Square-Planar Bis(triisopropylstibine)(olefin)iridium(I) Complexes and Their Rearrangement to (η^3-Allyl)hydridoiridium(III) Isomers

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In contrast to *trans*-[IrCl(C_2H_4)(Sb*i*Pr$_3$)$_2$] (**2**), which has been obtained from [IrCl(C_2H_4)$_2$-(Sb*i*Pr$_3$)$_2$] (**1**) by abstraction of ethene together with some byproducts, the corresponding cyclooctene iridium(I) complex *trans*-[IrCl(C_8H_{14})(Sb*i*Pr$_3$)$_2$] (**4**) can be prepared from [IrCl-(C_8H_{14})$_2$]$_2$ (**3**) and 4 equiv of Sb*i*Pr$_3$ in excellent yield. Compound **4** rearranges in hexane at room temperature to *anti,exo*-[IrHCl(η^3-C_8H_{13})(Sb*i*Pr$_3$)$_2$] (**5a**), which in benzene is in equilibrium with the *anti,endo* isomer **5b**. Compound **5a** is generated from **4** even in the solid state. Treatment of **4** with propene and 1-hexene results in the displacement of cyclooctene and affords *exo*-[IrHCl(η^3-C_3H_5)(Sb*i*Pr$_3$)$_2$] (**6a**) and *anti,exo*-[IrHCl(η^3-C_6H_{11})-(Sb*i*Pr$_3$)$_2$] (**7**), respectively. Similarly to **5a**, also **6a** isomerizes to *endo*-[IrHCl(η^3-C_3H_5)-(Sb*i*Pr$_3$)$_2$] (**6b**). The reaction of **6a** with HCl leads to the formation of [IrHCl$_2$(Sb*i*Pr$_3$)$_2$] (**8**), which forms the 1:1 adduct **9** with C_2H_4. The preparation of other bis(triisopropylstibine)-iridium complexes **10**−**12** has been achieved by using **4** as the starting material. Compounds **5a** and **6a** have been characterized crystallographically.

Introduction

A few years ago, we reported that square-planar carbenerhodium(I) complexes *trans*-[RhCl(=CRR′)(Sb*i*-Pr$_3$)$_2$] can be obtained from *trans*-[RhCl(C_2H_4)(Sb*i*Pr$_3$)$_2$] and diazoalkanes RR′CN_2 as the precursors.[1] The subsequent discovery that these rhodium carbenes provide a rich chemistry, including unusual C−C coupling reactions,[2] initiated our attempts to prepare also the (ethene)iridium counterpart *trans*-[IrCl(C_2H_4)(Sb*i*-Pr$_3$)$_2$] (**2**). However, instead of generating **2**, the reaction of the dimer [IrCl(C_2H_4)$_2$]$_2$ with excess Sb*i*Pr$_3$ yielded the five-coordinate [IrCl(C_2H_4)$_2$(Sb*i*Pr$_3$)$_2$] (**1**), which did not react with RR′CN_2 to give the desired complexes *trans*-[IrCl(=CRR′)(Sb*i*Pr$_3$)$_2$].[3] Therefore, we set out either to find another synthetic route to **2** or to prepare the related (olefin)iridium(I) compounds *trans*-[IrCl-(olefin)(Sb*i*Pr$_3$)$_2$] with the hope that they can be used as starting materials for the iridium carbenes. In the context of this work (which quite recently led to the synthesis of *trans*-[IrCl(=CRR′)(Sb*i*Pr$_3$)(P*i*Pr$_3$)])[4] we found that, in contrast to their rhodium analogues, square-planar (olefin)iridium(I) complexes *trans*-[IrCl-(olefin)(Sb*i*Pr$_3$)$_2$] are surprisingly labile and, at least in the case of cyclooctene, propene, and 1-hexene as ligands, rapidly rearrange by intramolecular oxidative addition to the (η^3-allyl)hydridoiridium(III) isomers. Some preliminary results of these studies have already been communicated.[5]

Results and Discussion

1. Preparation of (Olefin)iridium(I) Complexes *trans*-[IrCl(olefin)(Sb*i*Pr$_3$)$_2$] and Their (η^3-Allyl)-hydridoiridium(III) Isomers. In contrast to the bis-(phosphine) compounds [IrCl(C_2H_4)$_2$(PR$_3$)$_2$] (R = Ph,[6] Et[7]), the related bis(stibine) complex **1** is surprisingly inert and does not lose ethene upon stirring a solution in benzene at room temperature for 7 days. The generation of the four-coordinate compound **2** could only be achieved if a solution of **1** in pentane is refluxed under slightly reduced pressure for ca. 1 h. Under these conditions, the elimination of ethene is accompanied by both a change of color from light yellow to red and the formation of some unidentified byproducts. Since solutions of **2** in common organic solvents slowly decompose, attempts to obtain an analytically pure sample of the mono(olefin) complex failed. However, the spectroscopic data for the generated species leave no doubt that the proposed structure for **2**, shown in Scheme 1, is correct. In agreement with the square-planar coordination and the *trans* disposition of the stibine ligands, the ^{1}H NMR spectrum of **2** displays a single resonance for the olefin protons at δ 2.83 and a septet plus a doublet for the protons of the isopropyl groups at, respectively, δ 2.21

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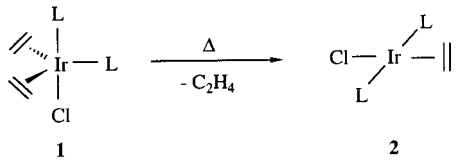
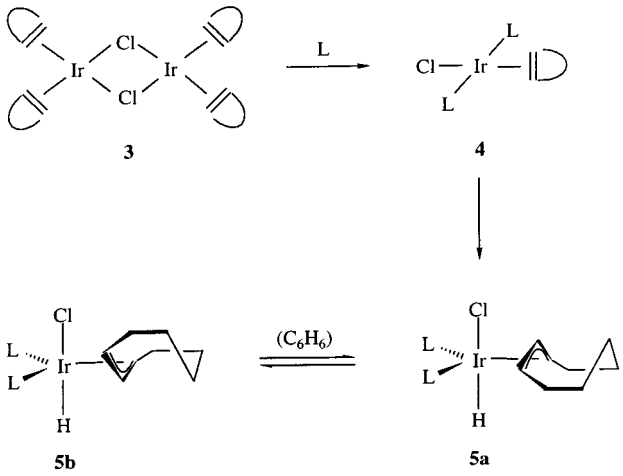
Scheme 1[a]



1 **2**

[a] L = Sb*i*Pr$_3$.

