Stable Carbeneiridium(I) Complexes with 16- and 18-Electron Configurations at the Metal Center

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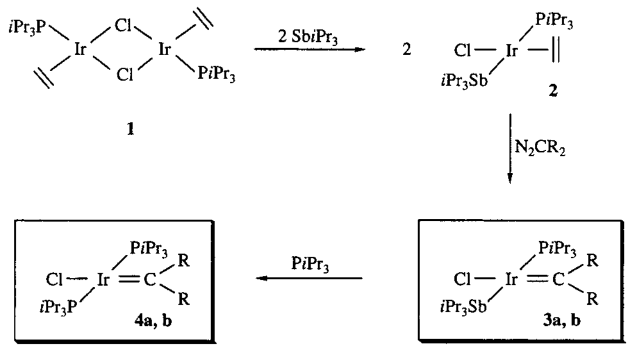
Summary: *Using the mixed phosphine−stibine compound* $[IrCl(C_2H_4)(PiPr_3)(SbiPr_3)]$ (***2***) *as the starting material, the square-planar carbeneiridium(I) complexes* $[IrCl(=CR_2)(PiPr_3)(SbiPr_3)]$ (***3a***,***b***) *and trans-*$[IrCl(=CR_2)(PiPr_3)_2]$ (***4a***,***b***) *were prepared. The cyclopentadienyl derivative* $[C_5H_5Ir(=CPh_2)(PiPr_3)]$ (***5***), *obtained from* ***3a*** *and* NaC_5H_5, *reacts with HCl by attack of the* $Ir=CPh_2$ *bond; in contrast, upon treatment of* ***4a*** *with HCl or* HBF_4, *hydridoiridium(III) complexes* ***8*** *and* ***9*** *with an intact* $Ir=CPh_2$ *unit are formed.*

Following the discovery that carbenerhodium(I) complexes of the general composition *trans*-$[RhCl(=CRR')(L)_2]$ ($L = PR_3, AsR_3, SbR_3$) are readily accessible[1] and provide a rich chemistry including novel C−C coupling reactions,[2] we set out to prepare the iridium counterparts. Since the methodology to obtain the square-planar rhodium carbenes *trans*-$[RhCl(=CRR')(L)_2]$ is based on the use of the bis(stibine) compound *trans*-$[RhCl(C_2H_4)(SbiPr_3)_2]$ as the starting material,[1,2] we initially attempted to generate the analogous carbeneiridium(I) complexes also from a precursor containing two $SbiPr_3$ ligands. However, these experiments failed. Although the bis(stibine) derivative $[IrCl(C_2H_4)_2(SbiPr_3)_2]$ reacts with $PhC\equiv CPh$ and $Me_3SiC\equiv CSiMe_3$ by ligand exchange to give the four-coordinate alkyne- and vinylideneiridium(I) complexes *trans*-$[IrCl(PhC\equiv CPh)(SbiPr_3)_2]$ and *trans*-$[IrCl\{=C=C(SiMe_3)_2\}(SbiPr_3)_2]$ in excellent yield,[3] it is completely inert toward Ph_2CN_2 under the same conditions. Therefore, the development of an alternative preparative route was necessary. Here we report the preparation, structure determination, and preliminary reactivity studies of both square-planar and half-sandwich-type iridium complexes that contain $Ir=C(aryl)_2$ as a molecular unit.

The synthetic pathways to obtain the carbeneiridium(I) compounds **3** and **4** are outlined in Scheme 1. The key to success was the use of the mixed phosphine−stibine complex **2** as the starting material, which was isolated upon treatment of the binuclear precursor **1** and 2 equiv of $SbiPr_3$ as a bright orange solid in nearly quantitative yield.[4] While compound **2** can be stored under argon at −30 °C for weeks, it is labile in solution and decomposes particularly in CH_2Cl_2 quite rapidly. The reaction of **2** with N_2CR_2 ($R = Ph$, p-Tol) in benzene proceeds cleanly and affords the carbene complexes **3a**,**b** in 60−70% isolated yield.[5] The most characteristic spectroscopic feature of **3a** and **3b** is the signal for the carbene carbon atom in the ^{13}C NMR spectrum at δ 240.9 (**3a**) and 244.7 (**3b**), which is split into a doublet due to P−C coupling.

