Novel Trialkylstibane Iridium(I) and Iridium(III) Complexes Including the X-ray Crystal Structure of Five-Coordinate $[IrCl(C_2H_4)_2(SbiPr_3)_2]$☆

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The reaction of $[IrCl(C_8H_{14})_2]_2$ (**2**) with $SbiPr_3$ in the presence of H_2 yields the dihydridoiridium(III) complex *cis,mer*-$[IrH_2Cl(SbiPr_3)_3]$ (**3**) which on treatment with CO and with HC≡CR (R = Ph, CO_2Me) affords the octahedral derivatives $[IrH_2Cl(CO)(SbiPr_3)_2]$ (**4**) and $[IrHCl(C{\equiv}CR)(SbiPr_3)_3]$ (**5**, **6**), respectively. The stibane ligand *trans* to hydride in **5** and **6** is rather labile and, therefore, **5** and **6** react with pyridine to give $[IrHCl(C{\equiv}CR)(py)(SbiPr_3)_2]$ (**7**, **8**). Five-coordinate bis(stibane)iridium(I) complexes $[IrCl(C_2H_4)_2(SbR_3)_2]$ (**10**–**12**) were prepared from $[IrCl(C_2H_4)_2]_2$ (**9**) and four equiv. of SbR_3 (R = *i*Pr, Me, Ph). The X-ray crystal structural analysis of **10** reveals a distorted trigonal-bipyramidal geometry around the metal center with one stibane ligand and the two olefinic ligands in the equatorial plane. Compound **10** reacts with NaC_5H_5 to yield $[C_5H_5Ir(C_2H_4)(SbiPr_3)]$ (**13**) and with different alkynes by partial or complete displacement of the ethene ligands to give *trans*-$[IrCl(PhC{\equiv}CPh)(SbiPr_3)_2]$ (**14**), $[IrHCl(C{\equiv}CTol)(C_2H_4)(SbiPr_3)_2]$ (**15**), and *trans*-$[IrCl\{{=}C{=}C(SiMe_3)R\}(SbiPr_3)_2]$ (**16**, **17**), respectively.

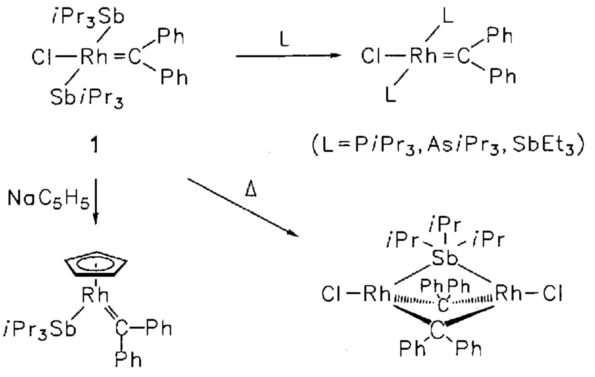
During investigations aimed to prepare carbenerhodium(I) complexes of the general composition *trans*-$[RhCl({=}CRR')(L)_2]$, we recently discovered that the type of ligand L has a remarkable influence on the reactivity of the precursor. While *trans*-$[RhCl(C_2H_4)(PiPr_3)_2]$ reacts with diphenyldiazomethane to give *trans*-$[RhCl(N_2CPh_2)(PiPr_3)_2]$, which on heating does not eliminate N_2 but instead yields *trans*-$[RhCl(N_2)(PiPr_3)_2]$[1], treatment of the corresponding bis(stibane) complex *trans*-$[RhCl(C_2H_4)(SbiPr_3)_2]$ with Ph_2CN_2 exclusively affords the carbene derivative *trans*-$[RhCl({=}CPh_2)(SbiPr_3)_2]$ (**1**)[2]. It was this result, combined with the observation that compound **1** is an excellent starting material for the preparation of a whole series of mono- and dinuclear carbenerhodium complexes (Scheme 1)[3], which prompted us to start an extensive research program concerned with the chemistry of low-valent transition-metal compounds having trialkylstibanes as ligands.

In this paper we describe the synthesis of a series of bis- and tris(stibane)iridium(I) and iridium(III) complexes in which, besides stibane, olefin, alkyne, and vinylidene ligands, hydride and alkynyl units are coordinated to the metal center. There are both similarities as well as differences in the structure and the behavior of related (triisopropylstibane)- and (triisopropylphosphane)iridium derivatives, which reflect not only the different size but also the unequal bonding capabilities of the two classes of ligands.

Dihydrido- and Alkynyl(hydrido)iridium(III) Complexes

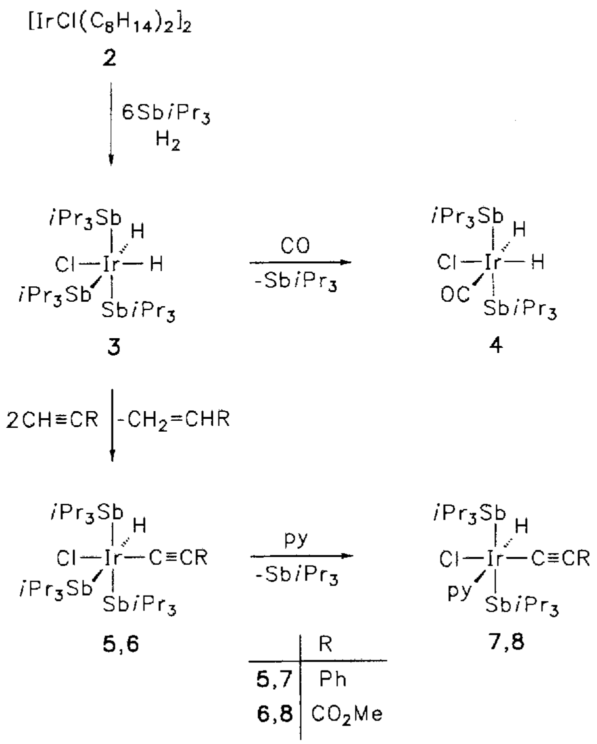
In contrast to the reaction of $[IrCl(C_8H_{14})_2]_2$ (**2**) with $PiPr_3$ which, in the presence of H_2, yields the five-coordinate compound $[IrH_2Cl(PiPr_3)_2]$[4], treatment of **2** with triisopropylstibane in hexane solution at −30 °C under hydrogen affords the octahedral iridium(III) complex $[IrH_2Cl(SbiPr_3)_3]$ (**3**) (Scheme 2). The composition of the white, only moderately air-sensitive solid was confirmed by elemental analysis and spectroscopic techniques. Whereas in the ^{1}H-NMR spectrum of $[IrH_2Cl(PiPr_3)_2]$ only one signal for the methyl protons of the isopropyl groups is observed, the ^{1}H-NMR spectrum of **3** displays two doublets for the $CH(CH_3)_2$ protons with the intensity ratio of 1:2 which illustrates the stereochemical inequivalence of the triisopropylstibane groups. Since also the two hydrido ligands are in a different environment (as confirmed by the two high-field NMR signals at δ = −14.94 and −28.24), there is no doubt that complex **3** has a *cis,mer* configuration. We note that in contrast to the sterically demanding triisopropylphosphane which gives the five-coordinate [IrH$_2$Cl(P-