Scheme 2[a]



3 **4** **5b** **5a**

[a] L = Sb*i*Pr$_3$.

and 1.38 in an intensity ratio of 1:6. These data are almost identical with those of *trans*-[RhCl(C$_2$H$_4$)-(Sb*i*Pr$_3$)$_2$].[8]

To avoid the dilemma which we had with the isolation of **2**, we tried next to prepare the analogous cyclooctene derivative *trans*-[IrCl(C$_8$H$_{14}$)(Sb*i*Pr$_3$)$_2$] (**4**). Treatment of a suspension of the dimer **3** in pentane with 4 equiv of Sb*i*Pr$_3$ led to the rapid formation of an orange-red solution from which, after removal of the solvent and low-temperature recrystallization of the residue from acetone, a product of analytical composition corresponding to **4** could be obtained. While the bright orange solid is stable under argon at −78 °C for weeks, in benzene solution at room temperature a relatively fast rearrangement occurs. The ^{1}H NMR spectrum (in C$_6$D$_6$) of **4**, taken immediately after the time of mixing, displays a resonance for the protons of the cyclooctene C═C bond at δ 3.52 as well as two signals for the CH and CH$_3$ protons of the isopropyl unit at δ 2.38 and 1.46, respectively. Already after a few minutes, in the ^{1}H NMR spectrum of the same solution new signals appear which are assigned to the isomer **5a** (Scheme 2). Typical features of this (η^3-cyclooctenyl)hydridoiridium(III) complex, which was isolated as a colorless crystalline solid from hexane, are both the hydride resonance at δ −29.24 and the two signals (a doublet of triplets and a triplet) for the allylic protons in the ^{1}H NMR spectrum. The ^{13}C NMR spectrum equally exhibits two signals at δ 98.1 and 49.3 for the −CH*C*HCH− and −*C*HCH*C*H− carbon atoms. The IR spectrum of **5a** shows a strong absorption at 2183 cm^{-1} for the Ir−H stretching mode.

Quite unexpectedly, **5a** partially rearranges in C$_6$D$_6$ to a second isomer, **5b**. The conversion stops if the ratio **5a**:**5b** = 1:5 is established, which does not change even if the solution is stored for 1 week. The ^{1}H NMR spectrum of **5b** displays a signal for the metal-bound proton at δ −28.02 (which is ca. 1.2 ppm downfield compared with **5a**) and resonances for the central and the terminal allylic protons at δ 4.96 (triplet) and 4.11 (doublet of triplets). We note that this order is the reverse of what had been observed for **5a**. Since the difference in the chemical shift for most of the other signals of **5a** and **5b** is rather small, we assume that the structures of the two isomers differ only in the orientation of the η^3-cyclooctenyl unit toward the IrHCl-(Sb*i*Pr$_3$)$_2$ moiety. If we take into consideration that, on the basis of the spectroscopic data, the two triisopropylstibine ligands of **5a** and **5b** are stereochemically equivalent and cis disposed in the octahedral coordination sphere, the central CH entity of the allylic system can point toward either the hydrido or the chloro ligand. When a boat conformation is assumed for the bidentate η^3-C$_8$H$_{13}$ unit, the *endo* configuration corresponding to **5b** might be favored in agreement with the ratio of the two isomers in solution. However, the kinetically preferred species is certainly the *exo* isomer **5a**, which is also (and exclusively) formed by storing the solid olefin complex **4** in a Schlenk tube under argon at room temperature for 4 weeks. We have confirmed that the isomerization of **5a** to **5b** takes place only in solution but not in the solid state.

Attempts to displace the cyclooctene ligand of **4** by propene and generate the analogous olefin complex *trans*-[IrCl(C$_3$H$_6$)(Sb*i*Pr$_3$)$_2$] led to the formation of the (η^3-allyl)hydridoiridium(III) isomer **6a** in good yield (Scheme 3). The same product is also obtained upon treatment of the dimer [IrCl(C$_3$H$_6$)$_2$]$_2$[9] with excess triisopropylstibine. The ^{1}H NMR spectrum of **6a** (which is a colorless, practically air-stable solid) exhibits a signal for the hydrido ligand at δ −28.61 and resonances for the allylic protons at δ 4.03 (central CH), 3.97 (*syn*-CH$_2$), and 2.51 (*anti*-CH$_2$), respectively. These data are slightly different from those of the related bis(phosphine) compound [IrH(O$_2$CCF$_3$)(η^3-C$_3$H$_5$)(P*i*Pr$_3$)$_2$], which was prepared from the monomeric iridium(I) precursor [Ir(η^3-C$_3$H$_5$)(P*i*Pr$_3$)$_2$] and CF$_3$CO$_2$H.[10]

Similarly to **5a**, **6a** also rearranges in C$_6$D$_6$ at room temperature to the corresponding *endo* isomer **6b**. In this case, the equilibrium lies almost entirely on the side of the thermodynamically preferred species **6b**. With regard to the spectroscopic data of **6b**, characteristic features are the position of the resonance of the central allylic proton in the ^{1}H NMR (which appears at δ 4.60 and thus ca. 0.6 ppm downfield compared to **6a**) and the chemical shifts of both the CH$_2$ and CH allylic carbon atoms in the ^{13}C NMR spectrum, the difference being much less than for **6a**. The proposal that **6b** is indeed the *endo* isomer is strongly supported by NOE measurements, which reveal, in agreement with earlier work by Fryzuk et al.,[11] that the intensity of the hydride signal at δ −28.30 is enhanced by irradiating the resonance of the allylic CH proton at δ 4.60 and vice versa.