Scheme 1[a]



[a] **a**: $R = C_6H_5$. **b**: $R = p\text{-}C_6H_4Me$.

In agreement with previous findings,[1,2] the $M-SbiPr_3$ bond in **3a**,**b** is more readily dissociable, and therefore the mixed phosphine−stibine derivatives react smoothly with $PiPr_3$ to give the bis(phosphine) iridium carbenes **4a** and **4b**, respectively.[6] Both complexes, which are thermally more stable than the precursors **3a**,**b**, have been characterized by elemental analysis and spectroscopic techniques.[7] The resonance for the $Ir=CR_2$ carbene carbon atom appears in the ^{13}C NMR spectra of

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[1] (1) Schwab, P.; Mahr, N.; Wolf, J.; Werner, H. *Angew. Chem.* **1993**, *105*, 1498−1500; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1480−1482.

[2] (2) (a) Werner, H. *J. Organomet. Chem.* **1995**, *500*, 331−336. (b) Werner H.; Schwab, P.; Bleuel, E.; Mahr, N.; Steinert, P.; Wolf, J. *Chem. Eur. J.* **1997**, *3*, 1375−1384. (c) Bleuel, E. Dissertation, Universität Würzburg, to be submitted.

[3] (3) Werner, H.; Ortmann, D. A.; Gevert, O. *Chem. Ber.* **1996**, *129*, 411−417.

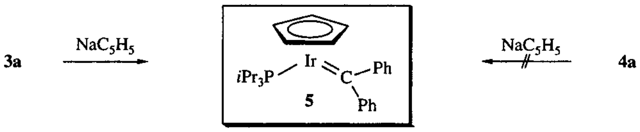
[4] (4) The preparation of **2** is as follows. A suspension of **1** (105 mg, 0.13 mmol) in 5 mL of pentane was treated under continuous stirring with $SbiPr_3$ (52 μL, 0.25 mmol). After benzene (5 mL) was added, the more volatile materials (mainly pentane) were removed in vacuo. The generated orange solution was stirred for 30 min and then brought to dryness in vacuo. The bright orange solid was washed twice with 2 mL of pentane and dried: yield 159 mg (95%); mp 88 °C dec.

[5] (5) The preparation of **3a** is as follows. A solution of **2** (121 mg, 0.18 mmol) in 10 mL of benzene was treated with Ph_2CN_2 (35 mg, 0.18 mmol) at room temperature and then stirred under slightly reduced pressure for 1 h. The solvent was removed, and the residue was recrystallized from acetone at −78 °C. A brown microcrystalline solid was obtained, which was washed twice with 1 mL of acetone (0 °C) and dried: yield 105 mg (72%); mp 42 °C dec. Compound **3b** was prepared analogously, using **2** (112 mg, 0.17 mmol) and $N_2C(C_6H_4\text{-p-}Me)_2$ (38 mg, 0.17 mmol) as starting materials: dark brown solid; yield 83 mg (59%); mp 24 °C dec.

[6] (6) The preparation of **4a** is as follows. A solution of **3a** (200 mg, 0.28 mmol) in 20 mL of pentane was treated with $PiPr_3$ (55 μL, 0.28 mmol) and stirred for 45 min at room temperature. The solvent was removed, and the residue was recrystallized from acetone at −78 °C. A brown, moderately air-stable solid was obtained, which was washed twice with 1 mL of acetone (0 °C) and dried: yield 112 mg (56%); mp 83 °C dec. Compound **4b** was prepared analogously, using **3b** (250 mg, 0.30 mmol) and $PiPr_3$ (64 μL, 0.33 mmol) as starting materials; dark brown solid; yield 136 mg (61%); mp 65 °C dec.