Scheme 1



$iPr_3)_2]$[4], less bulky phosphanes such as PPh_3, $PMePh_2$, or PMe_2tBu all form six-coordinate tris(phosphane) species $[IrH_2Cl(PR_3)_3]$ for which in analogy to **3** a *cis,mer* arrangement of the hydrido and the PR_3 ligands seems to be preferred[5]. Tri*phenyl*stibane also yields a complex of the analytical composition $[IrH_2Cl(SbPh_3)_3]$ the configuration of which, however, is unknown[6].

Scheme 2



Treatment of **3** with CO in hexane at room temperature smoothly generates the monocarbonyl derivative **4** in 60–65% yield. Due to the strong *trans*-labilizing effect of the hydrido ligand, we assume that it is the stibane group *trans* to the hydride in the starting material which has been displaced. In agreement with the proposed structure for compound **4** (which forms yellow, almost air-stable crystals), the IR spectrum displays two Ir–H stretching frequencies (at 2150 and 2045 cm^{-1}) and the ^1H-NMR spectrum two high-field signals (at $\delta = -8.90$ and -22.21) which indicate that the bonding situation of the two hydrido ligands is significantly different. Relating the spectroscopic data of **4** to those of $[IrH_2Cl(CO)(PiPr_3)_2]$[7], we assume that the ν(IrH) stretching vibration at 2045 and the doublet at $\delta = -8.90$ belong to the metal-bound hydride *trans* to CO while the corresponding absorption at 2150 cm^{-1} and the signal at $\delta = -22.21$ belong to the hydride *trans* to Cl. The two stibane units in **4** are stereochemically equivalent and thus definitely *trans* to each other since in the ^1H- and the ^{13}C-NMR spectra only one set of signals both for the CH and CH_3 protons and carbon atoms were observed.

Compound **3** reacts with terminal alkynes such as $HC{\equiv}CPh$ and $HC{\equiv}CCO_2Me$ to give the six-coordinate alkynyl(hydrido)iridium(III) complexes **5** and **6** in 60–70% yield. To complete the reaction, two equivalents of the alkyne have to be used since besides **5** and **6** equal quantities of the corresponding olefin $CH_2{=}CHR$ (R = Ph, CO_2Me) are formed. By comparison with the spectroscopic data of $[IrHCl(C{\equiv}CPh)(PMePh_2)_3]$ for which two isomers having the alkynyl ligand either *trans* to the phosphane or to the chloro ligand are known[8], we propose the structures shown in Scheme 2 for **5** and **6**. This proposal is supported, inter alia, by the position of the hydride signal in the ^1H-NMR spectra of **5** ($\delta = -13.52$) and **6** ($\delta = -13.00$) which appears in the same region as that of the hydrido ligand *trans* to $SbiPr_3$ in the starting complex **3**. The assignment of the ^{13}C-NMR signals to the α- and β-carbon atoms of the alkynyl groups in **5** and **6** follows the trend which was established for related octahedral alkynyl(hydrido)rhodium(III) derivatives[9].

Similar to the dihydrido compound **3**, the stibane ligand *trans* to hydride is quite labile in **5** and **6** and therefore can be easily replaced by pyridine. The reaction of **5** and **6** with pyridine in hexane at room temperature is complete after a few minutes and affords the complexes **7** and **8** in good to excellent yield. It is possible to prepare **7** and **8** also directly from **3** if this compound is treated first with the alkyne and then with pyridine. The spectroscopic data of **7** and **8**, which are yellow or orange, almost air-stable solids, are in complete agreement with what was expected by a comparison with complex **4** and need no further comment.

Attempts to transform compounds **5**, **6** or **7**, **8** to the corresponding vinylidene complexes *trans*-$[IrCl(=C=CHR)(SbiPr_3)_2]$ (R = Ph, CO_2Me) with concomitant elimination of a stibane or pyridine ligand failed. Neither on heating (in toluene at 110°C) nor on photolysis does a migration of the metal-bonded hydride to the β-carbon atom of the alkynyl group occur in contrast to the formation of *trans*-$[(IrCl(=C=CHR)(PiPr_3)_2]$ from alkynyl(hydrido)iridium(III) precursors[10]. Also the reaction of **5** or **6** with methyl iodide which was performed in the hope that the labilized $SbiPr_3$ ligand could be trapped by CH_3I and the coordinatively unsaturated intermediate $[IrHCl(C{\equiv}CR)(SbiPr_3)_2]$ thus formed would then rearrange to give *trans*-$[IrCl(=C=CHR)(SbiPr_3)_2]$, remained unsuccessful.

Preparation and Structure of Five-Coordinate Bis(ethene)iridium(I) Compounds

After the above-mentioned attempts to prepare square-planar vinylideneiridium(I) complexes containing two triisopropylstibane ligands had failed, we considered the displacement of ethene in *trans*-$[IrCl(C_2H_4)(SbiPr_3)_2]$ by $HC{\equiv}CR$ followed by an alkyne-to-vinylidene rearrangement as an alternative route to obtain *trans*-$[IrCl(=C=CHR)(SbiPr_3)_2]$. We knew that at least in *trans*-$[RhCl(C_2H_4)(SbiPr_3)_2]$[2,11] and *trans*-$[IrCl(C_8H_{14})(PiPr_3)_2]$[10] the olefinic moiety is rather labile and can be easily displaced by σ- as well as π-donor ligands.

In contrast to the reaction of $[IrCl(C_2H_4)_2]_2$ (**9**) with PPh_3[12] and $PiPr_3$[13] which affords *trans*-$[IrCl(C_2H_4)$-

$(PR_3)_2]$, the five-coordinate bis(ethene) complex **10** is formed quite unexpectedly quantitatively by treatment of **9** with four equivalents of Sb*i*Pr$_3$ in hexane at −30°C under ethene. The composition of the yellow crystalline solid was confirmed both by elemental analysis and spectroscopic techniques (Eq. 1). Compound **10** is air-stable and soluble in most organic solvents. The ^{1}H-NMR spectrum displays two sets of signals for the CH and CH$_3$ protons of the isopropyl groups and two multiplets for the eight protons of the two ethene ligands. In the ^{13}C-NMR spectrum of **10** also two sets of resonances for the CH and CH$_3$ carbon atoms appear as well as two signals for the CH$_2$ carbons of the olefins.

