Iridium-containing cumulenes: how to prepare and how to use

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Dedicated to Professor Pierre Braunstein for his continuous support of the collaborations in the frame of the Sonderforschungsbereich 347

Abstract

This microreview summarizes the work on iridium-containing cumulenes of the general compositions *trans*-[IrX{=C(=C)$_n$RR′}(PiPr$_3$)$_2$] with n = 1, 2, 3 and 4, which recently has been carried out in our laboratory. It is shown that all the parent compounds with X = Cl and an Ir=C=C, Ir=C=C=C, Ir=C=C=C=C or Ir=C=C=C=C=C chain can be prepared using [IrH$_2$Cl(PiPr$_3$)$_2$] as the starting material. Independent on the length of the chain, the iridiacumulenes are highly reactive to both nucleophiles and electrophiles. For n = 1 and 3, the corresponding chloro complexes can be converted to organometallic derivatives *trans*-[IrR″{=C(=C)$_n$RR′}(PiPr$_3$)$_2$], which in the presence of CO smoothly undergoe migratory insertion reactions. Upon treatment with CO, the azido compounds *trans*-[Ir(N$_3$){=C(=C)$_n$RR′}(PiPr$_3$)$_2$] (n = 1, 2 and 3) react similarly. A remarkable feature is that the hydroxoiridium(I) derivatives *trans*-[Ir(OH)(=C=CRR′)(PiPr$_3$)$_2$] and *trans*-[Ir(OH)(=C=C=CRR′)(PiPr$_3$)$_2$] behave as Broensted bases and react with HX (X = OPh, F, C≡CR) by elimination of water and the formation of new iridiacumulenes containing an Ir–X bond. While the reactions of the chloro complexes *trans*-[IrCl(=C=C=CRR′)(PiPr$_3$)$_2$] and *trans*-[IrCl(=C=C=C=CRR′)(PiPr$_3$)$_2$] with HCl proceed by oxidative addition to afford neutral iridium(III) compounds, the iridium allenylidenes react with CF$_3$CO$_2$H in polar solvents to generate cationic iridium carbynes *trans*-[IrCl(≡CCH=CRR′)(PiPr$_3$)$_2$]X, being the first representatives of this type.

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Keywords: Cumulenes; Iridium; C–C bond formation; Oxidative addition; Migratory insertion

1. Introduction

In the context of an extensive investigation on electron-rich transition-metal complexes which behave as typical Lewis-bases [1], we previously found that in contrast to the compounds *trans*-[RhCl(RC≡CR)(PiPr$_3$)$_2$] (where R is methyl or phenyl), which react with NaC$_5$H$_5$ to give the alkyne complexes [(η^5-C$_5$H$_5$)Rh(RC≡CR)(PiPr$_3$)], the corresponding starting materials *trans*-[RhCl(HC≡CR)(PiPr$_3$)$_2$] (where R is H, methyl or phenyl) afford upon treatment with NaC$_5$H$_5$ exclusively the vinylidene counterparts [(η^5-C$_5$H$_5$)Rh(=C=CHR)(PiPr$_3$)] [2]. While studying the mechanism of this reaction, we observed that in solution the four-

coordinate rhodium(I) precursors *trans*-[RhCl(HC≡CR)(PiPr$_3$)$_2$] are relatively labile and rearrange at ambient temperatures to the vinylidene isomers *trans*-[RhCl(=C=CHR)(PiPr$_3$)$_2$] [3,4].

Since these vinylidenerhodium(I) complexes offer a rich chemistry indeed [5,6], we continued our work in this field first by preparing the next generation of unsaturated rhodium(I) carbenes of the general composition *trans*-[RhCl(=C=C=CRR′)(PiPr$_3$)$_2$] [7], and second by generating the compound *trans*-[RhCl(=C=C=C=C=CPh$_2$)(PiPr$_3$)$_2$] with a linear RhC$_5$ chain [8]. We failed to find a synthetic entry to the related RhC$_4$ complex *trans*-[RhCl(=C=C=C=CPh$_2$)(PiPr$_3$)$_2$] but, most recently, developed a methodology to prepare the iridium analogue [9]. In the course of these studies we learned that despite the structural relationship between the rhodium(I) and iridium(I) compounds *trans*-[RhCl{=C(=C)$_n$RR′}(PiPr$_3$)$_2$] and *trans*-[IrCl{=C(=C)$_n$RR′}(PiPr$_3$)$_2$], the chemistry of these complexes