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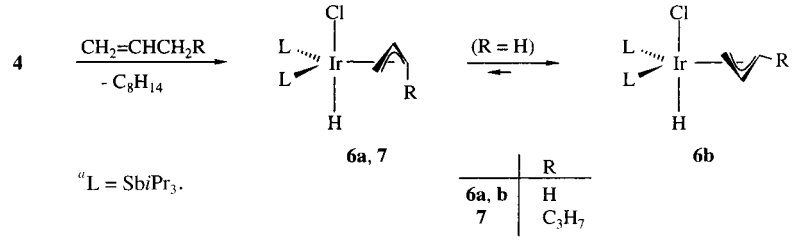
Scheme 3[a]



[a] L = Sb*i*Pr$_3$.

The reaction of the cycloocteneiridium(I) compound **4** with 1-hexene in pentane takes a course similar to that of **4** with propene. After the solution is stirred for 1 h at room temperature and the solvent is evaporated, a yellow oil is isolated, the analytical composition of which corresponds to **7**. The ^{1}H NMR spectrum of **7** (in C_6D_6) displays a hydride resonance at δ −28.56 which appears at almost the same position as that of **6a**. However, in contrast to **6a** (and also to **5a**), the (η^3-hexenyl)hydridoiridium(III) complex **7** is configurationally stable; even after it is stored for 1 week in benzene, **7** does not rearrange to the corresponding *endo* isomer. From a C−H correlation spectrum it can be concluded that the propyl substituent at one of the terminal allylic carbon atoms of **7** occupies an *anti* position, similar to what has been recently observed for the half-sandwich-type iridium(III) derivative *anti,exo*-[Tp*IrH(η^3-C_3H_4-Me)].[12] The signal for the *syn* proton H^4 (for assignment, see the Experimental Section) is split into a doublet of doublets of doublets, the coupling constant ^3J(H^{4}H^1) being of the order which is also found in other *anti*-η^3-C_3H_4R metal compounds.[11−13]

2. Molecular Structure of Compounds 5a and 6a. To prove that the kinetically preferred isomers of the (η^3-allyl)hydridoiridium(III) complexes obtained from (cyclooctene)- and (propene)iridium(I) precursors possess the *exo* configuration, the molecular structures of **5a** and **6a** were determined by X-ray crystallography. The results are shown in Figures 1 and 2, and the important bond lengths and bond angles are summarized in Tables 1 and 2, respectively.

The coordination geometry around the iridium center in both compounds is distorted octahedral, the cyclooctenyl or the allyl ligand occupying two basal coordination sites and the stibines the two others. The hydride (the position of which could only be localized for **6a**) and the chloride are in the apical positions. The Ir−Sb bond lengths in **5a** and **6a** are almost identical and quite similar to those found in [IrCl(C_2H_4)$_2$-(Sb*i*Pr$_3$)$_2$][3] and *trans*-[IrCl{κ^1(*N*)-$N_2C_5Cl_4$}(Sb*i*Pr$_3$)$_2$].[14] The Sb−Ir−Sb bond angles in both complexes are also nearly the same. In agreement with the structure proposed in solution on the basis of the NMR data, also in the crystals of **5a** and **6a** the allyl moiety points toward the chloro ligand. As expected, the distance between the metal and the central allylic carbon atom

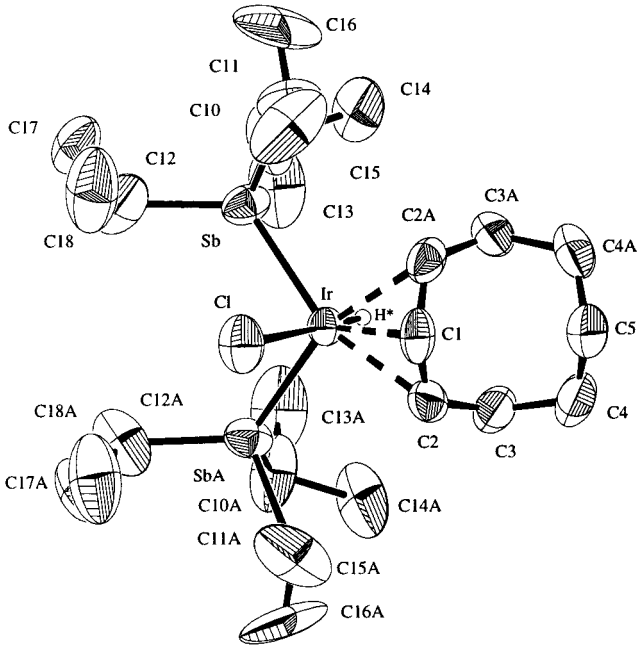


Figure 1. Solid-state structure of **5a**, with anisotropic uncertainty parameters depicting 50% probability. Hydrogen atoms other than H* have been omitted for clarity.

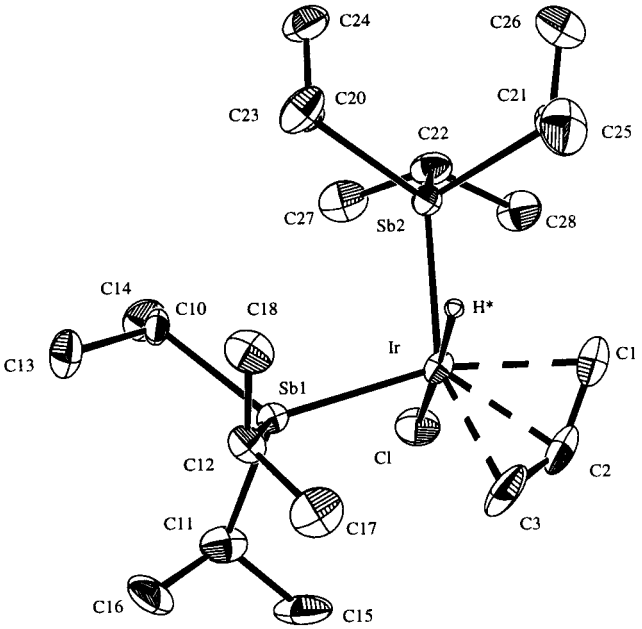


Figure 2. Solid-state structure of **6a**, with anisotropic uncertainty parameters depicting 50% probability. Hydrogen atoms other than H* have been omitted for clarity.