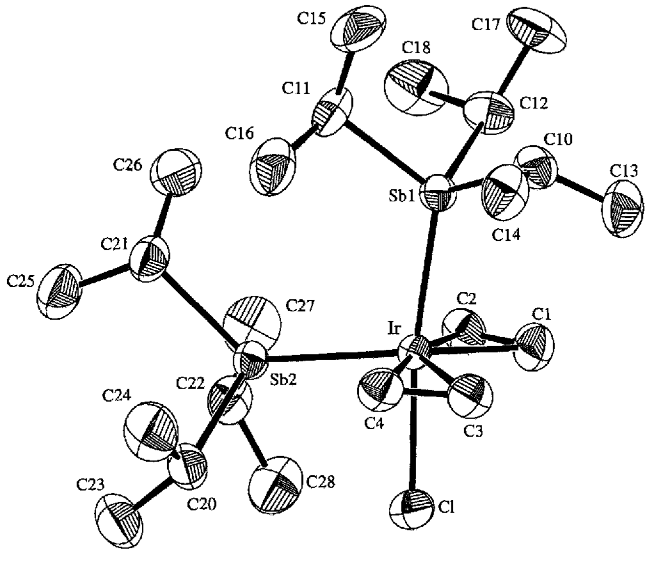
Trimethyl- and triphenylstibane behave similarly to Sb*i*Pr$_3$ and react with **9** in hexane at room temperature to give the five-coordinate compounds **11** and **12** (Eq. 1) in 90−95% yield. In complete analogy to the bis(triisopropylstibane) complex **10**, the stibane ligands in **11** and **12** are stereochemically different as is shown by the ^{1}H- and ^{13}C-NMR spectroscopic data. It should be noted that not only treatment of **9** with phosphanes gives monoethene complexes *trans*-$[IrCl(C_2H_4)(PR_3)_2]$[12,13]. Also the reaction of $[RhCl(C_2H_4)_2]_2$ (the rhodium analog of **9**) with Sb*i*Pr$_3$ leads to four-coordinate *trans*-$[RhCl(C_2H_4)(SbiPr_3)_2]$ instead of $[RhCl(C_2H_4)_2(SbiPr_3)_2]$[14]. Two compounds structurally related to **12** are $[IrCl(cod)(SbPh_3)_2]$[15] and $[IrCl(tfb)(SbPh_3)_2]$[16] (cod = 1,5-cyclooctadiene; tfb = tetrafluorobenzobarrelene) which have been prepared from $[IrCl(cod)]_2$ and $[IrCl(tfb)_2]$, respectively.

$$\underset{\textbf{9}}{[IrCl(C_2H_4)_2]_2} \xrightarrow{4SbR_3} 2\ [IrCl(C_2H_4)_2(SbR_3)_2] \qquad (1)$$

10: R = *i*Pr
11: R = Me
12: R = Ph

The structural proposal for **10** shown in Scheme 3 was confirmed by an X-ray crystal structural analysis. The ORTEP plot (Figure 1) reveals that the geometry around the metal center is distorted trigonal-bipyramidal. One of the stibane ligands is in an equatorial and one in an axial position, the latter being *trans* to the chloride atom. The Cl−Ir−Sb1 axis is only slightly bent [172.16(8)°] whereas the Cl−Ir−Sb2 [82.62(8)°] and even more so the Sb1−Ir−Sb2 angles [105.22(4)°] deviate significantly from 90°. The two Ir−Sb bond lengths are quite different [2.546(1) and 2.655(1) Å] which we attribute to the unequal position of the two stibanes together with the different *trans* influence of the chloride and the ethene ligands. Since to the best of our knowledge there are no structural data for *mononuclear* stibaneiridium(I) complexes, we can compare the Ir−Sb distances of **10** only with those of the dinuclear SbF$_2$-bridged compound $[Ir_2(\mu\text{-}SbF_2)(CO)_2Cl_2(\mu\text{-dpma})_2]^+$ [dpma = bis(diphenylphosphanylmethyl)phenylarsane] where Ir−Sb is 2.655(1) Å[17]. The four carbon atoms of the ethene ligands together with the iridium lie in a plane perpendicular to the Ir−Cl axis which is in agreement with theoretical studies[18].

Figure 1. Molecular structure (ORTEP diagram) of **10**; selected bond lengths [Å] and angles [°]: Ir−Sb1 2.546(1), Ir−Sb2 2.655(1), Ir−Cl 2.433(3), Ir−C1 2.14(1), Ir−C2 2.16(1), Ir−C3 2.13(1), Ir−C4 2.16(1), C1−C2 1.42(2), C3−C4 1.40(2), Cl−Ir−Sb1 172.16(8), Cl−Ir−Sb2 82.62(8), Cl−Ir−C1 86.0(4), Cl−Ir−C2 86.5(4), Cl−Ir−C3 83.6(4), Cl−Ir−C4 86.9(4), Sb1−Ir−C1 88.8(4), Sb1−Ir−C2 93.1(3), Sb1−Ir−C3 91.0(3), Sb1−Ir−C4 92.4(3), Sb1−Ir−Sb2 105.22(4), C1−Ir−C2 38.6(5), C3−Ir−C4 38.0(5)



Ligand Displacement Reactions of Complex 10

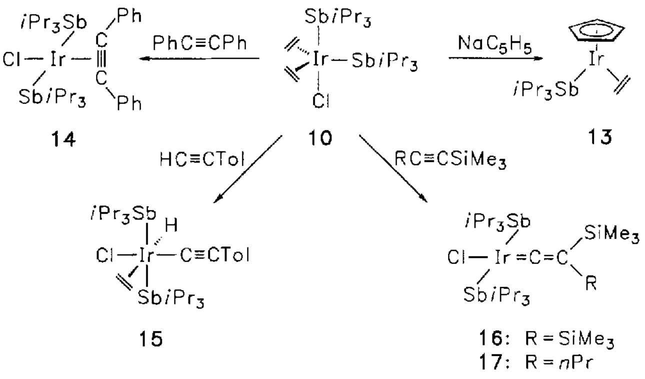
The reaction of the five-coordinate compound **10** with NaC$_5$H$_5$ in THF at ambient temperature leads to replacement of Cl$^-$ by C$_5$H$_5^-$ and, accompanied by elimination of one ethene and one stibane ligand, to the formation of complex **13**. The half-sandwich type compound is an analog of $[C_5H_5Ir(C_2H_4)(PiPr_3)]$ which was prepared by stepwise treatment of **9** with P*i*Pr$_3$ and LiC$_5$H$_5$[13]. As far as the spectroscopic data of **13** are concerned, the most characteristic feature is the ^{13}C-NMR signal for the ethene carbon atoms which appears at $\delta = -3.04$, i.e. at unusually high field.