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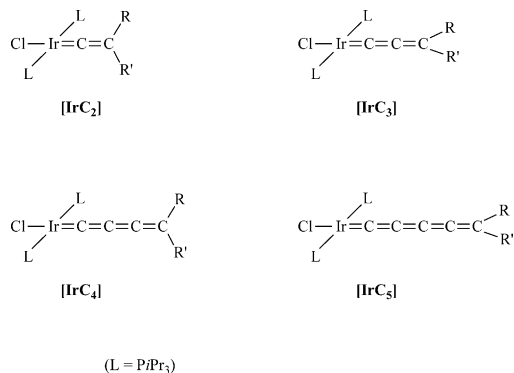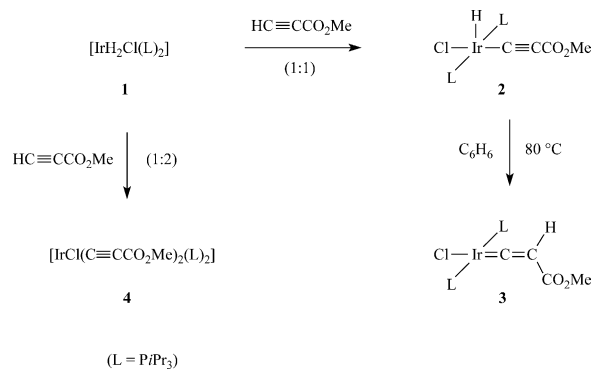
Scheme 1.

Scheme 2.

can be quite different. The present account summarizes our work regarding the synthesis and reactivity of iridiacumulenes (see Scheme 1), most of which has been carried out in the last 3-year period of the Sonderforschungsbereich 347. Published as well as unpublished results will be reported and, wherever it is appropriate, comparative lines to the related rhodium(I) compounds will be drawn.

2. [IrC$_2$]: the counterparts of allenes

There are two routes to prepare iridium(I) vinylidenes with a square-planar geometry: the first one uses the well-known bis(cyclooctene) derivative [IrCl(C$_8$H$_{14}$)$_2$]$_2$, which reacts stepwise with PiPr$_3$ and terminal alkynes to give *trans*-[IrCl(HC≡CR)(PiPr$_3$)$_2$]; subsequent rearrangement of these compounds yields *trans*-[IrCl(=C=CHR)(PiPr$_3$)$_2$] via the isolated and surprisingly stable alkynyl(hydrido)iridium(III) species [IrHCl(C≡CR)(PiPr$_3$)$_2$] [10]. With MeC≡CSiMe$_3$ instead of HC≡CMe or HC≡CSiMe$_3$ as substrate, the vinylidene complex *trans*-[IrCl{=C=C(SiMe$_3$)Me}(PiPr$_3$)$_2$] is formed from [IrCl(C$_8$H$_{14}$)$_2$]$_2$, PiPr$_3$ and the alkyne via the spectroscopically detectable intermediate *trans*-[IrCl(MeC≡CSiMe$_3$)(PiPr$_3$)$_2$] [11].

The second route uses the dihydridoiridium(III) compound [IrH$_2$Cl(PiPr$_3$)$_2$] (**1**) as the precursor which upon treatment with acetylene gives *trans*-[IrCl(=C=CH$_2$)(PiPr$_3$)$_2$] and with methylpropiolate the iridium(I) vinylidene **3** via the iridium(III) intermediate **2** (Scheme 2). The reaction of **1** with two equivalents of HC≡CCO$_2$Me affords the bis(alkynyl) complex **4** [12].

The reactivity of the rhodium(I) and iridium(I) compounds *trans*-[MCl(=C=CRR′)(PiPr$_3$)$_2$] (M = Rh, Ir) towards Grignard reagents is quite different. While the rhodium(I) vinylidenes react with R″MgX to give the expected substitution products *trans*-[Rh(R″)(=C=CRR′)(PiPr$_3$)$_2$] in good to excellent yield [6a], treatment of the iridium(I) counterparts with CH$_3$MgI or CH$_2$=CHMgBr in diethylether or THF leads to halide exchange and to the formation of the bromo and iodo

derivatives *trans*-[IrX(=C=CRR′)(PiPr$_3$)$_2$] (X = Br, I) [13]. These compounds are more conveniently prepared by salt metathesis from *trans*-[IrCl(=C=CRR′)(PiPr$_3$)$_2$] and NaBr or KI, respectively. The methyl, phenyl and alkynyl complexes *trans*-[Ir(R″)(=C=CRR′)(PiPr$_3$)$_2$] can be obtained, however, from the corresponding chloroiridium(I) species and R″Li. These results are exemplified in Scheme 3 with compound **5** as the precursor. The hydroxoiridium(I) derivative **9** can also be used as starting material for the synthesis of alkynyl(vinylidene) complexes such as **10** and **11** [13], thereby illustrating the fact that electron-rich transition-metal compounds of the general type [M(OH)(L)$_n$] (M = Ru, Rh, Ir, Pd, Pt) behave as Broensted bases [14].

The reactions of the methyl, phenyl and alkynyl complexes **6–8** and *trans*-[Ir(CH$_3$)(=C=CHPh)(PiPr$_3$)$_2$] (**12**) [10] with CO proceed by migratory insertion to give the four-coordinate carbonyl(vinyl)iridium(I) compounds **13–16** in excellent yields (Scheme 4). Due to the X-ray crystal structure analysis of **13** and the NMR

Scheme 3.

