg) in **9**: Pt(1)−C(1) 2.033(3), Pt(1)−N(1) 2.078(3), Pt(1)−C(19) 2.186(3), Pt(1)−C(22) 2.263(3), Pt(1)−C(23) 2.306(3), Pt(1)−C(26) 2.175(3), As(1)−C(2) 1.965(3); Pt(1)−C(1)−C(2) 120.9(2), As(1)−C(2)−C(1) 115.7(2), N(1)−Pt(1)−C(1) 91.02(11).

Compounds **9** and **15** are structurally similar to **7**. The Pt−C(aryl) bond lengths in **9** and **15** are similar to but slightly longer than the corresponding bonds in **7**. The Pt−C(COD) bond lengths trans to C(aryl) in **9** (2.2845 (av) Å) are similar to those in **7** (2.2790 (av) Å) but longer than the corresponding bonds in **15** (2.2276 (av) Å). The Pt−C(COD) bond lengths trans to iodide, nitrogen, and C(methyl) in **7** (2.1685 (av) Å), **9** (2.1805 (av) Å), and **15** (2.26045 (av) Å), respectively, reflect the trans influence in the order I < N < C.

The Pt−N(pyridine) bond length (2.078(3) Å) in **9** is smaller than the Pt−N(bpy) bond lengths in [PtPh(bpy)(1,5-COD)]PF_6 (2.238(8) and 2.211(8) Å).[26] The Pt−C(methyl) bond length (2.0655(17) Å) in **15** is similar to that of 2.057(10) Å in [PtMe(C≡CC_6H_4-4-F)(1,5-COD)][27] and shorter than those in [PtMe(OH)(1,5-COD)] (2.126(7) Å), [$PtMe_2$(1,5-COD)] (2.134(6) Å), and [PtMeCl(1,5-COD)] (2.164(8) Å).[28]

The X-ray structural analysis of **12** confirms that the halogen positions are occupied by both chlorine and iodine atoms. The molecular structure of **12** is shown in Figure 5; selected bond distances and angles are given in Table 3. In **12**, the Au···Pt separation (3.19993(17) Å) is consistent with the presence of a weak attractive interaction between the metal centers.[29] The As(1)−C(2) bond distance (1.936(3) Å) in **12** is shorter than

dx.doi.org/10.1021/om400961z | *Organometallics* 2013, 32, 7451−7459

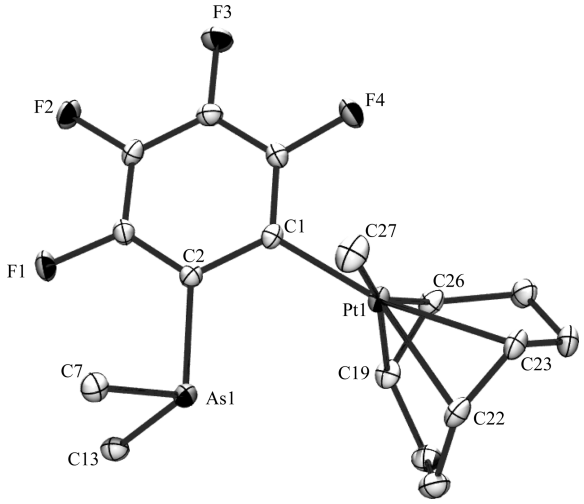


Figure 4. Molecular structure of **15**. Ellipsoids are shown at the 50% probability level, and hydrogen atoms have been omitted for clarity. The phenyl rings of the $AsPh_2$ groups only show the ipso carbons. Selected bond lengths (Å) and angles (deg) in **15**: Pt(1)−C(1) 2.0328(16), Pt(1)−C(27) 2.0655(17), Pt(1)−C(19) 2.2719(17), Pt(1)−C(22) 2.2160(16), Pt(1)−C(23) 2.2392(17), Pt(1)−C(26) 2.2490(16), As(1)−C(2) 1.9691(16); Pt(1)−C(1)−C(2) 121.27(11), As(1)−C(2)−C(1) 115.95(12), C(1)−Pt(1)−C(27) 87.33(7).