The reactions of **10** with PhC≡CPh and HC≡CTol (Tol = p-CH$_3$C$_6$H$_4$) take a different course. While diphenylacetylene gives almost quantitatively the square-planar alkyneiridium(I) complex **14** (a dark red air-sensitive solid), with *p*-tolylacetylene the alkynyl(hydrido)iridium(III) derivative **15** is obtained instead (Scheme 3). The ^{1}H-NMR spectrum of **15** displays, besides the resonances for the phenyl and the stibane protons, one singlet at $\delta = -8.55$ for the metal-bound hydride and one singlet for the olefinic protons which is in agreement with the structural proposal. Although the spectroscopic data are not unambiguous as to whether the hydrido ligand is *trans* to the ethene or *trans* to the chloride, we assume that in analogy to **5** and **6** the first possibility is correct.

Since not only the attempts to transform **5**−**8** into *trans*-$[IrCl(=C=CHR)(SbiPr_3)_2]$ but also those to convert **15** into the corresponding iridium(I) complex *trans*-[IrCl(=C=CH-

Tol)(SbiPr$_3$)$_2$] failed, we used trimethylsilyl-substituted alkynes as alternative precursors for the generation of vinylidene ligands. We recently showed that various alkynylsilanes RC≡CSiMe$_3$ and RC≡CSiPh$_3$ react with [RhCl(PiPr$_3$)$_2$]$_2$ to yield *trans*-[RhCl(RC≡CSiR'$_3$)(PiPr$_3$)$_2$] (R' = Me, Ph) which either thermally or photochemically rearrange to the isomeric complexes *trans*-[RhCl{=C=C(SiR'$_3$)R}(PiPr$_3$)$_2$][19].

Scheme 3



Compound **10** reacts with both Me$_3$SiC≡CSiMe$_3$ and nPrC≡CSiMe$_3$ in hexane at 65°C to give the vinylideneiridium complexes **16** and **17** in 60–70% yield. For the complete conversion of the starting material to the products, an excess of the alkyne has to be used; the reason why the reaction does not go to completion in the presence of only one equivalent of RC≡CSiMe$_3$ is not clear as yet. The new vinylideneiridium complexes are deep red (**16**) or violet (**17**) air-sensitive solids which are highly soluble in all common organic solvents. The most typical spectroscopic features in the ^{1}H-NMR spectra are the signals at δ = 0.35 (**16**) and 0.29 (**17**) for the SiMe$_3$ protons and in the ^{13}C-NMR spectra the low-field signals at δ = 232.38 (**16**) and 239.69 (**17**) for the α-carbon atoms of the vinylidene ligand[20]. Since in the ^{1}H- as well as in the ^{13}C-NMR spectrum of **17** only one set of signals for the protons and the carbon atoms of the stibane CH$_3$ groups are observed, a rapid rotation of the vinylidene unit around the Ir=C bond can be assumed.

Conclusions

Although trialkyl- and triarylstibanes are known to behave as Lewis bases[21], the coordination chemistry of SbR$_3$ derivatives has received limited attention to date[22]. The lack of information becomes particularly obvious if the extensive literature on tertiary phosphane and also tertiary arsane transition-metal complexes is compared with that on stibane analogs[23]. The remarkable difference is not only due to the availability and the easy access of PR$_3$ and AsR$_3$ species but even more so to the significantly weaker σ-donor and π-acceptor capacities of the related stibanes.

Despite the electronic properties, however, also steric effects have to be taken into account. Based on the cone angle concept of Tolman[24], McAuliffe calculated the cone angles of tertiary stibane ligands which are 2–5° smaller than those of the corresponding phosphanes[25]. The decrease in bulkiness should result in higher coordination numbers of SbR$_3$ compared with PR$_3$ metal complexes, and exactly this was found in our investigations. Neither [IrH$_2$Cl(PiPr$_3$)$_n$] nor [IrHCl(C≡CR)(PiPr$_3$)$_n$] compounds with n = 3 are accessible[4,10,26] while, as shown in this paper, the corresponding Ir(SbiPr$_3$)$_3$ derivatives are readily formed. The difference in size (possibly assisted by the different donor/acceptor properties) may equally explain why [IrCl(C$_2$H$_4$)$_2$]$_2$ (**9**) reacts with PiPr$_3$ to give *trans*-[IrCl(C$_2$H$_4$)(PiPr$_3$)$_2$] but with SbiPr$_3$ to give five-coordinate [IrCl(C$_2$H$_4$)$_2$(SbiPr$_3$)$_2$] (**10**).

Besides the diminished coordinating abilities of tertiary stibanes, the present work nevertheless illustrates that by starting from readily available precursors such as **2** and **9** a whole series of hydrido-, alkynyl-, alkyne-, vinylidene- as well as olefiniridium(I) and -iridium(III) complexes, mainly containing SbiPr$_3$ as ligand, can be obtained. Triisopropylstibane seems to be more useful than SbMe$_3$ or SbPh$_3$, probably for similar reasons which make PiPr$_3$ more favorable for the synthesis of low-valent transition-metal compounds than other phosphanes[27]. Recent studies[2,3] as well as work in progress from our laboratory indicate that not only in rhodium and iridium but also in ruthenium and osmium chemistry[28] the use of trialkylstibanes as ligands may help to develop new preparative routes.

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Experimental

All operations were carried out under argon with the Schlenk tube technique. The starting materials **2**[29], **9**[30], SbiPr$_3$[14], and SbMe$_3$[31] were prepared by published procedures. – IR: Perkin-Elmer 1420. – NMR: Bruker AC 200 and AMX 400.