	R	R'
12, 14	H	Ph
13, 15, 16	Me	SiMe₃

(L = P*i*Pr₃)

Scheme 4.

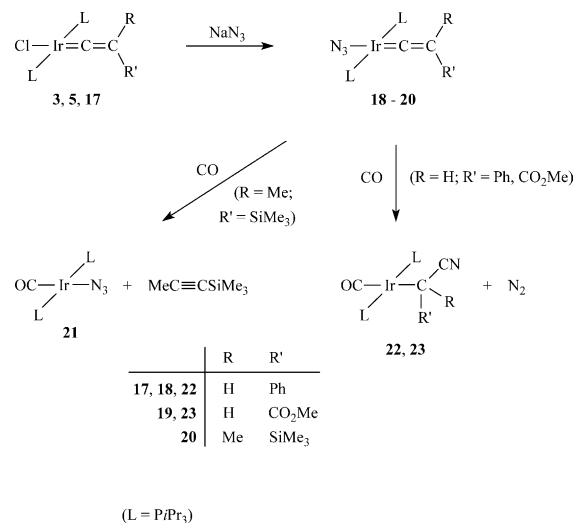|	R	R'
17, 18, 22	H	Ph
19, 23	H	CO₂Me
20	Me	SiMe₃
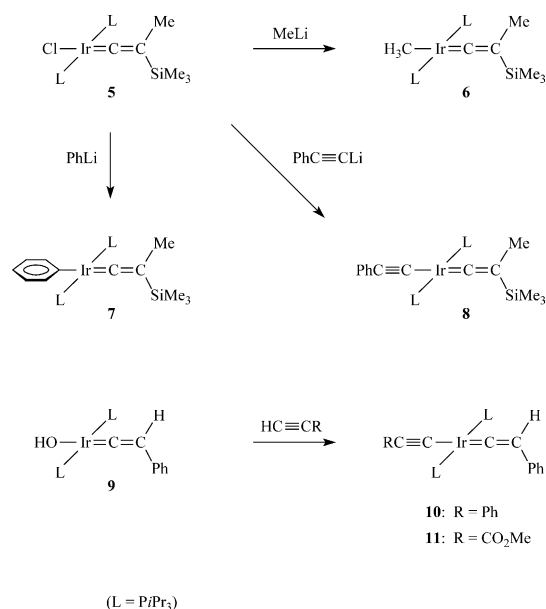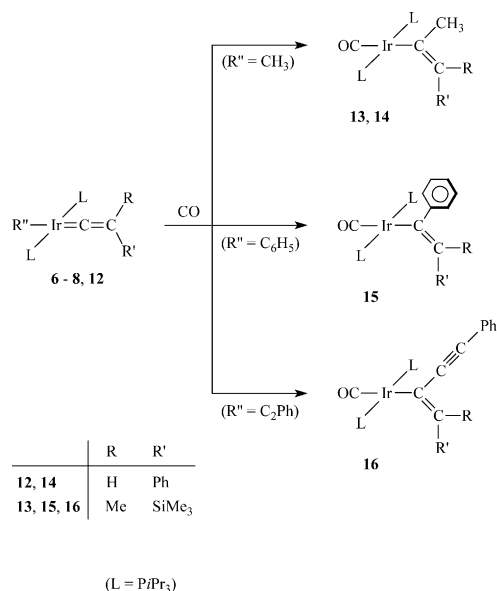
(L = P*i*Pr₃)

Scheme 5.

data of the other products, there is no doubt that the *Z* isomers with the more bulky substituents R' (SiMe₃, Ph) and [Ir(CO)(P*i*Pr₃)₂] in a *cis* orientation at the vinylic C=C double bond are exclusively formed [13]. With regard to the mechanism of formation of the iridium complexes **13–16**, we assume that the attack of carbon monoxide at the metal center of the starting materials is accompanied by a concerted shift of the group R″ to the α-carbon atom of the vinylidene unit. Although this proposal seems reasonable [15], the possibility that a short-lived five-coordinate intermediate [Ir(R″)(CO)-(=C=CRR')(P*i*Pr₃)₂] with a trigonal-bipyramidal geometry is generated cannot be excluded. If the sterically demanding phosphines are occupying the apical positions in this intermediate, the group R″ and the vinylidene ligand would approach each other, thus reducing the barrier for the C–C coupling process. It is probably for steric reasons that the migration of R″ is directed to that side of the Ir=C=CRR' fragment which is opposite to the phenyl or trimethylsilyl substituent. Indirect evidence for the stereochemical arrangement of the vinyl complexes **13**, **14** and **16** is also provided by the observation that acid cleavage of the Ir–C σ-bond under mild conditions (25 °C, benzene) affords besides *trans*-[Ir(κ¹-O₂CR)(CO)(P*i*Pr₃)₂] (R = CH₃, CF₃) the corresponding olefin R″CH=CRR' with the two most bulky substituents R″ and R' in *trans* disposition [13].