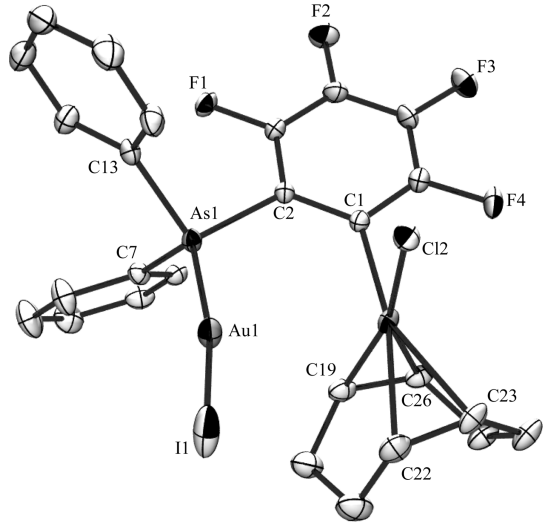


Figure 5. Molecular structure of **12**. Ellipsoids are shown at the 50% probability level. Hydrogen atoms have been omitted for clarity. The halide positions are occupied by both chlorine and iodine atoms. The ratios are 0.67 I, 0.33 Cl at Au(1) and 0.67 Cl, 0.33 I at Pt(1).

the corresponding bond in **7** (1.972(4) Å), as a consequence of coordination of the arsenic atom. The metal−halide bond lengths in **12** will not be discussed, as they are influenced by the Cl vs I occupancy disorder.

DISCUSSION

The only tractable complex containing $[2\text{-}C_6F_4AsPh_2]^-$ that we have been able to isolate is $[PtI(\kappa C\text{-}2\text{-}C_6F_4AsPh_2)(1,5\text{-COD})]$ (**7**), the notable features of which are that 1,5-COD is retained in the coordination sphere and that the arsenic atom is not coordinated. In these respects, $[2\text{-}C_6F_4AsPh_2]^-$ differs from $[C_6H_3\text{-}5\text{-Me-}2\text{-}AsPh_2]^-$ (see Introduction). When the iodide is removed (either by reaction with $TlPF_6$ or by reaction with dimethylzinc and subsequent protonolysis of the Pt−Me bond), the arsenic atom binds to the resulting cationic center to give $[Pt(\kappa^2As,C\text{-}2\text{-}C_6F_4AsPh_2)(1,5\text{-COD})]^+$, isolated as its PF_6 (**8**) or triflate salt (**16**), containing the As,C-four-membered ring. Moreover, the ring is readily reopened, with displacement of the coordinated arsenic atom, by reaction with halide ions to give $[PtX(\kappa C\text{-}2\text{-}C_6F_4AsPh_2)(1,5\text{-COD})]$ (X = Cl (**10**), Br (**11**), I (**7**)) and with pyridine to give the cation of **9**, $[Pt(py)(\kappa C\text{-}2\text{-}C_6F_4AsPh_2)(1,5\text{-COD})]^+$.

The fluorine substituents in $2\text{-}C_6F_4AsPh_2$ probably stabilize the platinum(II)−carbon bond, but they can also be expected to reduce the coordinating ability of the arsenic atom. Thus, although a limited number of complexes of $(C_6F_5)_3P$ with Pd(II), Pt(II), Rh(I), and Ir(I) are known, the ligand itself, unlike triphenylphosphine, displays no basic properties.[30−32]

The available evidence indicates that $(C_6F_5)_3P$ is a large, sterically bulky, poor σ-donor ligand with little or no π-acceptor ability.[33] Since tertiary arsines are weaker bases than corresponding tertiary phosphines, $(C_6F_5)_3As$ is likely to be an even poorer ligand than $(C_6F_5)_3P$ and indeed only two of its complexes, $[AgClO_4.As(C_6F_5)_3]$ and $[Ag\{As(C_6F_5)_3\}_2]ClO_4$, are known.[34] Our results indicate that the chelate four-membered-ring complexes of the carbanion $[2\text{-}C_6F_4AsPh_2]^-$ are more labile than those of $[2\text{-}C_6F_4PPh_2]^-$ and that they are most likely to be observed at a cationic center. Although no evidence was found for a chelate to bridging transformation in the salts **8** and **16**, the isolation of the Pt(II)−Au(I) complexes **12**−**14** demonstrates that $[2\text{-}C_6F_4AsPh_2]^-$ is capable of acting as a bridging ligand. However, this behavior is likely to be limited by both steric constraints and the poor donor ability of the arsenic center.

EXPERIMENTAL SECTION

Syntheses were performed under an atmosphere of dry argon with the use of standard Schlenk techniques, although the solid complexes, once isolated, were air stable. The compounds $[AuCl(tht)]$,[35] $[PtI_2(1,5\text{-COD})]$,[10a] and chlorodiphenylarsine[36] were prepared by the appropriate literature procedure. All other chemicals were commercially available.