is significantly shorter (ca. 0.14 Å in **5a** and ca. 0.07 Å in **6a**) than the distances between iridium and the

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Table 1. Selected Bond Distances and Angles with Esd's for Compound 5a

	Bond Distances (Å)		
Ir−Sb	2.565(1)	C1−C2	1.407(9)
Ir−Cl	2.513(3)	C2−C3	1.51(1)
Ir−C1	2.110(9)	C3−C4	1.54(1)
Ir−C2	2.254(7)	C4−C5	1.52(1)
	Bond Angles (deg)		
Cl−Ir−Sb	88.78(5)	C2−C1−C2A	121(1)
Cl−Ir−C2	99.5(2)	C2−C1−Ir	76.8(5)
Cl−Ir−C1	82.5(3)	C1−C2−Ir	65.7(5)
Sb−Ir−C1	126.51(5)	C1−C2−C3	124.5(8)
Sb−Ir−C2	159.0(2)	C2−C3−C4	112.6(7)
Sb−Ir−SbA	105.78(4)	C3−C4−C5	117.5(8)
C1−Ir−C2	37.4(2)	C4−C5−C4A	117(1)

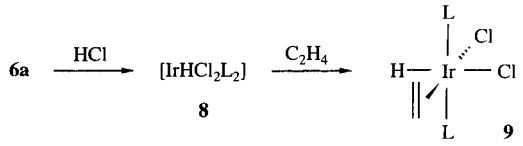
Table 2. Selected Bond Distances and Angles with Esd's for Compound 6a

	Bond Distances (Å)		
Ir−Sb1	2.5642(5)	Ir−C2	2.139(7)
Ir−Sb2	2.5569(7)	Ir−C3	2.227(7)
Ir−Cl	2.518(2)	C1−C2	1.36(1)
Ir−C1	2.214(7)	C2−C3	1.42(1)
	Bond Angles (deg)		
Cl−Ir−Sb1	90.51(4)	Sb2−Ir−C1	91.5(2)
Cl−Ir−Sb2	92.05(4)	Sb1−Ir−C3	94.9(2)
Cl−Ir−C1	96.3(2)	C1−C2−C3	122.8(9)
Cl−Ir−C2	81.8(3)	Sb1−Ir−Sb2	105.93(2)
Cl−Ir−C3	99.0(3)		

terminal allylic carbons, a fact which is equally reflected in the different chemical shifts of the respective ^{13}C nuclei in the NMR spectra. The C−C distances of the allylic units lie between those for a single and a double carbon−carbon bond and are in accordance with those of *syn,endo*-[IrHCl(η^3-C_3H_4Ph)(PPh_3)$_2$][15] and the Fryzuk compounds.[11] The Ir−H bond length in **6a** is approximately 1.85 Å and thus slightly longer than in some other hydridoiridium(III) complexes.[11,12,15,16]

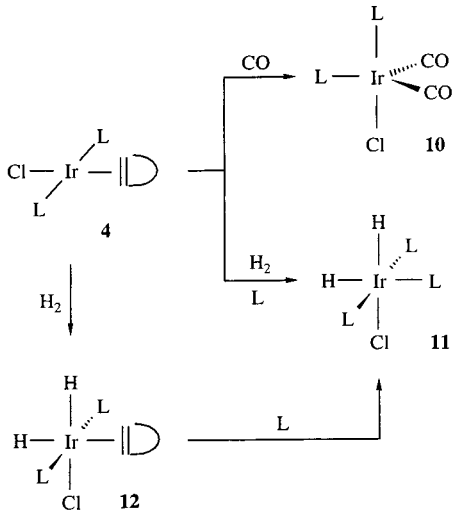
3. Five- and Six-Coordinate (Triisopropylstibine)iridium Complexes with Olefins, CO, and Hydride as Ligands. In agreement with earlier observations about the reactivity of (η^3-allyl)hydridoiridium(III) compounds with two triisopropylphosphine ligands,[10] the related stibine complex **6a** is thermally quite stable and upon heating in THF under reflux, either in the presence or in the absence of acetonitrile, does not eliminate propene. However, if a solution of **6a** in CH_2Cl_2 is stirred for 10 min under an atmosphere of HCl, a change of color occurs and, after removal of the solvent, an orange air-sensitive oil with the analytical composition corresponding to **8** can be isolated. Although **8** slowly decomposes in solutions of most common organic solvents, the ^1H and ^{13}C NMR spectra (in CD_2Cl_2) indicate that the two Sb*i*Pr$_3$ ligands are stereochemically nonequivalent. Therefore, we assume that the configuration of **8** corresponds to either a trigonal bipyramid or a square pyramid with one stibine in a (or the) apical position. In this context it is worth mentioning that also in the five-coordinate starting material **1** the two stibines occupy two different coordination sites, the reason probably being steric in nature.

Scheme 4[a]



[a] L = Sb*i*Pr$_3$.

Scheme 5[a]



[a] L = Sb*i*Pr$_3$.