The chloroiridium(I) derivatives **3**, **5** and *trans*-[IrCl(=C=CHPh)(P*i*Pr₃)₂] (**17**) [10] react not only with NaBr and KI but also with excess NaN₃ by salt metathesis to afford the azido complexes **18–20** in about 90% yield (Scheme 5) [13]. The preparative procedure is quite similar to that used for the related rhodium compounds *trans*-[Rh(N₃)(CO)(PR₃)₂] (R = Ph, Cy) [16] and *trans*-[Rh(N₃)(=C=C=CRR')(P*i*Pr₃)₂] [17], re-

spectively. The azido derivatives **18** and **19** undergo in the presence of CO a migratory insertion reaction to give the cyano substituted alkyliridium(I) complexes **22**, **23** and N₂. Compound **20** behaves similarly to some chloro(vinylidene) counterparts *trans*-[MCl(=C= CRR')(P*i*Pr₃)₂] (M = Rh, Ir) and affords upon treatment with CO by elimination of the free alkyne the azido(carbonyl) complex **21**. Regarding the course of the reaction of **18–20** with carbon monoxide, we assume (in analogy to the formation of **13–16**) that in the initial step an attack of CO at the iridium(I) center occurs and that the azido ligand migrates to the α-carbon atom of the vinylidene moiety. This migration is probably followed by elimination of N₂ and a subsequent 1,2-shift of the metal from α-C to β-C of the IrC₂ unit. In analogy to the behavior of the vinyl compounds **13–16**, the acid-induced cleavage of the Ir–C σ-bond in **22** and **23** leads to the acetonitrile derivatives R'CH₂CN.

Vinylideneiridium(I) complexes with the alkynyl group C≡CSiMe₃ as a substituent at the β-carbon atom have been prepared from the dihydridoiridium(III) compound **1** and diynes [11]. Similarly to the reaction of **1** with HC≡CCO₂Me (see Scheme 2), treatment of **1** with an equimolar amount of HC≡CC≡CSiMe₃ affords the five-coordinate, very air-sensitive diynyl(hydrido) complex **24** (Scheme 6), which rearranges in toluene at 60 °C to give the vinylideneiridium(I) isomer **25** in good yield. The corresponding derivative **26** with SiMe₃ instead of H at the β-carbon atom of the IrC₂ chain can be obtained either on thermal or photochemical isomerization of the diyne precursor *trans*-[IrCl(η²-Me₃SiC≡CC≡CSiMe₃)(P*i*Pr₃)₂] or on photolysis of a 1:1 mixture of **1** and Me₃SiC≡CC≡CSiMe₃ by elimination of H₂ [11]. In contrast to the related rhodium compound *trans*-[RhCl(η²-Me₃SiC≡CC≡CSiMe₃)-(P*i*Pr₃)₂], the iridium analogue **26** is surprisingly inert toward hydrolysis. In this context it is interesting to note
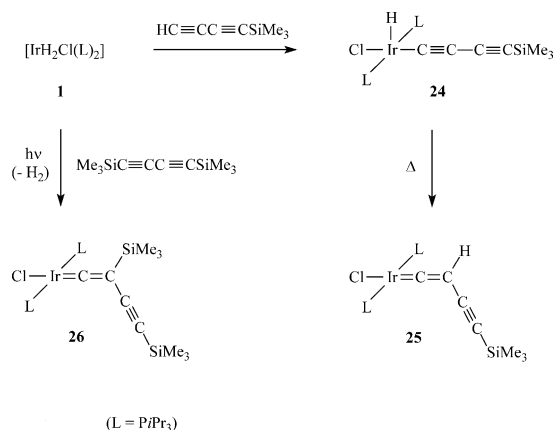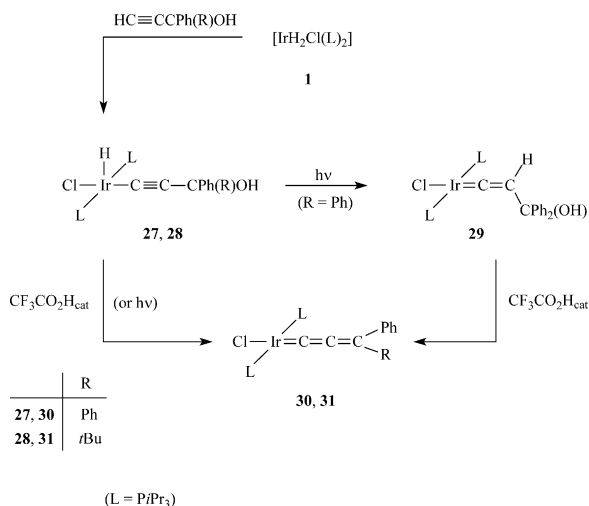
Scheme 6.

that both **5** (see Scheme 3) and *trans*-[IrCl{=C=C(SiMe$_3$)Ph}(P*i*Pr$_3$)$_2$] react with deactivated Al$_2$O$_3$ (activity grade V) in hexane to give the β-CH derivatives *trans*-[IrCl(=C=CHR)(P*i*Pr$_3$)$_2$] (R = Me, Ph) by protolytic cleavage of the C–Si bond [11].