1. *Preparation of [IrH$_2$Cl(SbiPr$_3$)$_3$]* (**3**): A suspension of 135 mg (0.15 mmol) of **2** in 10 ml of hexane was treated at room temp. with 187 µl (0.90 mmol) of SbiPr$_3$. A rapid change of color from yellow to deep red occurred. The solution was cooled to −30°C and, after the argon was replaced by hydrogen, stirred for 10 min. The pale yellow solution was warmed to 25°C, then filtered, and the filtrate was stored at 0°C. White crystals precipitated, the formation of which was complete after storage for 1 h at −78°C. The crystals were filtered, washed with three 1-ml portions of pentane (0°C), and dried in vacuo; yield 201 mg (68%), m.p. 87°C. – IR (KBr): $\tilde{\nu}$ = 2120, 2040 cm^{-1} [ν(IrH)]. – ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ = 2.15 (m, 9H, SbCHCH$_3$), 1.44 [d, J(HH) = 7.3 Hz, 36H, SbCHCH_3], 1.31 [d, J(HH) = 7.3 Hz, 18H, SbCHCH_3], −14.94 [d, J(HH) = 7.2 Hz, 1H, IrH], – 28.24 [d, J(HH) = 7.2 Hz, 1H, IrH]. – ^{13}C NMR (C$_6$D$_6$, 100.6 MHz): δ = 22.11, 21.64, 21.57 (all s, SbCHCH$_3$), 21.24, 19.65 (both s, SBCHCH$_3$). – C$_{27}$H$_{65}$ClIrSb$_3$ (982.7): calcd. C 32.99, H 6.67; found C 32.96, H 6.93.

2. *Preparation of [IrH$_2$Cl(CO)(SbiPr$_3$)$_2$]* (**4**): A slow stream of CO was passed for 5 min through a solution of 94 mg (0.09 mmol) of **3** in 5 ml of hexane. After the solution had been stirred for 1 h at room temp., it was cooled to −78°C and stored for 3 h. A light

yellow microcrystalline solid precipitated which was separated from the mother liquor at −78 °C, washed with three 1 ml portions of pentane (−78 °C) and dried in vacuo; yield 45 mg (62%), m.p. 78 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 2150, 2045 cm^{-1} [ν(IrH)], 1935 [ν(CO)]. – ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ = 2.16 [sept, *J*(HH) = 7.3 Hz, 6H, SbC*H*CH$_3$], 1.29 [d, *J*(HH) = 7.3 Hz, 36H, SbCHC*H*$_3$], −8.90 [d, *J*(HH) = 5.8 Hz, 1H, IrH], −22.21 [d, *J*(HH) = 5.8 Hz, 1H, IrH]. – ^{13}C NMR (C$_6$D$_6$, 50.3 MHz): δ = 181.26 (s, CO), 21.21, 21.16 (both s, SbCH*C*H$_3$), 18.05 (s, Sb*C*HCH$_3$). – C$_{19}$H$_{44}$ClIrOSb$_2$ (759.7): calcd. C 30.04, H 5.84; found C 29.67, H 5.94.

3. *Preparation of [IrHCl(C≡CPh)(SbiPr$_3$)$_3$]* (**5**). – a) A solution of 169 mg (0.17 mmol) of **3** in 10 ml of hexane was treated with 38 μl (0.34 mmol) of phenylacetylene and stirred for 2 h at room temp. The solution was then heated for 5 min to 60 °C, which led to a change of color from light yellow to brown-yellow. After the reaction mixture had been cooled to 25 °C, the solvent was removed, the oily residue was dissolved in 2 ml of hexane, and the solution was chromatographed on Al$_2$O$_3$ (neutral, activity grade V, height of column 8 cm). With hexane, a yellow fraction was eluted which, after removal of the solvent, gave a yellow oil; yield 113 mg (60%).

b) A suspension of 183 mg (0.20 mmol) of **2** in 10 ml of hexane was treated at room temp. with 253 μl (1.225 mmol) of Sb*i*Pr$_3$. A dark red solution rapidly formed to which 45 μl (0.41 mmol) of phenylacetylene was added. The reaction mixture was stirred for 20 min at 25 °C, and then the solvent was removed. A brown oily residue remained which was purified by column chromatography as described for a). After recrystallization from 2 ml of hexane at −78 °C light yellow crystals were obtained; yield 309 mg (70%), m.p. 76 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 2095 cm^{-1} [overlap of ν(IrH) and ν(C≡C)]. – ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ = 7.28–6.87 (m, 5H, C$_6$H$_5$), 2.56 [sept, *J*(HH) = 7.3 Hz, 6H, SbC*H*CH$_3$], 2.44 [sept, *J*(HH) = 7.3 Hz, 3H, SbC*H*CH$_3$], 1.60 [d, *J*(HH) = 7.3 Hz, 18H, SbCHC*H*$_3$], 1.52 [d, *J*(HH) = 7.3 Hz, 36H, SbCHC*H*$_3$], −13.52 (s, 1H, IrH). – ^{13}C NMR (C$_6$D$_6$, 100.6 MHz): δ = 131.41, 130.64, 128.05, 123.97 (all s, C$_6$H$_5$), 105.10, 56.79 (both s, C≡C), 22.42 (s, SbCH*C*H$_2$), 21.83 (s, Sb*C*HCH$_3$), 21.75, 21.72 (both s, SbCH*C*H$_3$), 19.79 (s, Sb*C*HCH$_3$). – C$_{35}$H$_{69}$ClIrSb$_3$ (1082.9): calcd. C 38.82, H 6.42; found C 38.70, H 6.38.

4. *Preparation of [IrHCl(C≡CCO$_2$Me)(SbiPr$_3$)$_3$]* (**6**): A solution of 135 mg (0.14 mmol) of **3** in 10 ml of hexane was treated with 25 μl (0.28 mmol) of HC≡CCO$_2$Me and stirred for 1 h at 25 °C. After the reaction mixture had been heated for 10 min at 60 °C and then cooled to room temp., the solvent was removed in vacuo. The oily residue was dissolved in 2 ml of pentane, and the solution was stored for 12 h at −78 °C. Bright red crystals precipitated which were washed several times with small portions of pentane (−20 °C) and dried; yield 104 mg (70%), m.p. 77 °C. – IR (KBr): $\tilde{\nu}$ = 2083 cm^{-1} [overlap of ν(IrH) and ν(C≡C)], 1675 [ν(C=O)]. – ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ = 3.37 (s, 3H, CO$_2$CH$_3$), 2.58 [sept, *J*(HH) = 7.3 Hz, 6H, SbC*H*CH$_3$], 2.42 [sept, *J*(HH) = 7.3 Hz, 3H, SbC*H*CH$_3$], 1.57 [d, *J*(HH) = 7.3 Hz, 18H, SbCHC*H*$_3$], 1.50 [d, *J*(HH) = 7.3 Hz, 36H, SbCHC*H*$_3$], −13.08 (s, 1H, IrH). – ^{13}C NMR (C$_6$D$_6$, 50.3 MHz): δ = 153.12 (s, *C*O$_2$CH$_3$), 100.39, 73.32 (both s, C≡C), 50.72 (s, CO$_2$*C*H$_3$), 22.34 (s, SbCH*C*H$_3$), 22.01 (s, SbCHCH$_3$), 21.75, 21.70 (both s, SbCH*C*H$_3$), 20.10 (s, Sb*C*HCH$_3$). – C$_{31}$H$_{67}$ClIrO$_2$Sb$_3$ (1064.8): calcd. C 34.97, H 6.34; found C 34.99, H 6.62.