10.1021/om980984p CCC: $18.00

Scheme 2



4a,**b** at δ 234.7 (**4a**) and 245.5 (**4b**) and thus at significantly higher field than in the case of the rhodium counterparts *trans*-[RhCl(=CR$_2$)(P*i*Pr$_3$)$_2$].[1,2b]

The reactivity of the structurally related compounds **3a** and **4a** toward NaC$_5$H$_5$ is quite different (see Scheme 2). While the bis(phosphine) compound **4a** is completely inert toward NaC$_5$H$_5$ (THF, 25 °C), the mixed-ligand derivative **3a** reacts under the same conditions with sodium cyclopentadienide to afford the half-sandwich-type complex **5** in 70% isolated yield.[8] In contrast to the related methyleneiridium compound [C$_5$Me$_5$Ir(=CH$_2$)(PMe$_3$)], generated by Klein and Bergman upon photolysis of the metallacycle [C$_5$Me$_5$Ir(κ^2-CH$_2$CMe$_2$O)(PMe$_3$)] at −60 °C,[9] the diphenylcarbene complex **5** is exceptionally thermally stable and decomposes only at temperatures above 93 °C. The X-ray crystal structure analysis of **5** (Figure 1)[10] reveals that the iridium has a somewhat distorted trigonal coordination sphere if the midpoint of the cyclopentadienyl ring is taken as one coordination site. The metal−C(carbene) distance Ir−C is almost identical to the Rh−C bond length (1.907(3) Å) of the analogous carbenerhodium(I) complex [C$_5$H$_5$-Rh(CPh$_2$)(CO)][11] but slightly longer than in the iridium methylene derivative [Ir(=CH$_2$){κ^3-N(SiMe$_2$CH$_2$PPh$_2$)$_2$}] (1.868(9) Å).[12] To the best of our knowledge, compound **5** is the first structurally characterized cyclopentadienyliridium complex of the general composition [C$_5$H$_5$-Ir(PR$_3$)(L)], where L is a carbene, vinylidene, or allenylidene ligand.[13]

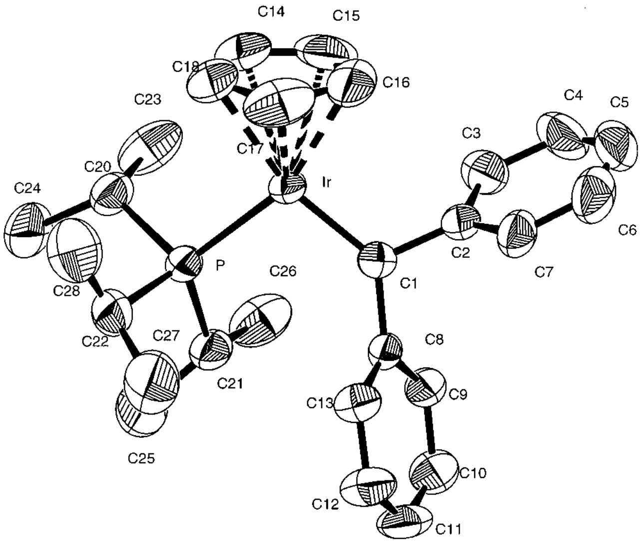


Figure 1. ORTEP diagram of compound **5**. Selected bond distances (Å) and angles (deg): Ir−P 2.262(2), Ir−C1 1.904(5), Ir−C14 2.308(7), Ir−C15 2.266(7), Ir−C16 2.210(7), Ir−C17 2.239(7), Ir−C18 2.316(6), C1−C2 1.499(7), C1−C8 1.492(7); P−Ir−C1 99.9(2), Ir−C1−C2 116.2(4), Ir−C1−C8 134.5(4), C2−C1−C8 109.2(4).