The hydrido complex **8** reacts with CO (CH_2Cl_2, 25 °C) to give a mixture of products which we could not separate by fractional crystallization or other techniques. However, upon treatment of **8** with ethene under the same conditions a single compound **9** is formed which according to the elemental analysis is an 1:1 adduct of **8** and ethene. The ^1H and ^{13}C NMR data of **9** suggest that, in contrast to **8**, the two Sb*i*Pr$_3$ ligands are stereochemically equivalent and therefore an octahedral coordination geometry with the stibines in *trans* and the chlorides in *cis* disposition seems most likely (see Scheme 4). The hydride resonance appears in the ^1H NMR spectrum of **9** at δ −26.40, which is also consistent with a *trans* H−Ir−Cl arrangement.[3]

The studies undertaken about the reactivity of the new (cyclooctene)iridium(I) compound **4** toward CO and H_2 are outlined in Scheme 5. If a solution of **4** in pentane is exposed for 10 s to an atmosphere of carbon monoxide at −78 °C (i.e., at low temperature in order to avoid the isomerization of **4** to **5a**) and then warmed to 25 °C, a lemon yellow microcrystalline solid is obtained which owing to the analytical data and the mass spectrum is not the 16-electron monocarbonyl species but the 18-electron dicarbonyl complex **10**. While the IR spectrum clearly indicates that more than one CO ligand is present, the ^1H NMR spectrum of **10** displays at room temperature only one set of signals for the CH and CH_3 protons of the Sb*i*Pr$_3$ ligands, therefore suggesting that the two stibines are equivalent. However, when the solution is cooled to −30 °C, two sets of resonances for the methine and methyl protons are observed, which indicates that probably one of the triisopropylstibine

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ligands is in an apical and one in an equatorial position of a trigonal bipyramid. Such a sterochemical arrangement has also been found for the related bis(phosphine)-iridium(I) derivative $[Ir(SiMe_3)(CO)_2(PMe_3)_2]$,[17] which similarly to **10** is fluxional in solution.

Treatment of **4** with dihydrogen in hexane at −30 °C in the presence of Sb*i*Pr$_3$ affords the octahedral dihydridoiridium(III) complex **11** which was recently prepared in our laboratory from **3**, excess of Sb*i*Pr$_3$ and H_2.[3] If the reaction of **4** with H_2 is carried out in C_6D_6 at room temperature and monitored by ^{1}H NMR spectroscopy, the formation of an intermediate **12** is observed, the spectroscopic data of which are partly similar to those of **11**. The most typical features of the ^{1}H NMR spectrum of **12** are the two doublet resonances in the high-field region at δ −12.52 and −29.08 which are assigned to the hydrido ligands *trans* to cyclooctene and chloride. If 1 equiv of Sb*i*Pr$_3$ is added to the solution containing the in situ generated species **12**, the tris-(stibine)iridium(III) compound **11** is formed in practically quantitative yield. The presence of cyclooctene as the byproduct has been confirmed by GC/MS measurements.

To summarize the results discussed in this paper, we have shown that d^8 systems of the general composition *trans*-[IrCl(olefin)(Sb*i*Pr$_3$)$_2$] are thermodynamically unstable compared with their (η^3-allyl)hydridoiridium(III) isomers. Regardless of whether the olefinic ligand is propene, 1-hexene, or cyclooctene, a rearrangement of the isolated or in situ generated four-coordinate (olefin)-iridium(I) compound occurs under unusually mild conditions to give the stable six-coordinate iridium(III) complexes by intramolecular C−H activation. It should be emphasized that in no case, for **5a**,**b**, **6a**,**b**, or **7**, does a reductive elimination of the respective olefin from the (η^3-allyl)hydridoiridium(III) compound take place below the melting or decomposition temperature. This result is in contrast to numerous observations made in the context of studies about the transition-metal-catalyzed isomerization of olefins where (η^3-allyl)hydridometal species are postulated as reactive intermediates.[18] The reason that reductive elimination is less favored for the (η^3-allyl)hydrido complexes prepared in this work possibly lies in the nature of iridium as a 5d element, for which the oxidation state +III with an octahedral coordination geometry is strongly preferred.

Experimental Section

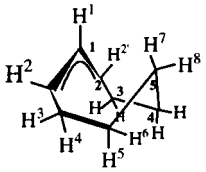
All reactions were carried out under an atmosphere of argon by Schlenk techniques. Solvents were dried by known procedures and distilled before use. The starting materials **1**[3] and **3**[6] were prepared as described in the literature. NMR spectra were recorded at room temperature on Bruker AC 200 and Bruker AMX 400 instruments. IR spectra were measured on a Perkin-Elmer 1420 and a Bruker IFS 25 spectrometer. Mass spectroscopic data were collected using a Finnigan 90 MAT instrument. Melting and decomposition points were determined by DTA.

Preparation of *trans*-[IrCl(C$_2$H$_4$)(Sb*i*Pr$_3$)$_2$] (2). A solution of **1** (87 mg, 0.11 mmol) in pentane (40 mL) was refluxed at ca. 20 mbar for 1 h. After the solution was cooled to room temperature, all volatiles were slowly removed in vacuo. During the evaporation the color of the mixture changed from pale yellow to red. The ^{1}H NMR spectrum of the resulting red solid showed, besides the signals of unidentified decomposition products, the expected resonances for **2.** Repeated recrystallization of the crude reaction product from acetone at −78 °C afforded ca. 8 mg (10%) of a bright red solid, which was dried in vacuo and characterized spectroscopically. Data for **2**: ^{1}H NMR (C_6D_6, 400 MHz) δ 2.83 (s, 4 H, C_2H_4), 2.21 (sept, J(HH) = 7.3 Hz, 6 H, SbC*H*CH$_3$), 1.38 (d, J(HH) = 7.3 Hz, 36 H, SbCHC*H*$_3$).

Preparation of *trans*-[IrCl(C$_8$H$_{14}$)(Sb*i*Pr$_3$)$_2$] (4). A suspension of **3** (74 mg, 0.08 mmol) in pentane (5 mL) was treated under continuous stirring with Sb*i*Pr$_3$ (69 μL, 0.33 mmol) at room temperature. The addition of the stibine led to a change of color from yellow to orange and at the same time to the formation of a clear solution. After the solvent was evaporated in vacuo, the residue was recrystallized from acetone at −78 °C to give bright orange crystals. These were washed with a small amount of acetone and dried in vacuo: yield 106 mg (79%); mp 40 °C dec; ^{1}H NMR (C_6D_6, 400 MHz) δ 3.52 (br m, 2H, CH of C_8H_{14}), 2.38 (sept, J(HH) = 7.3 Hz, 6H, SbC*H*CH$_3$), 1.46 (d, J(HH) = 7.3 Hz, 36H, SbCHC*H*$_3$). (The signals displayed by the CH_2 protons of **4** and **5a** are overlapping). Anal. Calcd for $C_{26}H_{56}ClIrSb_2$: C, 37.18; H, 6.72; Sb, 28.99. Found: C, 37.08; H, 6.88; Sb, 28.17.