5. *Preparation of [IrHCl(C≡CPh)(py)(SbiPr$_3$)$_2$]* (**7**): A solution of 184 mg (0.17 mmol) of **5** in 4 ml of hexane was treated dropwise with 14 μl (0.17 mmol) of pyridine. After the solution had been stirred for 5 min, a yellow precipitate began to form. The reaction mixture was stored for 3 h at −78 °C, the microcrystalline yellow solid was separated, washed twice with 2 ml of pentane each and dried; yield 138 mg (89%), m.p. 132 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 2185 cm^{-1} [ν(IrH)], 2095 [ν(C≡C)]. – ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ = 10.35 (m, 2H, *o*-H of NC$_5$H$_5$), 7.47–6.52 (m, 8H, C$_6$H$_5$ and *m*-, *p*-H of NC$_5$H$_5$), 2.36 [sept, *J*(HH) = 7.3 Hz, 6H, SbC*H*CH$_3$], 1.29 [d, *J*(HH) = 7.3 Hz, 36H, SbCHC*H*$_3$], −21.86 (s, 1H, IrH). – ^{13}C NMR (C$_6$D$_6$, 100.6 MHz): δ = 154.13, 136.01, 131.49, 131.14, 127.88, 124.05, 124.00 (all s, NC$_5$H$_5$ and C$_6$H$_5$), 106.58, 71.22 (both s, C≡C), 21.29 (s, SbCH*C*H$_3$), 17.60 (s, Sb*C*HCH$_3$). – C$_{31}$H$_{53}$ClIrNSb$_2$ (910.9): calcd. C 40.87, H 5.86, N 1.54; found C 40.73, H 5.98, N 1.43.

6. *Preparation of [IrHCl(C≡CCO$_2$Me)(py)(SbiPr$_3$)$_2$]* (**8**): Analogously as described or **7**, using 192 mg (0.18 mmol) of **6** and 15 μl (0.18 mmol) of pyridine as starting materials we obtained orange-brown crystals; yield 127 mg (79%), m.p. 98 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 2175 cm^{-1} [ν(IrH)], 2080 [ν(C≡C)], 1680 [ν(C=O)]. – ^{1}H NMR (C$_6$D$_6$, 200 MHz): δ = 10.21 (m, 2H, *o*-H of NC$_5$H$_5$), 6.88–6.52 (m, 3H, *m*-, *p*-H of NC$_5$H$_5$), 3.50 (s, 3H, CO$_2$CH$_3$), 2.42 [sept, *J*(HH) = 6.9 Hz, 6H, SbC*H*CH$_3$], 1.32 [d, *J*(HH) = 6.9 Hz, 36H, SbCHC*H*$_3$], −21.42 (s, 1H, IrH). – ^{13}C NMR (C$_6$D$_6$, 50.3 MHz): δ = 154.32 (s, *C*O$_2$CH$_3$), 153.87, 136.32, 124.23 (all s, NC$_5$H$_5$), 101.33, 86.29 (both s, C≡C), 50.89 (s, CO$_2$*C*H$_3$), 21.23 (s, SbCH*C*H$_3$), 17.83 (s, Sb*C*HCH$_3$). – C$_{27}$H$_{51}$ClIrNO$_2$Sb$_2$ (892.9): calcd. C 36.32, H 5.76, N 1.57; found C 36.18, H 5.83, N 1.41.

7. *Preparation of [IrCl(C$_2$H$_4$)$_2$(SbiPr$_3$)$_2$]* (**10**): A solution of 167 mg (0.29 mmol) of **9** in 7 ml of hexane was stored under ethene at −30 °C. After the solution had become colorless, 244 μl (1.17 mmol) of Sb*i*Pr$_3$ was added. The reaction mixture was then warmed to room temp. and stirred for 30 min. Thereafter it was stored for 1 h at −78 °C which led to the precipitation of a pale yellow solid. This was filtered, washed with three 1-ml portions of pentane (−20 °C) and dried; yield 425 mg (93%), m.p. 64 °C (dec.). – ^{1}H NMR (C$_6$D$_6$, 400 MHz): δ = 3.64 (m, 2H, C$_2$H$_4$), 3.17 (m, 6H, C$_2$H$_4$), 2.54, 1.77 [both sept, *J*(HH) = 7.4 Hz, 3H each, SbC*H*CH$_3$], 1.45, 0.98 [both d, *J*(HH) = 7.4 Hz, 18H each, SbCHC*H*$_3$]. – ^{13}C NMR (C$_6$D$_6$, 50.3 MHz): δ = 22.30, 21.49 (both s, SbCH*C*H$_3$), 20.61, 18.02 (both s, C$_2$H$_4$), 19.85, 17.72 (both s, Sb*C*HCH$_3$). – C$_{22}$H$_{50}$ClIrSb$_2$ (785.8): calcd. C 33.63, H 6.41; found C 33.29, H 6.27.

8. *Preparation of [IrCl(C$_2$H$_4$)$_2$(SbMe$_3$)$_2$]* (**11**): A solution of 49 mg (0.09 mmol) of **9** in 5 ml of hexane was treated with 40 μl (0.36 mmol) of SbMe$_3$ and stirred for 1 h at room temp. A change of color from red to yellow occurred. After the reaction mixture had been stored at −78 °C for 30 min, a light yellow solid had formed which was separated from the solution, washed with three 5-ml portions of pentane and dried in vacuo; yield 104 mg (94%). – ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 2.82 (m, 2H, C$_2$H$_4$), 2.36 (m, 6H, C$_2$H$_4$), 1.18, 0.78 (both s, 9H each, SbCH$_3$). – ^{13}C NMR (CDCl$_3$, 100.6 MHz): δ = 21.45, 21.28 (both s, SbCH$_3$), −4.73, −7.38 (both s, C$_2$H$_4$). – C$_{10}$H$_{26}$ClIrSb$_2$ (617.5): calcd. C 19.45, H 4.24; found C 19.29, H 4.16.