3. [IrC$_3$]: the counterparts of butatrienes

The synthetic route leading to the iridium(I) allenylidenes *trans*-[IrCl{=C=C=C(Ph)R}(P*i*Pr$_3$)$_2$] (**30**, **31**) followed the methodology originally developed by Selegue for cationic half-sandwich type ruthenium compounds [(η^5-C$_5$H$_5$)Ru(=C=C=CRR′)(PPh$_3$)$_2$]X [18]. Treatment of **1** with propargylic alcohols HC≡CCPh(R)OH in pentane or hexane at ambient temperatures leads to the formation of the iridium(III) derivatives **27** and **28** (Scheme 7), which were isolated as red crystalline solids in 80–85% yield [11,19]. If instead of HC≡CCPh$_2$(OH) or HC≡CCPh(*t*Bu)OH the diisopropyl-substituted alcohol HC≡CC(*i*Pr)$_2$OH is used as substrate, the corresponding alkynyl(hydrido)iridi-
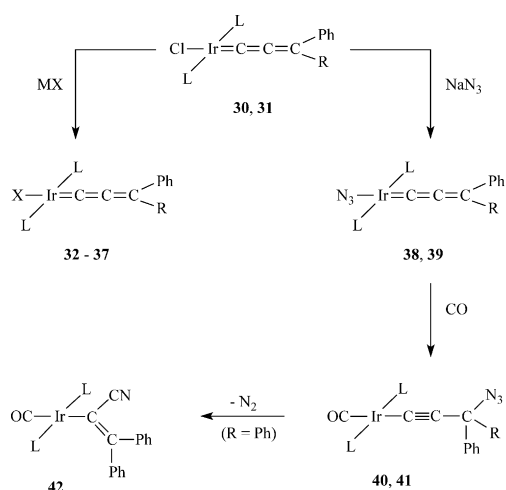

Scheme 7.

um(III) complex [IrHCl{C≡CC(*i*Pr)=CMe$_2$}(P*i*Pr$_3$)$_2$] is generated by elimination of water. The conversion of **27** and **28** to the metal allenylidenes **30** and **31** occurs almost quantitatively in the presence of trace amounts of CF$_3$CO$_2$H. Without acid, **27** rearranges slowly in toluene at 70 °C to the vinylidene isomer **29** that subsequently reacts with CF$_3$CO$_2$H to afford **30**. The isomerization of **27**–**29** is strongly facilitated by UV irradiation in hexane and the same is true for the water abstraction from **27** to give **30** [11]. The iridium allenylidenes **30** and **31** are deeply colored, only moderately air-sensitive solids, which can be stored under argon at room temperature for weeks. Since in the ^{1}H-, ^{13}C- and ^{31}P-NMR spectra of **30** only one set of signals for the hydrogen, carbon and phosphorus atoms of the P*i*Pr$_3$ ligands is observed, we assume in agreement with bonding considerations [20] that the barrier for rotation around the Ir–C bond is quite small on the NMR time scale.

In contrast to the vinylidene complexes *trans*-[IrCl(=C=CRR′)(P*i*Pr$_3$)$_2$] (**5**, **17**), the allenylidene derivatives **30** and **31** do not react with organolithium compounds R″Li (R″ = Me, Ph, C≡CPh) by substitution of the chloro ligand. If instead of R″Li the corresponding Grignard reagent R″MgX (X = Br or I) is used, a mixture of products is formed, among which the bromo or iodo complexes *trans*-[IrX{=C=C=C(Ph)R}(P*i*Pr$_3$)$_2$] (X=Br, I) were the major components. These compounds (illustrated with **30** as the starting material) have been obtained in nearly quantitative yields by salt metathesis from the chloro complex and NaBr or KI [19]. The preparation of the azido-, cyanato-, thiocyanato- and hydroxoiridium(I) derivatives **32–39** takes place on a similar route (Scheme 8). In analogy to the metal vinylidenes **18** and **19** (see Scheme 5), the azido compounds **38** and **39** react smoothly in acetone with carbon monoxide to afford the complexes **40** and **41** in excellent yields [19]. Since the migratory step is not directly accompanied by the elimination of N$_2$, the functionalized iridium alkynyls can be isolated and have been fully characterized. The proposed structure is supported by the appearance of two strong absorptions in the IR spectra at, respectively, 2098 and 1933 cm^{-1} for **40** and at 2104 and 1932 cm^{-1} for **41**, assigned to the ν(N$_3$) and ν(CO) stretching modes.