Physical Measurements. Melting points were determined on a Gallenkamp melting point apparatus in open glass capillaries. ^1H (300 MHz) and ^{19}F (282 MHz) NMR spectra were recorded on a Bruker Avance 300 spectrometer in $CDCl_3$, unless otherwise stated. Coupling constants (J) are given in Hertz, and chemical shifts (δ) are given in ppm, internally referenced to residual solvent signals (^1H) or internal $CFCl_3$ (^{19}F). Elemental analyses were performed by the Micro-

Table 3. Selected Bond Lengths (Å) and Angles (deg) in 12

Pt(1)−C(1)	2.027(3)	Pt(1)−C(19)	2.162(3)
As(1)−C(2)	1.936(3)	Pt(1)−C(26)	2.172(3)
As(1)−Au(1)	2.3496(3)	Pt(1)−C(22)	2.297(3)
Au(1)−Pt(1)	3.19993(17)	Pt(1)−C(23)	2.251(3)
Au(1)−As(1)−C(2)	116.21(8)	Pt(1)−Au(1)−As(1)	79.753(8)
Cl(1)−Au(1)−Pt(1)	108.7(3)		

dx.doi.org/10.1021/om400961z | *Organometallics* 2013, 32, 7451−7459

analytical Unit of the Research School of Chemistry at the Australian National University (ANU), Canberra, Australia. Mass spectra were recorded on a Bruker Apex 3 FTICR mass spectrometer.

X-ray Crystallography. Crystals suitable for single-crystal X-ray diffraction were obtained by layering a CH_2Cl_2 solution with hexane (**7**–**9** and **16**) or methanol (**12** and **15**).

X-ray diffraction data were collected on a D8 Bruker diffractometer with an APEX2 area detector using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) from a 1 μS microsource. Geometric and intensity data were collected using SMART software.[37] The data were processed using SAINT,[38] and corrections for absorption were applied using SADABS.[39] The structures were solved by direct methods and refined with full-matrix least-squares methods on F^2 using the SHELXTL package.[40] For the structures of **7** data collection was performed on a Stoe IPDS-2/2T diffractometer with Mo Kα radiation. For the COD olefinic C/H atoms an sp^2 model was used to attach the H atoms to the respective C atoms.

Syntheses. *2-$BrC_6F_4AsPh_2$ (**6**).* To a solution of 1,2-dibromotetrafluorobenzene (9.28 g, 30 mmol) in ether (100 mL), cooled to −78 °C, was added ^{n}BuLi (1.6 M in hexanes, 20.0 mL, 30 mmol) dropwise. After the mixture had been stirred for 30 min, chlorodiphenylarsine (5.6 mL, 30 mmol) was slowly added. The solution was stirred at −78 °C for 2 h and then warmed to room temperature overnight. The resulting suspension was hydrolyzed, the ether layer was separated, and the aqueous phase was extracted with ether (3 × 50 mL). The combined organic phases were dried ($MgSO_4$) and filtered, and the solvent was removed in vacuo. The yellow gummy solid was recrystallized from methanol to give the title product as a colorless solid (9.8 g, 71%).

Mp: 64–66 °C. ^{1}H NMR: δ 7.34–7.42 (m, 6H, aromatic), 7.42–7.49 (m, 4H, aromatic). ^{19}F NMR: δ −119.6 (ddd, J_{FF} = 5.7, 11.5, 24.5 Hz), −126.2 (ddd, J_{FF} = 3.1, 11.4, 21.5 Hz), −151.0 (ddd, J_{FF} = 5.8, 20.1, 21.4 Hz), −153.9 (ddd, J_{FF} = 3.2, 19.6, 24.4 Hz). ESI-MS (m/z): 455.9 $[M]^+$. Anal. Calcd for $C_{18}H_{10}BrAsF_4$: C, 47.30; H, 2.21; F, 16.63. Found: C, 47.46; H, 2.24; F, 16.57.