9. *Preparation of [IrCl(C$_2$H$_4$)$_2$(SbPh$_3$)$_2$]* (**12**): Analogously as described for **11**, from 52 mg (0.09 mmol) of **9** and 127 mg (0.36 mmol) of SbPh$_3$ as starting materials a light yellow microcrystalline solid was obtained; yield 162 mg (91%). – ^{1}H NMR (CD$_2$Cl$_2$, 200 MHz): δ = 7.47–6.92 (m, 30H, C$_6$H$_5$), 3.42 (s, br, 2H, C$_2$H$_4$), 2.88 (s, br, 6H, C$_2$H$_4$). – ^{13}C NMR (CD$_2$Cl$_2$, 50.3 MHz): δ = 136.93, 136.12, 134.52, 131.12, 130.17, 129.82, 129.47, 127.05 (all s, C$_6$H$_5$), 26.23, 24.80 (both s, C$_2$H$_4$). – C$_{40}$H$_{38}$ClIrSb$_2$ (989.9): calcd. C 48.53, H 3.87; found C 48.56, H 4.10.

10. *Preparation of* $[C_5H_5Ir(C_2H_4)(SbiPr_3)]$ (**13**): A solution of 200 mg (0.25 mmol) of **10** in 20 ml of THF was treated at −78 °C with 27 mg (0.30 mmol) of NaC_5H_5. After the solution had been stirred for 10 min, it was slowly warmed to room temp. which led to the formation of a finely divided precipitate. The solvent was removed, the oily residue was extracted twice with 10 ml of pentane each, and the extract was evaporated to dryness in vacuo. The residue was dissolved in 2 ml of hexane, and the solution was chromatographed on Al_2O_3 (neutral, activity grade V, height of column 5 cm). With hexane, an almost colorless fraction (containg Sb*i*Pr_3) and then with THF a yellow fraction were eluted. The latter was concentrated in vacuo to give a yellow oil which was characterized by NMR spectroscopy; yield 60 mg (45%). – ^1H NMR (C_6D_6, 200 MHz): δ = 4.94 (s, 5H, C_5H_5), 2.36, 2.00 (both m, 2H each, C_2H_4), 1.76 [scpt, *J*(HH) = 7.1 Hz, 3H, $\mathrm{SbC}\mathit{H}\mathrm{CH_3}$], 1.10 [d, *J*(HH) = 7.1 Hz, 18H, $\mathrm{SbCHC}\mathit{H}_3$]. – ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 75.09 (s, C_5H_5), 21.25 (s, $\mathrm{SbCH}\mathit{C}\mathrm{H_3}$), 16.14 (s, $\mathrm{Sb}\mathit{C}\mathrm{HCH_3}$), −3.04 (s, C_2H_4).

11. *Preparation of trans-*$[IrCl(PhC{\equiv}CPh)(SbiPr_3)_2]$ (**14**): A solution of 176 mg (0.22 mmol) of **10** in 5 ml of hexane was treated with a solution of 40 mg (0.22 mmol) of diphenylacetylene. The reaction mixture was stirred for 2 h at room temp. which led to a change of color from orange to dark red. The solvent was removed in vacuo, and the oily residue was dissolved in 3 ml of pentane. Upon addition of 3 ml of methanol, the solution was concentrated until a precipitate began to form. The mother liquor was separated, the dark red microcrystalline solid was repeatedly washed with small portions of methanol and dried in vacuo; yield 186 mg (92%), m.p. 72 °C (dec.). – IR (C_6H_6): $\tilde{\nu}$ = 1835 cm^{-1} [ν(C≡C)]. – ^1H NMR (C_6D_6, 200 MHz): δ = 8.32 [d, *J*(HH) = 6.9 Hz, 4H, *o*-H of C_6H_5], 7.18–6.96 (m, 6H, *m*-, *p*-H of C_6H_5), 1.93 [sept, *J*(HH) = 6.9 Hz, 6H, $\mathrm{SbC}\mathit{H}\mathrm{CH_3}$], 1.16 [d, *J*(HH) = 6.9 Hz, 36H, $\mathrm{SbCHC}\mathit{H}_3$]. – ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 131.89, 130.19, 127.39, 126.29 (all s, C_6H_5), 66.76 (s, C≡C), 22.00 (s, $\mathrm{SbCH}\mathit{C}\mathrm{H_3}$), 17.81 (s, $\mathrm{Sb}\mathit{C}\mathrm{HCH_3}$). – $C_{32}H_{52}ClIrSb_2$ (907.9): calcd. C 42.33, H 5.77; found C 42.04, H 5.57.

12. *Preparation of* $[IrHCl(C{\equiv}CC_6H_4\text{-}p\text{-}CH_3)(C_2H_4)(SbiPr_3)_2]$ (**15**): A solution of 144 mg (0.18 mmol) of **10** in 10 ml of benzene was treated with 24 μl (0.18 mmol) of *p*-tolylacetylene and stirred for 3 h at room temp. A gradual change of color from pale yellow to yellow-brown occurred. The solvent was removed, the oily residue was dissolved in 3 ml of acetone, and the solution was stored at −78 °C for 12 h. Light yellow crystals formed which were filtered, washed twice with 1 ml of acetone each and dried in vacuo; yield 95 mg (59%), m.p. 68 °C (dec.). – IR (KBr): $\tilde{\nu}$ = 2110 cm^{-1} [overlap of ν(IrH) and ν(C≡C)]. – ^1H NMR (C_6D_6, 200 MHz): δ = 7.22, 7.00 [both d, *J*(HH) = 7.9 Hz, 2H each, C_6H_4], 3.82 (s, 4H, C_2H_4), 2.65 [sept, *J*(HH) = 7.9 Hz, 36H, $\mathrm{SbC}\mathit{H}\mathrm{CH_3}$], 2.16 (s, 3H, $\mathrm{C_6H_4C}\mathit{H}_3$), 1.53 [d, *J*(HH) = 7.9 Hz, 36H, $\mathrm{SbCHC}\mathit{H}_3$], −8.55 (s, 1H, IrH). – ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 133.78, 131.66, 128.76, 126.94 (all s, C_6H_4), 99.28, 57.65 (both s, C≡C), 44.92 (s, C_2H_4), 21.41 (s, $\mathrm{SbCH}\mathit{C}\mathrm{H_3}$), 21.08 (s, $\mathrm{C_6H_4}\mathit{C}\mathrm{H_3}$), 18.55 (s, $\mathrm{Sb}\mathit{C}\mathrm{HCH_3}$). – $C_{29}H_{54}ClIrSb_2$ (873.9): calcd. C 39.86, H 6.23; found C 39.60, H 6.25.