Treatment of **5** with dry HCl in pentane results in a rapid change of color from violet to orange-yellow and leads to the formation of the alkyl(chloro)iridium(III) complex **6** (Scheme 3) in virtually quantitative yield.[14] Diagnostic of an Ir−CHPh$_2$ moiety in **6** is a resonance in the ^{1}H NMR at δ 5.75 for the CH proton and a signal in the ^{13}C NMR spectrum at δ 24.9 for the substituted methyl carbon atom. Due to P−H and P−C coupling,

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(7) Selected spectroscopic data for **3a**, **4a**, and **5**−**9** (omitting the ^{1}H and ^{13}C NMR data for the aryl groups) are as follows. **3a**: ^{1}H NMR (200 MHz, C$_6$D$_6$) δ 2.39 (m, 3 H, PC*H*CH$_3$), 2.11 (sept, ^3J(HH) = 7.3 Hz, 3 H, SbC*H*CH$_3$), 1.32 (d, ^3J(HH) = 7.3 Hz, 18 H, SbCHC*H*$_3$), 1.19 (dd, ^3J(PH) = 13.2, ^3J(HH) = 7.3 Hz, 18 H, PCHC*H*$_3$); ^{13}C NMR (50.3 MHz, C$_6$D$_6$) δ 240.9 (d, ^2J(PC) = 7.6 Hz, Ir=C), 24.8 (d, ^1J(PC) = 24.2 Hz, P*C*HCH$_3$), 22.0 (s, SbCH*C*H$_3$), 20.0 (s, PCH*C*H$_3$), 18.9 (d, ^3J(PC) = 5.1 Hz, Sb*C*HCH$_3$); ^{31}P NMR (81.0 MHz, C$_6$D$_6$) δ 8.8 (s). **4a**: ^{1}H NMR (400 MHz, C$_6$D$_6$) δ 2.44 (m, 6 H, PC*H*CH$_3$), 1.20 (dvt, *N* = 13.2, ^3J(HH) = 7.0 Hz, 36 H, PCHC*H*$_3$); ^{13}C NMR (100.6 MHz, C$_6$D$_6$) δ 234.7 (t, ^2J(PC) = 8.9 Hz, Ir=C), 25.2 (vt, *N* = 25.4 Hz, P*C*HCH$_3$), 20.4 (s, PCH*C*H$_3$); ^{31}P NMR (81.0 MHz, C$_6$D$_6$) δ 4.2 (s). **5**: ^{1}H NMR (200 MHz, C$_6$D$_6$) δ 4.92 (d, ^3J(PH) = 1.1 Hz, 5 H, C$_5$H$_5$), 1.54 (m, 3 H, PC*H*CH$_3$), 0.98 (dd, ^3J(PH) = 13.1, ^3J(HH) = 6.9 Hz, 18 H, PCHC*H*$_3$); ^{13}C NMR (50.3 MHz, C$_6$D$_6$) δ 217.2 (d, ^2J(PC) = 12.7 Hz, Ir=C), 82.3 (d, ^2J(PC) = 3.8 Hz, C$_5$H$_5$), 28.0 (d, ^1J(PC) = 28.0 Hz, P*C*HCH$_3$), 20.8 (s, PCH*C*H$_3$); ^{31}P NMR (81.0 MHz, C$_6$D$_6$) δ 27.8 (s). **6**: ^{1}H NMR (200 MHz, CD$_2$Cl$_2$) δ 5.75 (d, ^3J(PH) = 2.2 Hz, 1 H, C*H*(C$_6$H$_5$)$_2$), 5.09 (d, ^3J(PH) = 1.5 Hz, 5 H, C$_5$H$_5$), 2.44 (m, 3 H, PC*H*CH$_3$), 1.20 (dd, ^3J(PH) = 14.4, ^3J(HH) = 7.1 Hz, 12 H, PCHC*H*$_3$), 0.81 (dd, ^3J(PH) = 12.6, ^3J(HH) = 7.1 Hz, 6 H, PCHC*H*$_3$); ^{13}C NMR (50.3 MHz, C$_6$D$_6$) δ 83.4 (d, ^2J(PC) = 2.8 Hz, C$_5$H$_5$), 24.9 (d, ^2J(PC) = 6.5 Hz, *C*HPh$_2$), 23.5 (d, ^1J(PC) = 27.8 Hz, P*C*HCH$_3$), 20.8, 19.1 (both s, PCH*C*H$_3$); ^{31}P NMR (81.0 MHz, C$_6$D$_6$) δ 5.5 (s). **7**: ^{1}H NMR (200 MHz, C$_6$D$_6$) δ 5.70 (d, ^3J(PH) = 2.2 Hz, 1 H, C*H*Ph$_2$), 4.93 (m, 2 H, C$_5$H$_4$), 4.49, 4.31 (both m, 1 H each, C$_5$H$_4$), 2.13 (m, 3 H, PC*H*CH$_3$), 0.96 (dd, ^3J(PH) = 13.9, ^3J(HH) = 7.3 Hz, 18 H, PCHC*H*$_3$), −14.40 (d, ^2J(PH) = 33.4 Hz, 1 H, IrH); ^{13}C NMR (50.3 MHz, C$_6$D$_6$) δ 121.8 (d, ^2J(PC) = 4.6 Hz, *C*CHPh$_2$), 84.0 (s, C$_5$H$_4$), 77.1 (d, ^2J(PC) = 9.2 Hz, C$_5$H$_4$), 74.8, 67.6 (both s, C$_5$H$_4$), 47.9 (s, *C*HPh$_2$), 26.6 (d, ^1J(PC) = 31.4 Hz, P*C*HCH$_3$), 19.8, 19.5 (je s, PCH*C*H$_3$); ^{31}P NMR (81.0 MHz, C$_6$D$_6$) δ 37.5 (s). **8**: ^{1}H NMR (200 MHz, C$_6$D$_6$) δ 2.61 (m, 6 H, PC*H*CH$_3$), 1.27, 1.19 (both dvt, *N* = 14.6, ^3J(HH) = 7.3 Hz, 18 H each, PCHC*H*$_3$), −19.23 (br s, 1 H, IrH); ^{31}P NMR (81.0 MHz, C$_6$D$_6$) δ 1.65 (s). **9**: ^{1}H NMR (200 MHz, CD$_2$Cl$_2$) δ 2.30 (m, 6 H, PC*H*CH$_3$), 1.11, 1.03 (both dvt, *N* = 14.5, ^3J(HH) = 7.3 Hz, 18 H each, PCHC*H*$_3$), −28.8 (t, ^2J(PH) = 11.6 Hz, 1 H, IrH); ^{13}C NMR (50.3 MHz, CD$_2$Cl$_2$) δ 266.5 (s, Ir=C), 24.9 (vt, *N* = 28.0 Hz, P*C*HCH$_3$), 19.7 (s, PCH*C*H$_3$); ^{31}P NMR (81.0 MHz, CD$_2$Cl$_2$) δ 38.2 (s).