*[PtI(κC-2-$C_6F_4AsPh_2$)(1,5-COD)] (**7**).* To a solution of 2-$BrC_6F_4AsPh_2$ (1.17 g, 2.56 mmol) in ether (20 mL), cooled to −78 °C, had been added ^{n}BuLi (1.6 M, 1.6 mL, 2.56 mmol) dropwise. After the mixture was stirred for 30 min, $[PtI_2(1,5\text{-COD})]$ (1.28 g, 2.3 mmol) was added. The mixture was stirred at −78 °C for several hours and warmed to room temperature overnight. The orange solution was removed by cannula from the off-white solid, which was washed with Et_2O (5 mL) and MeOH (5 mL) and recrystallized from CH_2Cl_2/MeOH to give complex **7** as a colorless solid (1.53 g, 83%).

^{1}H NMR: δ 1.81–2.03 (m, 1H, aliphatic COD), 2.03–2.32 (m, 3H, aliphatic COD), 2.32–2.58 (m, 2H, aliphatic COD), 2.58–2.84 (m, 2H, aliphatic COD), 4.34 (m, 1H, J_{PtH} = 64.3 Hz, olefinic COD), 5.08 (m, 1H, J_{PtH} = 71.8 Hz, olefinic COD), 5.89 (m, 1H, J_{PtH} = 43.6 Hz, olefinic COD), 6.09 (m, 1H, J_{PtH} = 42.7 Hz, olefinic COD), 7.24–7.35 (m, 3H, aromatic), 7.38–7.43 (m, 3H, aromatic), 7.43–7.50 (m, 2H, aromatic), 7.50–7.58 (m, 2H, aromatic). ^{19}F NMR: δ −119.6 (dd, J_{FF} = 14.1, 27.8 Hz, J_{PtF} = 282 Hz), −122.7 (ddd, J_{FF} = 5.1, 14.7, 23.7 Hz, J_{PtF} = 38.9 Hz), −153.3 (ddd, J_{FF} = 5.2, 19.1, 27.7 Hz, J_{PtF} = 83.4 Hz), −158.8 (dd, J_{FF} = 19.0, 23.7 Hz, J_{PtF} = 17.6 Hz). ESI-MS (m/z): 829.9 $[M + Na]^+$. Anal. Calcd for $C_{26}H_{22}AsF_4IPt$: C, 38. 68; H, 2.75; F, 9.41. Found: C, 38.85; H, 2.67; F, 9.21.

*$[Pt(\kappa^2As,C\text{-}2\text{-}C_6F_4AsPh_2)(1,5\text{-COD})]PF_6$ (**8**).* To a solution of $[PtI(\kappa C\text{-}2\text{-}C_6F_4AsPh_2)(1,5\text{-COD})]$ (**7**; 400 mg, 0.50 mmol) in CH_2Cl_2 (40 mL) was added $TlPF_6$ (260 mg, 0.74 mmol). The mixture was shielded from light and stirred overnight. The resulting orange suspension was filtered through Celite, and the solvent was removed in vacuo. The residue was dissolved in the minimum amount of dichloromethane, and ether was slowly added, precipitating a colorless solid. The volume was reduced in vacuo, and more ether was added. The colorless solid was isolated by filtration, washed with ether, and dried. The yield of **8** was 381 mg (93%).

^{1}H NMR: δ 2.64 (br. s, 8H, aliphatic COD), 6.04 (m, 2H, J_{PtH} = 43.2 Hz, olefinic COD), 6.58 (m, 2H, J_{PtH} = 64.7 Hz, olefinic COD), 7.56–7.68 (m, 10H, aromatic). ^{19}F NMR: δ −73.1 (d, J_{PF} = 713 Hz), −128.2 (ddd, J_{FF} = 5.3, 18.1, 23.7 Hz, J_{PtF} = 82.3 Hz), −132.5 (ddd, J_{FF} = 5.1, 18.0, 22.7 Hz), −146.2 (ddd, J_{FF} = 5.0, 18.0, 23.5 Hz, J_{PtF} = 68.7 Hz), −149.9 (ddd, J_{FF} = 5.5, 18.2, 22.4 Hz). ESI-MS (m/z): 680.1 $[M - PF_6]^+$. Anal. Calcd for $C_{26}H_{22}AsF_{10}PPt$: C, 37.83; H, 2.69; F, 23.02. Found: C, 37.90; H, 2.63; F, 23.26.

*$[Pt(py)(\kappa C\text{-}2\text{-}C_6F_4AsPh_2)(1,5\text{-COD})]PF_6$ (**9**).* To solution of $[Pt(\kappa^2As,C\text{-}2\text{-}C_6F_4AsPh_2)(1,5\text{-COD})]PF_6$ (**8**; 113 mg, 0.14 mmol) in dichloromethane (5 mL) was added pyridine (11 μL, 0.14 mmol), and the mixture was stirred overnight. Hexane was added to the colorless solution, and the volume was reduced in vacuo. The precipitated colorless solid was separated by filtration, washed with hexane, and dried in vacuo to give **9** (118 mg, 95%).