Preparation of *anti,exo*-[IrHCl(η^3-C$_8$H$_{13}$)(Sb*i*Pr$_3$)$_2$] (5a). (a) A solution of **4** (67 mg, 0.08 mmol) in hexane (20 mL) was stirred at room temperature for 4 h, which resulted in a change of color from orange to pale yellow. The solution was concentrated to ca. 3 mL in vacuo and then stored at −78 °C for 12 h. Colorless crystals precipitated which were separated from the mother liquor and dried in vacuo: yield 58 mg (87%); mp 90 °C dec.

(b) A Schlenk flask containing **4** (194 mg, 0.23 mmol) was stored at room temperature for 4 weeks. A slow change of color from bright orange to pale yellow occurred. The quantitative conversion of **4** to **5a** was confirmed by ^{1}H NMR spectroscopy. Data for **5a** are as follows. IR (KBr): ν(IrH) 2183 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 5.01 (dt, $J(H^2H^1)$ = 8.0, $J(H^2H^3)$ = $J(H^2H^4)$ = 8.7 Hz, 2H, H$^{2,2'}$), 4.66 (t, $J(H^1H^2)$ = $J(H^1H^{2'})$ = 8.0 Hz, 1H, H^1), 2.44 (m, 2H, H$^{3,3'}$), 2.22 (m, 2H, H$^{4,4'}$), 2.27 (sept, J(HH) = 7.3 Hz, 6H, SbC*H*CH$_3$), 1.82−1.08 (br m, 6H, H$^{5,5',6,6',7,8}$), 1.41, 1.35 (both d, J(HH) = 7.3 Hz, 18H each, SbCHC*H*$_3$), −29.24 (s, 1H, IrH). ^{13}C{^{1}H} NMR (C_6D_6, 50.3 MHz): δ 98.1 (s, C^1), 49.3 (s, C$^{2,2'}$), 39.1, 29.7 (both s, C$^{3,3'}$ and C$^{4,4'}$), 25.3 (s, C^5), 21.9 (s, SbCH*C*H$_3$), 20.6 (s, Sb*C*HCH$_3$). Anal. Calcd for $C_{26}H_{56}ClIrSb_2$: C, 37.18; H, 6.72. Found: C, 37.47; H, 6.67.



Preparation of *anti,endo*-[IrHCl(η^3-C$_8$H$_{13}$)(Sb*i*Pr$_3$)$_2$] (5b). A solution of **5a** (35 mg, 0.04 mmol) in C_6D_6 (0.4 mL) was investigated by ^{1}H NMR spectroscopy at room temperature. After a few minutes, the generation of isomer **5b** was observed. Storing the solution for 2 days led to the formation of a mixture of **5a** and **5b** in the ration of 5:1. The removal of the solvent in vacuo resulted in the complete recovery of **5a**. Spectroscopic data for **5b** are as follows. IR (CH_2Cl_2): ν(IrH) 2171 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 4.96 (t, $J(H^1H^2)$ = $J(H^1H^{2'})$ = 7.2 Hz, 1H, H^1), 4.11 (dt, $J(H^2H^1)$ = 7.2, $J(H^2H^3)$ = $J(H^2H^4)$ = 9.0 Hz, 2H, H$^{2,2'}$), 2.43 (m, 2H, H$^{3,3'}$), 2.15 (sept, J(HH) = 7.2 Hz, 6H, SbC*H*CH$_3$), 1.92 (m, 2H, H$^{4,4'}$), 1.81−1.45 (br m, 6H, H$^{5,5',6,6',7,8}$), 1.35, 1.31 (both d, J(HH) = 7.2 Hz,

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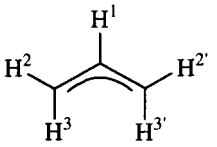
18H each, SbCHCH_3), −28.02 (s, 1H, IrH). $^{13}C\{^1H\}$ NMR (C_6D_6, 50.3 MHz): δ 74.2 (s, C^1), 45.0 (s, $C^{2,2'}$), 28.3, 25.7 (both s, $C^{3,3'}$ and $C^{4,4'}$), 25.4 (s, C^5), 21.7, 21.6 (both s, SbCHCH_3), 20.4 (s, SbCHCH_3).

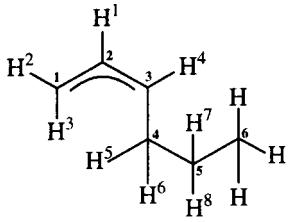
Preparation of *exo*-[IrHCl(η^3-C_3H_5)(Sb*i*Pr$_3$)$_2$] (6a). A solution of **4** (175 mg, 0.21 mmol) in hexane (10 mL) was exposed to an atmosphere of propene for 60 s at room temperature. After the resulting solution was stirred for 30 min, the solvent was removed in vacuo, and acetone (2 mL) was added to the oily residue. After the mixture was stored for 12 h at −78 °C, colorless crystals were formed. They were separated from the mother liquor and dried in vacuo: yield 104 mg (65%); mp 68 °C. IR (KBr): ν(IrH) 2141 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 4.03 (tt, $J(H^1H^3) = J(H^1H^{3'}) = 10.2$, $J(H^1H^2) = J(H^1H^{2'}) = 7.3$ Hz, 1H, H^1), 3.97 (d, $J(H^2H^1) = 7.3$ Hz, 2H, $H^{2,2'}$), 2.51 (d, $J(H^3H^1) = 10.2$ Hz, 2H, $H^{3,3'}$), 2.18 (sept, J(HH) = 7.3 Hz, 6H, SbCHCH_3), 1.32 (d, J(HH) = 7.3 Hz, 36H, SbCHCH_3), −28.61 (s, 1H, IrH). $^{13}C\{^1H\}$ NMR (C_6D_6, 50.3 MHz): δ 95.7 (s, CH_2CHCH_2), 28.1 (s, CH_2CHCH_2), 21.6, 21.5 (both s, SbCHCH_3), 20.0 (s, SbCHCH_3). Anal. Calcd for $C_{21}H_{48}ClIrSb_2$: C, 32.68; H, 6.27. Found: C, 32.36; H, 5.98.