The thermal stability of the products **40** and **41** generated by migratory insertion is remarkably different. While solutions of **41** in benzene can be stirred for 24 h at room temperature without decomposition or rearrangement, the diphenyl derivative **40** is relatively labile and, under the same conditions, slowly reacts to give first a (non-isolated) intermediate and then the new exceedingly stable carbonyl(vinyl) complex **42** (see Scheme 8). Owing to the spectroscopic data, we assume that the intermediate is the four-coodinate allenyliridium(I) compound *trans*-[Ir{C(N$_3$)=C=CPh$_2$}(CO)-
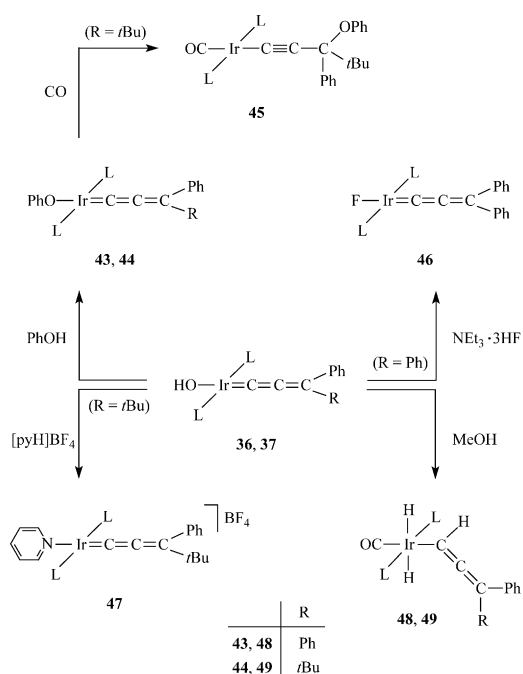
Scheme 8.

Scheme 9.

(PiPr$_3$)$_2$] generated by migration of the N$_3$ unit from the γ-carbon to the α-carbon atom of the C$_3$ moiety. Subsequent elimination of N$_2$ from the intermediate accompanied (or followed) by a 1,2-shift of the metal along the C=C=CPh$_2$ chain would lead to **42**. Notably, a rhodium complex related to **42** with *p*-anisyl instead of phenyl substituents at the terminal carbon atom is known and has been characterized by X-ray crystallography [17].

Likewise to the vinylidene counterpart **9**, the allenylidene(hydroxo)iridium(I) compounds **36** and **37** also behave as Broensted bases. Some examples of the reactions illustrating this property are outlined in Scheme 9. It should be emphasized that the phenolato complex **44** reacts analogously to the azido derivatives **38** and **39** with CO by migratory insertion to give the functionalized iridium(I) alkynyl **45** in 83% yield [19]. The trifluoroacetato compound *trans*-[Ir(κ^1-O$_2$CCF$_3$){= C=C=C(Ph)*t*Bu}(PiPr$_3$)$_2$], prepared from **37** and CF$_3$CO$_2$H by acid–base reaction, also reacts with CO but in this case, in contrast to **45**, no analytically pure product could be isolated.

Under similar conditions as used for the synthesis of **43** and **44**, the neutral allenylidene(fluoro)- and the cationic allenylidene(pyridine)iridium(I) complexes **46** and **47** have been obtained. The key to success for the preparation of **46** (a species which according to the HSAB concept of Pearson [21] should be rather labile) is the use of NEt$_3$·3HF, which has been shown for the first time by Grushin et al. to be a versatile fluorinating reagent in late-transition metal chemistry [22]. Besides a small difference in the Ir–P distances of **46** and the

chloro analogue **30**, the crucial bond lengths (Ir–C1, C1–C2, C2–C3) and angles (Ir–C1–C2, C1–C2–C3, X–Ir–C1) of the two compounds are almost the same indicating that the electronic influence of the chloro or fluoro ligand in *trans* disposition to the allenylidene unit is quite small [19].

Attempts to perform substitution reactions of the hydroxo complexes **36** and **37** in methanol as the solvent led to an unusual result (see Scheme 9). After dissolving one of the starting materials in CH$_3$OH at room temperature, in a fairly short period of time a change of color from orange or green to pale brown takes place and, after recrystallization of the crude product from pentane, the octahedral allenyldihydrido compounds **48** and **49** are obtained in about 90% yield [19]. Since the NMR spectra of **48** and **49** display only a single resonance for the two Ir–H protons and only one signal for the two phosphorus atoms, there is no doubt that the two hydrides as well as the two PiPr$_3$ ligands are in *trans* disposition. The fact that treatment of **36** with CD$_3$OD exclusively yields the tris(deuterio) derivative [IrD$_2$(CD=CH=CPh$_2$)(CO)(PiPr$_3$)$_2$] supports the assumption that the carbonyl as well as the hydrido ligands of **48** and **49** are generated by fragmentation of the alcohol.