^{1}H NMR (CD_2Cl_2): δ 2.38–2.96 (m, 8H, aliphatic COD), 5.28 (m, 2H, J_{PtH} = 64.1 Hz, olefinic COD), 5.71 (m, 2H, J_{PtH} = 38.6 Hz, olefinic COD), 7.24–7.62 (m, 11H, aromatic/py), 7.95 (t, 1H, J_{HH} = 7.8 Hz, py), 8.74 (d, 2H, J_{HH} = 5.2 Hz, py). ^{19}F NMR (CD_2Cl_2): δ −73.1 (d, J_{PtF} = 711 Hz), −122.9 (ddd, J_{FF} = 5.8, 15.0, 21.7 Hz, unresolved J_{PtF}), −123.9 (br. s, $J_{PtF} \approx$ 230 Hz), −151.1 (m), −156.1 (m). ESI-MS (m/z): 759.1 $[M - PF_6]^+$. Anal. Calcd for $C_{31}H_{27}NAsF_{10}PPt$: C, 41.16; H, 3.01; N, 1.55; F, 21.00. Found: C, 40.87; H, 2.99; N, 1.69; F, 20.60.

*$[PtCl(\kappa C\text{-}2\text{-}C_6F_4AsPh_2)(1,5\text{-COD})]$ (**10**).* To a solution of $[Pt(\kappa^2As,C\text{-}2\text{-}C_6F_4AsPh_2)(1,5\text{-COD})]PF_6$ (**8**; 150 mg, 0.18 mmol) in dichloromethane (5 mL) was added a solution of LiCl (10 mg, 0.24 mmol) in methanol (5 mL). The mixture was stirred for 10 min, during which time a white precipitate formed, and the solvent was removed in vacuo. The residue was extracted with dichloromethane, and the suspension was filtered through Celite. Addition of methanol to the filtrate and evaporation in vacuo caused the product to precipitate as a colorless solid, which was isolated by filtration, washed with methanol, and dried in vacuo. The yield of **10** was 125 mg (97%).

^{1}H NMR: δ 2.01–2.62 (m, 6H, aliphatic COD), 2.62–2.98 (m, 2H, aliphatic COD), 4.26 (m, 1H, J_{PtH} = 64.9 Hz, olefinic COD), 4.94 (m, 1H, J_{PtH} = 73.1 Hz, olefinic COD), 5.87 (m, 1H, J_{PtH} = 39.3 Hz, olefinic COD), 6.06 (m, 1H, J_{PtH} = 38.9 Hz, olefinic COD), 7.26–7.36 (m, 3H, aromatic), 7.38–7.50 (m, 5H, aromatic), 7.50–7.61 (m, 2H, aromatic). ^{19}F NMR: δ −122.1 (dd, J_{FF} = 14.9, 27.4 Hz, J_{PtF} = 270 Hz), −122.4 (ddd, J_{FF} = 4.9, 14.8, 23.5 Hz, $J_{PtF} \approx$ 38 Hz), −153.1 (ddd, J_{FF} = 5.0, 18.9, 27.4 Hz, J_{PtF} = 82.8 Hz), −158.5 (dd, J_{FF} = 18.9, 23.5 Hz, $J_{PtF} \approx$ 19 Hz). ESI-MS (m/z): 739.0 $[M + Na]^+$. Anal. Calcd for $C_{26}H_{22}AsClF_4Pt$: C, 43.67; H, 3.10; Cl, 4.95; F, 10.62. Found: C, 43.42; H, 3.06; Cl, 5.13; F, 10.54.

*$[PtBr(\kappa C\text{-}2\text{-}C_6F_4AsPh_2)(1,5\text{-COD})]$ (**11**).* Complex **11** was made analogously to complex **10** from **8** (150 mg, 0.18 mmol) and LiBr (20 mg, 0.23 mmol) to give the product as a colorless solid (130 mg, 95%).