Preparation of *endo*-[IrHCl(η^3-C_3H_5)(Sb*i*Pr$_3$)$_2$] (6b). A solution of **6a** (25 mg, 0.032 mmol) in C_6D_6 (0.4 mL) was stored at room temperature for 12 h. The IR and NMR spectra confirmed the quantitative conversion of **6a** to **6b**. Data for **6b** are as follows. IR (CH_2Cl_2): ν(IrH) 2170 cm^{-1}. ^{1}H NMR (C_6D_6, 200 MHz): δ 4.60 (tt, $J(H^1H^3) = J(H^1H^{3'}) = 11.6$, $J(H^1H^2) = J(H^1H^{2'}) = 5.8$ Hz, 1H, H^1), 3.96 (d, $J(H^2H^1) = 5.8$ Hz, 2H, $H^{2,2'}$), 2.41 (d, $J(H^3H^1) = 11.6$ Hz, 2H, $H^{3,3'}$), 2.14 (sept, J(HH) = 7.3 Hz, 6H, SbCHCH_3), 1.32, 1.24 (both d, J(HH) = 7.3 Hz, 18H each, SbCHCH_3), −28.30 (s, 1H, IrH). $^{13}C\{^1H\}$ NMR (C_6D_6, 50.3 MHz): δ 78.4 (s, CH_2CHCH_2), 42.6 (s, CH_2CHCH_2), 21.5, 21.4 (both s, SbCHCH_3), 19.7 (s, SbCHCH_3).

Preparation of *anti,exo*-[IrHCl(η^3-C_6H_{11})(Sb*i*Pr$_3$)$_2$] (7). A solution of **4** (60 mg, 0.07 mmol) in pentane (10 mL) was treated dropwise with 1-hexene (500 μL, excess) at −78 °C. After a few seconds a change of color from bright orange to light yellow was observed. The reaction mixture was then warmed to room temperature and stirred for 1 h. The solvent was removed in vacuo and the resulting yellow oil recrystallized from hexane at −78 °C to give a small quantity of pale yellow crystals. These were used to determine the melting point (56 °C) and to perform the elemental analysis. The spectroscopic measurements were done by using the yellow oil which was found pure by ^{1}H NMR spectroscopy. Yield of the yellow oil: 56 mg (quantitative). IR (C_6H_6): ν(IrH) 2146 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 4.59 (m, 1H, H^1), 3.74 (d, $J(H^2H^1) = 6.8$ Hz, 1H, H^2), 3.34 (ddd, $J(H^4H^5) = 10.3$, $J(H^4H^1) = 7.2$, $J(H^4H^6) = 2.9$ Hz, 1H, H^4), 2.43 (m, 1H, H^5), 2.26 (d, $J(H^3H^1) = 10.3$ Hz, 1H, H^3), 2.25, 2.14 (both sept, J(HH) = 7.6 Hz, 3H each, SbCHCH_3), 1.70 (m, 1H, H^6), 1.62, 1.55 (both m, 1H each, $H^{7,8}$), 1.42 (d, J(HH) = 7.5 Hz, 9H, SbCHCH_3), 1.34 (d, J(HH) = 7.9 Hz, 9H, SbCHCH_3), 1.32 (d, J(HH) = 7.9 Hz, 9H, SbCHCH_3), 1.25 (d, J(HH) = 7.6 Hz, 9H, SbCHCH_3), 1.00 (t, J(HH) = 7.5 Hz, 3H, CH_2CH_3), −28.56 (s, 1H, IrH). $^{13}C\{^1H\}$ NMR (C_6D_6, 50.3 MHz): δ 83.0 (s, C^2), 67.4 (s, C^3), 41.6 (s, C^4), 40.1 (s, C^1) 27.7 (s, C^5), 21.8, 21.4 (both s, SbCHCH_3), 20.1, 19.8 (both s, SbCHCH_3), 14.0 (s, C^6). Anal. Calcd for $C_{24}H_{54}ClIrSb_2$: C, 35.42; H, 6.69. Found: C, 35.18; H, 6.34.

Preparation of [IrHCl$_2$(Sb*i*Pr$_3$)$_2$] (8). A solution of **6a** (108 mg, 0.14 mmol) in dichloromethane (15 mL) was exposed to an atmosphere of HCl for 10 min at room temperature. A gradual change of color from pale yellow to yellow occurred.



After removal of the volatiles in vacuo, an orange oil was obtained which was dried in vacuo for 1 h: yield 110 mg (quantitative). IR (C_6H_6): ν(IrH) 2189 cm^{-1}. ^{1}H NMR (CD_2Cl_2, 200 MHz): δ 2.30 (m, 6H, SbCHCH_3), 1.32, 1.28 (both d, J(HH) = 7.3 Hz, 18H each, SbCHCH_3), −27.82 (s, 1H, IrH). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 100.6 MHz): δ 21.7, 21.6, 21.5, 21.4 (all s, SbCHCH_3), 21.3, 21.2 (both s, SbCHCH_3). Anal. Calcd for $C_{18}H_{43}Cl_2IrSb_2$: C, 28.22; H, 5.66. Found: C, 28.26; H, 5.38.