The reaction of the allenylidene(hydroxo) complexes **36** and **37** with acidic 1-alkynes HC≡CR′ takes a different course to that of the vinylidene counterpart **9** (see Scheme 3). While we anticipated that the alkynyl compounds   *trans*-[Ir(C≡CR′){=C=C=C(Ph)*t*Bu}- (PiPr$_3$)$_2$] would be formed, the isolated products ob-
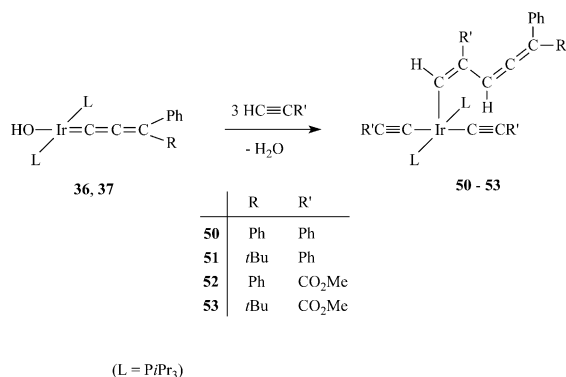
Scheme 10.

Scheme 11.

tained after chromatographic workup are the novel five-coordinate iridium(III) complexes **50–53** (Scheme 10). The X-ray crystal structure analysis of **50** confirmed that the coordination geometry around the metal center is square-pyramidal and that the σ-bonded allenylvinyl unit, possibly generated via the insertion of one phenylacetylene molecule into a Ir–CH=C=CPh$_2$ bond, occupies the apical position [23]. It should be mentioned that in contrast to **50**, **52** and **53** the ^{31}P-NMR spectrum of **51** is temperature-dependent, which is probably due to the linkage of two different substituents (Ph and tBu) at the terminal carbon atom of the C$_5$ chain. Provided that the rotation around the C–C single bond between the vinyl and allenyl moieties is slow on the NMR time scale, the two phosphine ligands are stereochemically non-equivalent and thus two separate ^{31}P-NMR signals should appear. The fact that a similar phenomenon is not observed for **53** could be due to the smaller size of the CO$_2$Me group. The reaction of **36** with DC≡CPh affords the bis(deuterio) derivative [Ir(C≡CPh)$_2$\{CD=C(Ph)–CD=C=CPh$_2$\}(PiPr$_3$)$_2$], the ^{1}H-NMR spectrum of which does not exhibit a resonance for an IrCH or CH=C=CPh$_2$ proton [19].

Taking into consideration that the bonding capabilities of CO and unsaturated carbenes :C=CRR′ and :C=C=CRR′ are similar [24], we also attempted to find out whether the iridium allenylidenes *trans*-[IrCl(=C=C=CRR′)(PiPr$_3$)$_2$] would react in analogy to the Vaska-type compounds *trans*-[IrCl(CO)(PR$_3$)$_2$] (R = Me, Ph) with electrophilic substrates such as CH$_3$I, HX or H$_2$ by oxidative addition. Although we learned that this is partly true, the outcome of these investigations was rather surprising indeed. First we observed that methyl iodide behaves as a source of CH$_2$ toward the Ir=C=C=CPh$_2$ derivatives **30** and **54** (Scheme 11). Treatment of these compounds with excess CH$_3$I in benzene at room temperature leads without the presence of a base to the formation of the butatriene complexes **55** and **56** in high yield [25]. The proposed stereochemistry including the coordination of the metal to the central C=C bond of the butatriene was substantiated by an X-ray crystal
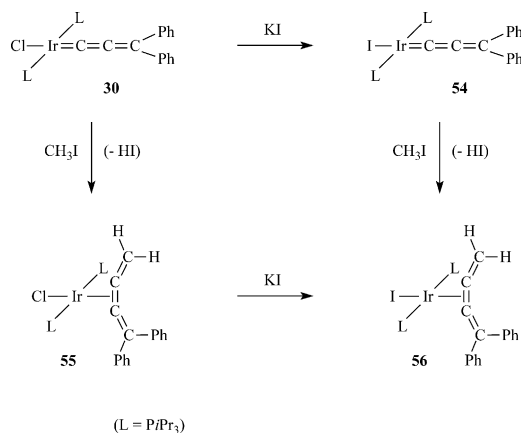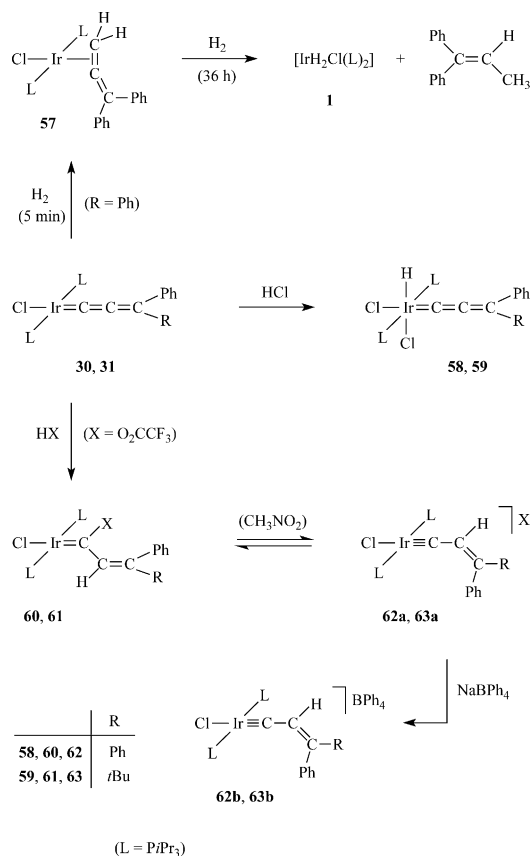
structure analysis of **55**. As expected, the C$_4$ chain is bent possessing C–C–C bond angles that are similar to those in related butatrienerhodium(I) complexes [26]. Regarding the mechanism of the reactions of **30** and **54** with CH$_3$I, we assume that in the initial step the anticipated oxidative addition of the electrophile at the iridium center takes place followed by the insertion of the allenylidene unit into the Ir–CH$_3$ bond. The so-formed intermediate could react via a β-H shift to afford a butatriene(hydrido)iridium(III) species which reductively eliminates HI to yield the product. There is precedence for the insertion step insofar as both we [10] and Fryzuk et al. [27] found that the vinylideneiridium(I) compounds *trans*-[IrCl(=C=CH$_2$)(PiPr$_3$)$_2$] and [Ir(=C=CH$_2$)\{η^3-N(SiMe$_2$CH$_2$PPh$_2$)$_2$\}] react with methyl iodide to give the five-coordinate vinyl complexes *trans*-[IrCl(I)\{C(CH$_3$)=CH$_2$)\}(PiPr$_3$)$_2$] and [IrI\{C(CH$_3$)=CH$_2$)\}\{η^3-N(SiMe$_2$CH$_2$PPh$_2$)$_2$\}], respectively. In these cases, a subsequent β-H shift does not occur.