^{1}H NMR: δ 1.86–2.12 (m, 1H, aliphatic COD), 2.12–2.40 (m, 3H, aliphatic COD), 2.40–2.60 (m, 2H, aliphatic COD), 2.68–2.90 (m, 2H, aliphatic COD), 4.29 (m, 1H, J_{PtH} = 68.6 Hz, olefinic COD), 4.98 (m, 1H, J_{PtH} = 72.2 Hz, olefinic COD), 5.88 (m, 1H, J_{PtH} = 42.6 Hz, olefinic COD), 6.08 (m, 1H, J_{PtH} = 36.6 Hz, olefinic COD), 7.26–7.36 (m, 4H, aromatic), 7.38–7.50 (m, 4H, aromatic), 7.50–7.61 (m, 2H, aromatic). ^{19}F NMR: δ −121.4 (dd, J_{FF} = 14.8, 27.6 Hz, J_{PtF} = 272 Hz), −122.6 (ddd, J_{FF} = 5.2, 14.6, 23.6 Hz, $J_{PtF} \approx$ 38 Hz), −153.1 (ddd, J_{FF} = 5.1, 19.2, 27.6 Hz, J_{PtF} = 80.8 Hz), −158.6 (dd, J_{FF} = 19.0, 23.6 Hz, $J_{PtF} \approx$ 17 Hz). ESI-MS (m/z): 783.0 $[M + Na]^+$. Anal. Calcd for $C_{26}H_{22}AsBrF_4Pt$: C, 41.07; H, 2.92; Br. 10.51; F, 9.99. Found: C, 40.96; H, 2.91; Br. 10.72; F, 9.45.

*$[PtI(\mu\text{-}2\text{-}C_6F_4AsPh_2)(1,5\text{-COD})AuCl]$ (**12**).* To a stirred solution of $[PtI(\kappa C\text{-}2\text{-}C_6F_4AsPh_2)(1,5\text{-COD})]$ (**7**; 151 mg, 0.19 mmol) in dichloromethane (150 mL) cooled to 0 °C was added [AuCl(tht)] (60 mg, 0.19 mmol). After the mixture had been stirred for 10 min, MeOH (20 mL) was added and the solution was filtered through Celite. The filtrate was evaporated under reduced pressure, and the precipitated colorless solid was isolated by filtration, washed with MeOH, and dried. The yield of **12** was 174 mg (90%).

^{1}H NMR: δ 1.80–3.25 (m, 8H, aliphatic COD), 4.23 (m, 0.5H, J_{PtH} = 61.5 Hz, olefinic COD), 4.37 (m, 0.5H, J_{PtH} = 68.5 Hz, olefinic COD), 4.53–4.88 (m, 1H, unresolved J_{PtH}, olefinic COD), 6.21–6.65 (m, 2H, unresolved J_{PtH}, olefinic COD), 7.35–7.70 (m, 8H, aromatic), 7.73–7.92 (m, 2H, aromatic). ^{19}F NMR: δ −109.5 (ddd, J_{FF} = 2.4,

dx.doi.org/10.1021/om400961z | Organometallics 2013, 32, 7451–7459

12.8, 28.8 Hz, J_{PtF} = 312 Hz), −110.0 (ddd, J_{FF} = 2.4, 12.9, 29.0 Hz, J_{PtF} = 309 Hz), −111.9 (ddd, J_{FF} = 2.6, 12.8, 28.8 Hz, J_{PtF} = 302 Hz), −112.3 (ddd, J_{FF} = 2.4, 12.8, 28.8 Hz, J_{PtF} = 302 Hz), −121.1 (m), −121.4 (m), −148.7 (ddd, J_{FF} = 6.8, 19.5, 28.7 Hz, unresolved J_{PtF}), −148.9 (ddd, J_{FF} = 6.7, 19.2, 28.5 Hz, unresolved J_{PtF}), −149.2 (ddd, J_{FF} = 6.4, 19.4, 28.9 Hz, unresolved J_{PtF}), −149.4 (ddd, J_{FF} = 6.5, 19.5, 29.1 Hz, unresolved J_{PtF}), −156.6 (ddd, J_{FF} = 2.6, 19.8, 22.3 Hz, unresolved J_{PtF}), −156.7 (ddd, J_{FF} = 2.8, 19.6, 22.5 Hz, unresolved J_{PtF}), −156.8 (ddd, J_{FF} = 2.5, 19.6, 22.4 Hz, unresolved J_{PtF}), −157.0 (ddd, J_{FF} = 2.4, 19.6, 22.2 Hz, unresolved J_{PtF}). ESI-MS (m/z): 1061.9 $[M + Na]^+$ for **12**, 1153.8 and 970.9 $[M + Na]^+$ for **13** and **14**, respectively. Anal. Calcd for $C_{26}H_{22}AsAuClF_4IPt$: C, 30.03; H, 2.13; F, 7.31; I, 12.20. Found: C, 29.50, H, 2.11; F, 7.13; I, 12.05.