(8) The preparation of **5** is as follows. A solution of **3a** (138 mg, 0.19 mmol) in 25 mL of THF was treated with small portions of NaC$_5$H$_5$ (85 mg, 0.97 mmol) and stirred for 1 h at room temperature. After the solvent was removed in vacuo, the residue was suspended in 20 mL of pentane and the solution was filtered. The filtrate was brought to dryness in vacuo, and the oily residue was recrystallized from pentane (2 mL) at −78 °C. Dark violet crystals were obtained, which were separated from the mother liquor, washed with small quantities of pentane (0 °C), and dried: yield 77 mg (70%); mp 93 °C dec.

(9) Klein, D. P.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 3079−3080.

(10) Crystal data for **5**: crystals from pentane; crystal size 0.22 × 0.16 × 0.13 mm; monoclinic, space group $P2_1/n$ (No. 14), $Z = 4$; a = 11.017(2) Å, b = 14.709(2) Å, c = 15.374(3) Å, β = 96.01(1)°, V = 2477.7(7) Å^3, d_{calcd} = 1.565 g cm^{-3}; 2θ(max) = 49.90° (Mo−Kα, λ = 0.710 73 Å, graphite monochromator, ω/θ scan, Zr filter with factor 15.4, T = 293(2) K.; 4496 reflections scanned, 4328 unique, 3565 observed ($I > 2\sigma(I)$), Lorentz-polarization and empirical absorption corrections (ψ scans, minimum transmission 83.92%); direct methods (SHELXS-86), 269 parameters, reflex/parameter ratio 16.08; R1 = 0.0287, wR2 = 0.0696; residual electron density +0.697/−0.568 e Å^{-3}.