13. *Preparation of trans-*$[IrCl\{{=}C{=}C(SiMe_3)_2\}(SbiPr_3)_2]$ (**16**): A solution of 150 mg (0.19 mmol) of **10** in 10 ml of hexane was treated with 85 μl (0.38 mmol) of $C_2(SiMe_3)_2$ at room temp. and then stirred for 2 h at 65 °C. A change of color from pale yellow to red occured. After cooling to 25 °C, the solvent was removed, the residue was dissolved in 2 ml of pentane, and the solution was stored at −78 °C for 5 h. A deep red solid precipitated which was filtered, washed twice with 1 ml of pentane (−20 °C) each and dried in vacuo; yield 103 mg (60%), m.p. 132 °C (dec.). – IR (hexane): $\tilde{\nu}$ = 1610 cm^{-1} [ν(C=C)]. – ^1H NMR (C_6D_6, 200 MHz): δ = 2.56 [sept, *J*(HH) = 7.3 Hz, 6H, $\mathrm{SbC}\mathit{H}\mathrm{CH_3}$], 1.49 [d, *J*(HH) = 7.3 Hz, 36H, $\mathrm{SbCHC}\mathit{H}_3$], 0.35 (s, 18H, $SiCH_3$). – ^{13}C NMR (C_6D_6, 100.6 MHz): δ = 232.38 (s, Ir=C), 87.42 (s, $={\mathit{C}}\mathrm{R_2}$), 22.38 (s, $\mathrm{SbCH}\mathit{C}\mathrm{H_3}$), 18.69 (s, $\mathrm{Sb}\mathit{C}\mathrm{HCH_3}$), 2.31 (s, $SiCH_3$). – ^{29}Si NMR (C_6D_6, 39.7 MHz): δ = −28.43 (s). – $C_{26}H_{60}ClIrSb_2Si_2$ (900.1): calcd. C 34.69, H 6.72; found C 34.46, H 6.86.

14. *Preparation of trans-*$[IrCl\{{=}C{=}C(SiMe_3)nPr\}(SbiPr_3)_2]$ (**17**): Analogously as described for **16**, from 172 mg (0.22 mmol) of **10** and 81 μl (0.44 mmol) of 1-(trimethylsilyl)-1-pentyne as starting materials a violet microcrystalline solid was obtained; yield 136 mg (71%), m.p. 40 °C (dec.). – IR (hexane): $\tilde{\nu}$ = 1635 cm^{-1} [ν(C=C)]. – ^1H NMR (C_6D_6, 200 MHz): δ = 2.74 (m, 2H, $\mathrm{C}\mathit{H}_2\mathrm{CH_2CH_3}$), 2.51 [sept, *J*(HH) = 7.3 Hz, 6H, $\mathrm{SbC}\mathit{H}\mathrm{CH_3}$], 1.64 (m, 2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CH_3}$), 1.48 [d, *J*(HH) = 7.3 Hz, 36H, $\mathrm{SbCHC}\mathit{H}_3$], 0.96 [t, *J*(HH) = 7.3 Hz, 3H, $\mathrm{CH_2CH_2C}\mathit{H}_3$], 0.29 (s, $SiCH_3$). – ^{13}C NMR (C_6D_6, 50.3 MHz): δ = 239.69 (s, Ir=C), 99.69 (s, $={\mathit{C}}\mathrm{RR'}$), 26.58 (s, $\mathit{C}\mathrm{H_2CH_2CH_3}$), 22.14 (s, $\mathrm{SbCH}\mathit{C}\mathrm{H_3}$), 18.37 (s, $\mathrm{Sb}\mathit{C}\mathrm{HCH_3}$), 14.94 (s, $\mathrm{CH_2CH_2}\mathit{C}\mathrm{H_3}$), 13.57 (s, $\mathrm{CH_2}\mathit{C}\mathrm{H_2CH_3}$), 0.18 (s, $SiCH_3$). – ^{29}Si NMR (C_6D_6, 39.7 MHz): δ = −28.67 (s). – $C_{26}H_{58}ClIrSb_2Si$ (870.0): calcd. C 35.89, H 6.72; found C 35.56, H 6.65.

15. *Determination of the X-ray Crystal Structure of* **10**: Single crystals were grown from toluene. Crystal data (from 23 reflections, 10° < Θ < 13°): triclinic, space group $P\text{-}\bar{1}$ (No. 2); a = 8.865(3), b = 10.940(4), c = 17.386(6) Å, α = 92.27(2), β = 91.58, γ = 112.84°, V = 1551(1) $Å^3$, Z = 2, d_{calcd} = 1.683 g cm^{-3}, μ(Mo-K_α) = 1.86 mm^{-1}; crystal size 0.25 × 0.45 × 0.53 mm; Enraf-Nonius CAD4 diffractometer, Mo-K_α radiation (0.70930 Å), graphite monochromator, zirconium filter (factor 15.41); T = 293 K; ω/Θ scan, max 2Θ = 48.8°; 5248 reflections measured, 4870 independent reflections, 4423 reflections with $I > 2\sigma(I)$, all 4870 independent reflections included in data set. Intensity data were corrected for Lorentz and polarization effects, a linear decay correction (loss of intensity 40.0%) and an empirical absorption correction (Ψ-scan method) were applied (minimum transmission 37.16%). The structure was solved by the Patterson method (SHELXS-86). Atomic coordinates and the anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares on F^2 {235 parameters, weighting scheme applied in the last cycle: $w = 1/[\sigma^2(F_o^2) + (0.0772 \cdot P)^2 + 16.7651 \cdot P]$ where $P = (F_o^2 + 2F_c^2)/3$, SHELXL-93}. The positions of all hydrogen atoms were calculated according to ideal geometry and were refined by using the riding method. Conventional R = 0.0409 [for 4423 reflections with $I > 2\sigma(I)$] and weighted $wR2$ = 0.1426 for all 4870 data reflections; reflex/parameter ratio 20:1; residual electron density +2.796/−1.557 e $Å^{-3}$. A ^1H-NMR spectrum of the crystal charge showed that toluene was present in the crystal. The atomic positions of this solvent molecule could not be refined due to multi-disordering. This explains both the high decay during the measurement and the high residual electron densities which were all found at the probable position of the multi-disordered solvent molecule.

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* Dedicated to Professor *Erwin Weiss* on the occasion of his 70th birthday.

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[32] Further details of the crystal structure investigations are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-404547, the names of the authors, and the journal citation.

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