*[PtI(μ-2-$C_6F_4AsPh_2$)(1,5-COD)AuI] (**13**).* To a solution of [PtI(κC-2-$C_6F_4AsPh_2$)(1,5-COD)AuCl] (**12**; 130 mg, 0.13 mmol) in CH_2Cl_2 (5 mL) was added NaI (55 mg, 0.37 mmol) in MeOH (5 mL). Workup as described for **10** gave complex **13** as a colorless solid (131 mg, 93%).

^{1}H NMR: δ 1.81−2.12 (m, 3H, aliphatic COD), 2.12−2.36 (m, 1H, aliphatic COD), 2.41−2.64 (m, 1H, aliphatic COD), 2.64−2.81 (m, 2H, aliphatic COD), 2.83−3.09 (m, 1H, aliphatic COD), 4.35 (m, 1H, J_{PtH} = 62.2 Hz, olefinic COD), 4.66 (m, 1H, J_{PtH} = 70.2 Hz, olefinic COD), 6.30−6.58 (m, 2H, unresolved J_{PtH}, olefinic COD), 7.33−7.68 (m, 8H, aromatic), 7.81−7.93 (m, 2H, aromatic). ^{19}F NMR: δ −110.0 (ddd, J_{FF} = 2.3, 12.8, 29.0 Hz, J_{PtF} = 307 Hz), −121.4 (6.4, 12.8, 22.4 Hz, J_{PtF} = 42.4 Hz), −149.4 (ddd, J_{FF} = 6.3, 19.5, 28.9 Hz, J_{PtF} = 80 Hz), −156.8 (ddd, 2.5, 19.6, 22.3 Hz, J_{PtF} ≈ 13 Hz). ESI-MS (m/z): 1153.8 $[M + Na]^+$. Anal. Calcd for $C_{26}H_{22}AsAuI_2F_4Pt$: C, 27.61; H, 1.96; F, 6.72; I, 22.44. Found: C, 27.38; H, 2.02; F, 6.87; I, 22.30.

*[PtCl(μ-2-$C_6F_4AsPh_2$)(1,5-COD)AuCl] (**14**).* This complex was made similarly to **12** from [PtCl(κC-2-$C_6F_4AsPh_2$)(1,5-COD)] (**10**; 154 mg, 0.22 mmol) and [AuCl(tht)] (69 mg, 0.22 mmol) and obtained as a colorless solid (194 mg, 95%).

^{1}H NMR: δ 1.96−2.23 (m, 2H, aliphatic COD), 2.23−3.98 (m, 5H, aliphatic COD), 3.02−3.25 (m, 1H, aliphatic COD), 4.24 (m, 1H, J_{PtH} = 63.6 Hz, olefinic COD), 4.67 (m, 1H, J_{PtH} = 73.5 Hz, olefinic COD), 6.32 (m, 1H, J_{PtH} ≈ 45 Hz, olefinic COD), 6.54 (m, 1H, J_{PtH} ≈ 41 Hz, olefinic COD), 7.37−7.54 (m, 5H, aromatic), 7.54−7.68 (m, 3H, aromatic), 7.74−7.87 (m, 2H, aromatic). ^{19}F NMR: δ −111.9 (ddd, J_{FF} = 2.7, 12.9, 28.8 Hz, J_{PtF} = 303 Hz), −121.1 (ddd, J_{FF} = 6.5, 12.7, 22.2 Hz, J_{PtF} ≈ 37 Hz), −148.7 (ddd, J_{FF} = 6.7, 19.5, 28.8 Hz, J_{PtF} = 80.4 Hz), −156.7 (ddd, J_{FF} = 2.6, 19.6, 22.0 Hz). ESI-MS (m/z): 970.9 $[M + Na]^+$. Anal. Calcd for $C_{26}H_{22}AsAuCl_2F_4Pt$: C, 32.93; H, 2.34; Cl, 7.48; F, 8.01. Found: C, 32.96; H, 2.40; Cl, 7.79; F, 8.10.