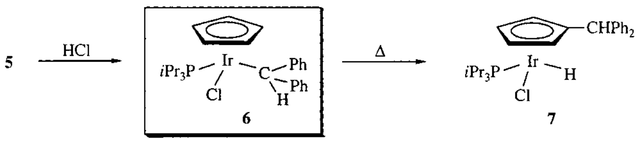
(11) Mahr, N. Dissertation, Universität Würzburg, 1994.

(12) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 6708−6710.

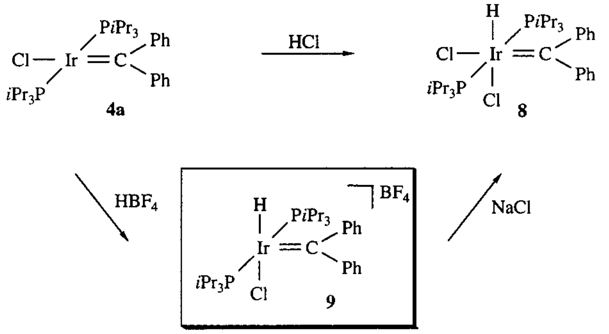
(13) (a) Dötz, K. H.; Fischer, H.; Hofmann, P.; Kreissl, F. R.; Schubert, U.; Weiss, K. *Transition Metal Carbene Complexes*; Verlag Chemie: Weinheim, 1983. (b) Bruce, M. I. *Chem. Rev.* **1991**, *91*, 197−257.

(14) The preparation of **6** is as follows. A slow stream of dry HCl was passed through a solution of **5** (69 mg, 0.12 mmol) in 5 mL of pentane at room temperature. After a few minutes, a change of color from violet to orange-yellow occurred and an orange-yellow solid precipitated. After the solution was stirred at −30 °C for 2 h, the solid was separated from the mother liquor, washed with 1 mL of pentane (0 °C), and dried: yield 71 mg (97%), mp 60 °C dec. For the isomerization from **6** to **7**, a solution of **6** (120 mg, 0.19 mmol) in 10 mL of benzene was refluxed for 2 min. After the solution was cooled to room temperature, the solvent was removed and the oily residue dissolved in 1 mL of CH$_2$Cl$_2$. Upon addition of 10 mL of hexane and careful concentration of the solution in vacuo, pale yellow air-sensitive crystals were obtained. They were separated from the mother liquor, washed with 1 mL of pentane (−20 °C), and dried: yield 114 mg (95%), mp 106 °C dec.

Scheme 3



Scheme 4



both of these signals are split into doublets.[7] Upon warming a solution of **6** in benzene for 2 min to reflux temperature, an isomerization occurs and the chloro(hydrido)iridium derivative **7** is formed.[14] We assume that the initial step of the conversion of **6** to **7** consists of the migration of the $CHPh_2$ unit from the metal center to the five-membered C_5H_5 ring forming an intermediate with a η^4-coordinated $C_5H_5CHPh_2$ cyclopentadiene ligand. We note that if the isomerization process of **6** to **7** is followed (in C_6D_6) by ^1H NMR spectroscopy, the formation of a new compound can be observed for which the appearance of two doublets at δ 3.42 and 3.19 (with a H−H coupling of ca. 10 Hz) is characteristic. In agreement with earlier observations,[15] we conclude that these signals belong to the four-coordinate iridium(I) species $[IrCl(\eta^4\text{-}C_5H_5CHPh_2)(P\textit{i}Pr_3)]$, which subsequently rearranges via a 1,2-hydrogen shift from the ring to iridium to give **7**. The ^1H NMR spectrum of **7** exhibits a resonance for the hydrido ligand at δ −14.4, which is shifted by ca. 2.2 ppm to higher field compared with the rhodium compound $[(\eta^5\text{-}C_5H_4CHPh_2)RhHCl(P\textit{i}Pr_3)]$.[15]