Preparation of [IrHCl$_2$(C_2H_4)(Sb*i*Pr$_3$)$_2$] (9). A solution of **8** (107 mg, 0.14 mmol) in dichloromethane (10 mL). was exposed to an atmosphere of ethylene for 10 min. After the solution was stirred for 20 min at room temperature, the solvent was evaporated in vacuo. The residue was dissolved in dichloromethane (ca. 1 mL), and hexane (3 mL) was added. The mixture was stored at −78 °C for 12 h, which led to the precipitation of yellow crystals. These were separated from the mother liquor, washed with a small quantitiy of pentane, and dried in vacuo: yield 99 mg (89%); mp 138 °C. IR (C_6H_6): ν(IrH) 2146 cm^{-1}. ^{1}H NMR (C_6D_6, 400 MHz): δ 2.77 (s, C_2H_4, 4H), 2.61 (sept, J(HH) = 7.3 Hz, 6H, SbCHCH_3), 1.41, 1.35 (both d, J(HH) = 7.3 Hz, 18H each, SbCHCH_3), −26.40 (s, 1H, IrH). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6): δ 25.7 (s, C_2H_4), 21.4, 21.3 (both s, SbCHCH_3), 19.2 (s, SbCHCH_3). Anal. Calcd for $C_{20}H_{47}Cl_2IrSb_2$: C, 30.25; H, 5.96. Found: C, 29.91; H, 5.65.

Preparation of [IrCl(CO)$_2$(Sb*i*Pr$_3$)$_2$] (10). A suspension of **4** (56 mg, 0.07 mmol) in pentane (10 mL) was exposed to an atmosphere of CO for 10 s at −78 °C. The reaction mixture was then warmed to room temperature and stirred for 20 min. A change of color from orange to yellow occurred. After the solution was concentrated to ca. 1 mL in vacuo, it was stored at −78 °C for 12 h. Lemon yellow crystals precipitated which were separated from the mother liquor, washed with small amounts of pentane, and dried in vacuo: yield 52 mg (94%);

Table 3. Crystallographic Data for 5a and 6a

	$C_{26}H_{56}ClIrSb_2$ (**5a**)	$C_{21}H_{48}ClIrSb_2$ (**6a**)
fw	839.90	771.79
cryst size, mm^3	0.2 × 0.3 × 0.4	0.35 × 0.15 × 0.12
cryst syst	orthorhombic	monoclinic
space group	*Pnma* (No. 62)	*C*2/*c* (No. 15)
cell dimens determn	25 rflns, 10° < θ < 15°	25 rflns, 10° < θ < 15°
a, Å	16.985(9)	42.07(1)
b, Å	20.150(9)	8.7348(9)
c, Å	9.374(3)	14.658(3)
β, deg		93.631(9)
V, Å^3	3208(2)	5375(2)
Z	4	8
d_{calcd}, g cm^{-3}	1.739	1.907
temp, K	293(2)	173(2)
μ, mm^{-1}	1.804	2.145
scan method	ω/θ	ω/θ
2θ(max), deg	64	54
total no. of rflns	6495	6125
no. of unique rflns	3312 (*R*(int) = 0.0577)	5501 (*R*(int) = 0.0221)
no. of obsd rflns ($I > 2\sigma(I)$)	2770	4593
no. of rflns used for refinement	4245	5501
no. of params refined	234	259
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0407, wR2 = 0.0864	R1 = 0.0324, wR2 = 0.0662
R indices (all data)	R1 = 0.0820, wR2 = 0.1136	R1 = 0.0456, wR2 = 0.0728
resid. electron density, e Å^{-3}	1.163/−0.833	0.865/−0.890

mp 77 °C dec. IR (C_6H_6): ν(CO) 1977 (sh), 1952 (vs), 1924 (s), 1898 (vs) cm^{-1}. ^1H NMR (C_6D_6, 200 MHz): δ 2.33 (sept, J(HH) = 7.3 Hz, 6H, SbC*H*CH_3), 1.36 (d, J(HH) = 7.3 Hz, 36H, SbCHC*H*$_3$). $^{13}C\{^1H\}$ NMR (C_6D_6, 100.6 MHz): δ 180.1 (br s, CO), 21.5 (s, SbCH*C*H$_3$), 19.6 (s, Sb*C*HCH$_3$); MS: m/z (I_r) 786 (0.2) [M^+], 758 (6) [M^+ − CO], 250 (46) [Sb*i*Pr_3^+]. Anal. Calcd for $C_{20}H_{42}ClIrO_2Sb_2$: C, 30.57; H, 5.39. Found: C, 30.38; H, 5.39.

Reaction of 4 with H_2. A solution of **4** (35 mg, 0.04 mmol) in C_6D_6 (0.4 mL) was exposed to an atmosphere of dihydrogen. The orange solution became immediately colorless, and the generation of the dihydridoiridium(III) compound **12** was observed by NMR spectroscopy. After addition of one equiv of Sb*i*Pr_3, the color of the solution changed to yellow and a grayish solid precipitated. After filtration the solid was identified as **11**, which can be prepared alternatively by reaction of **3** with 3 equiv of Sb*i*Pr_3/Ir in the presence of H_2.[3]

X-ray Structural Determination of Compounds 5a and 6a. Single crystals of **5a** and **6a** were grown from solutions in acetone at −30 and −60 °C, respectively. Crystal data and data collection parameters are summarized in Table 3. Intensity data were corrected by Lorentz and polarization effects, and an empirical absorption correction was applied in each case (minimum transmission 0.81 (**5a**), 0.89 (**6a**)). The structures were solved by direct methods (SHELXS-86),[19] while atomic coordinates and the anisotropic thermal parameters of non-hydrogen atoms were refined by full-matrix least squares on F^2 (SHELXL-93).[20] For **5a** a linear decay correction (intensity loss 6.7%) was applied. The isopropyl groups of the stibine ligands of **5a** are disordered. Two geometrically independent positions were found and refined anisotropically with occupancy factors 0.6:0.4. In the case of **6a**, the hydrogen atoms H1a/b, H2, H9a/b, and the hydridic hydrogen atom H* could be found in a differential Fourier analysis and refined without restrictions. The positions of all remaining hydrogen atoms in **6a** were calculated according to ideal geometry and were refined by using the riding method.

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Supporting Information Available: Tables of data collection parameters, bond lengths and angles, positional and thermal parameters, and least-squares planes for **5a** and **6a**; data for these compounds are also given in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OM001078R

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