*[PtMe(κC-2-$C_6F_4AsPh_2$)(1,5-COD)] (**15**).* To an ice-cooled solution of [PtI(κC-2-$C_6F_4AsPh_2$)(1,5-COD] (7; 500 mg, 0.62 mmol) in dichloromethane (40 mL) was added $ZnMe_2$ (2.0 M solution in toluene, 200 μL, 0.4 mmol). The turbid solution was stirred for 15 min and then warmed to room temperature and evaporated to dryness. The residue was dissolved in dichloromethane and the solution filtered through Celite. Methanol was added to the filtrate, and the volume of the solution was reduced in vacuo. The precipitated colorless solid was filtered off, washed with methanol, and dried. The yield of **15** was 408 mg (95%).

^{1}H NMR: δ 0.78 (s, 3H, J_{PtH} = 78.7 Hz, methyl), 2.10−2.76 (m, 8H, aliphatic COD), 4.57 (m, 1H, J_{PtH} = 54.1 Hz, olefinic COD), 5.06 (m, 2H, unresolved J_{PtH}, olefinic COD), 5.24 (m, 1H, J_{PtH} = 43.7 Hz, olefinic COD), 7.28−7.44 (m, 8H, aromatic), 7.46−7.54 (m, 2H, aromatic). ^{19}F NMR: δ −119.7 (dd, J_{FF} = 16.1, 31.0 Hz, J_{PtF} = 450 Hz), −123.3 (ddd, J_{FF} = 4.4, 16.2, 23.7 Hz, J_{PtF} = 67.2 Hz), −155.2 (ddd, J_{FF} = 4.5, 19.1, 31.0 Hz, J_{PtF} = 128 Hz), −161.3 (dd, J_{FF} = 19.2, 23.7 Hz, J_{PtF} = 18.4 Hz). ESI-MS (m/z): 696.1 $[M + H]^+$. Anal. Calcd for $C_{27}H_{25}AsF_4Pt$: C, 46.63; H, 3.62; F, 10.93. Found: C, 46.31; H, 3.48; F, 10.83.

*[Pt(κ^{2}As,C-2-$C_6F_4AsPh_2$)(1,5-COD)]OTf (**16**).* A solution of [PtMe-(κC-2-$C_6F_4AsPh_2$)(1,5-COD)] (**15**; 360 mg, 0.52 mmol) in dichloromethane (10 mL) was cooled to −78 °C and treated dropwise with triflic acid (46 μL, 0.52 mmol) in dichloromethane (5 mL). After it was stirred for 5 min, the solution was warmed to room temperature and the solvent was removed in vacuo. Toluene (10 mL) was added to the residue, and the suspension was stirred for 10 min. After the mixture had been set aside for 1 h, the solid was filtered off and dissolved in a small amount of dichloromethane and ether was slowly added, precipitating a colorless solid. The volume was reduced in vacuo, more ether was added, and the solid was isolated by filtration. The colorless precipitate was washed with ether and dried in vacuo. The yield of **15** was 340 mg (79%).

^{1}H NMR: δ 2.67 (br. s, 8H, aliphatic COD), 6.17 (m, 2H, J_{PtH} = 39 Hz, olefinic COD), 6.70 (m, 2H, J_{PtH} = 63 Hz, olefinic COD), 7.55−7.73 (m, 10H, aromatic). ^{19}F NMR: δ −78.2 (s), −128.5 (m), −132.4 (m), −146.7 (ddd, J_{FF} = 5.8, 19.1, 22.7 Hz, J_{PtF} = 67.4 Hz), −150.3 (apparent t, J_{FF} = 20.1 Hz, unresolved J_{PtF}). ESI-MS (m/z): 680.1 $[M - OTf]^+$. Anal. Calcd for $C_{27}H_{22}AsF_7O_3PtS$: C, 39.09; H, 2.67; F, 16.03; S, 3.86. Found: C, 39.27; H, 2.67; F, 16.02; S, 3.77.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

CIF files giving crystallographic data and a table giving crystal data and details of data collection and structure refinement for compounds **7** (two modifications), **8**, **9**, **12**, **15**, and **16**. This material is available free of charge via the Internet at http://pubs.acs.org. The CCDC entries 963185 (**7**, in *Pna*2$_1$), 963184 (**7**, in *P*2$_1$), 963187 (**8**), 963190 (**9**), 963186 (**12**), 963188 (**15**), and 963189 (**16**) also contain supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank Mr. Erik Wächtler for his help in the structural analysis of compound **12**.

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