We have also examined the reactivity of the square-planar carbeneiridium(I) complex **4a** toward acids HX. Upon exposure of a solution of **4a** in benzene to dry HCl, a deep green compound is formed which is very labile and could not be isolated in analytically pure state. On the basis of its ^1H NMR spectrum, the reaction product from **4a** and HCl is the dichlorohydridoiridium(III) complex **8** (Scheme 4), which is generated via oxidative addition of the electrophile to the electron-rich metal center. The most typical spectroscopic feature of **8** is the hydride resonance at δ −19.2 which appears in the same region as that of related octahedral hydridobis(triisopropylphosphine) iridium derivatives.[16]

In contrast to compound **8**, the product obtained upon treatment of **4a** with aqueous HBF_4 is quite stable and has been characterized by elemental analysis and spectroscopic techniques.[17] The red air-sensitive solid **9** is soluble in acetone and CH_2Cl_2 (but insoluble in benzene and ether) and can be stored under argon for days. While it is conceivable that in acetone a 1:1 adduct is formed, the elemental analysis reveals that in the solid state an unsolvated species is present. The ^1H NMR spectrum of **9** displays a high-field signal (triplet) at δ −28.8 for the hydrido ligand, while the ^{13}C NMR spectrum exhibits a low-field resonance at 266.5 for the carbene carbon atom.[7] The appearance of this carbon signal at significantly lower field compared to **4a** (δ 234.7) and the methyleneiridium complex $[Ir({=}CH_2)\{\kappa^3\text{-}N(SiMe_2CH_2PPh_2)_2\}]$ (δ 200.1) could be due at least partly to the fact that the complex is cationic. Since according to the spectroscopic data the two phenyl groups are inequivalent, we tentatively propose a square-pyramidal geometry for the five-coordinate cation of **9** with the carbene ligand in the apical position. The free coordination site of **9** is readily occupied by chloride, and thus upon addition of NaCl to a solution of **9** in benzene/water the neutral species **8** is formed. In this context we note that most recently Kaska, Mayer, and co-workers discussed the generation of a labile, five-coordinate carbene(carbonyl)hydridoiridium species in which, however, the metal is in the +I and not, like in **9**, in the +III oxidation state.[18]

In conclusion, we have shown that by choosing the mixed-ligand system **2** as the starting material the preparation of a variety of new carbeneiridium complexes with different structural features can be achieved. The square-planar representative **4a**, containing a metal center with a 16-electron configuration, and the half-sandwich-type compound **5**, containing a metal center with an 18-electron configuration, behave differently toward acids HX, the former yielding a product with $IrH({=}CPh_2)$ and the latter with $Ir{-}CHPh_2$ as a molecular unit. We are currently exploring the scope and mechanism of C−C coupling reactions of the diarylcarbeneiridium complexes, particularly with olefins as substrates.

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Supporting Information Available: A table with the elemental analyses of compounds **2**, **3a**, **3b**, **4a**, **4b**, **5**, **6**, **7**, and **9** as well as fully labeled diagrams and tables of crystallographic data, data collection, solution and refinement details, positional and thermal parameters, and both distances and angles for **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) (a) Werner, H.; Höhn, A. *Z. Naturforsch., B* **1984**, *39*, 1505−1509. (b) Höhn, A.; Werner, H. *J. Organomet. Chem.* **1990**, *382*, 255−272.

(17) The preparation of **9** is as follows. A solution of **4a** (61 mg, 0.09 mmol) in 10 mL of CH_2Cl_2/pentane (1:1) was treated dropwise with an aqueous solution (50%) of HBF_4 as long as the formation of a red precipitate occurred. After 5 mL of distilled water was added to the solution, the liquid phase was removed and the residue extracted with 10 mL of CH_2Cl_2. The extract was concentrated to ca. 5 mL in vacuo and then layered with pentane. Upon storing for 2 h, the almost colorless mother liquor was separated, and the remaining red solid was washed with 5 mL of pentane and dried: yield 65 mg (95%); mp 91 °C dec.

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