The allenylidene ligand of **30** can be converted not only to a butatriene but also to an allene. Passing a slow stream of H$_2$ through a solution of **30** in CH$_2$Cl$_2$ affords very cleanly the five-coordinate complex **57** (Scheme 12) in which, as indicated by the NMR spectroscopic data and confirmed crystallographically, the unsubstituted double bond of the allene is coordinated to the metal [11]. Under the conditions to generate **57**, no hydrogenation of the allene ligand takes place. However, if a solution of **57** in benzene is stirred for 36 h under a hydrogen atmosphere, the 3,3-diphenylallene is transformed into the olefin CH$_3$CH=CPh$_2$, while the dihydridoiridium(III) derivative **1** used for the preparation of **30** is reformed. One should note that during the various steps of the processes, shown in Schemes 7 and 12, the corresponding propargylic alcohol HC≡CCPh$_2$(OH) is converted to the trisubstituted olefin CH$_3$CH=CPh$_2$.

The remarkable reactivity of the iridium allenylidenes **30** and **31** toward Broensted acids is illustrated in

57 → (H₂, 36 h) → [IrH₂Cl(L)₂] **1** + Ph₂C=C(H)CH₃

(structures with labels)

30, 31 → HCl → **58, 59**

60, 61 ⇌ (CH₃NO₂) **62a, 63a**

62b, 63b ← NaBPh₄

	R
58, 60, 62	Ph
59, 61, 63	tBu

(L = PiPr₃)

Scheme 12.

Scheme 12. With HCl in benzene, an oxidative addition at the metal center occurs and the allenylidene(hydrido)iridium(III) compounds **58** and **59** are formed in practically quantitative yields [25]. The diphenylcarbene complex trans-[IrCl(=CPh₂)(PiPr₃)₂] behaves similarly and upon treatment with HCl affords trans-[IrHCl₂(=CPh₂)(PiPr₃)₂] [28]. The X-ray crystal structure analysis of **58** revealed that the coordination geometry around iridium corresponds to a slightly distorted octahedron in which the P–Ir–P axis is somewhat bent toward the hydride. The two chloro ligands are cis disposed, the bond length Ir–Cl1 (trans to C₃Ph₂) being ca. 0.07 Å shorter than the distance Ir–Cl2 (trans to hydride).

In contrast to the reactions of **30** and **31** with HCl, those of the same starting materials with CF₃CO₂H take a different course. Instead of six-coordinate iridium(III), four-coordinate iridium(I) compounds **60** and **61** are generated in which, as already indicated by the IR spectra, an allenylidene ligand is no longer present. Based on the ¹H- and ¹³C-NMR spectroscopic data, complemented by NOE measurements, we conclude that trifluoroacetic acid reacts like a nucleophile (e.g. ROH, RNH₂) with **30**, **31** and afford, via addition of the proton to the β-C and of the carboxylate anion to the α-C atom of the IrC₃ fragment, the carbene derivatives. Both **60** and **61** were isolated in ca. 90% yield [25].

While the 1:1 adducts **60** and **61**, if dissolved in benzene, are non-electrolytes, solutions of the same iridium(I) complexes in CH₂Cl₂ and CH₃NO₂ exhibit a significant conductivity. The Λ values (in cm² Ω^{-1} mol^{-1}) measured in nitromethane point to a nearly complete dissociation of the neutral compounds into the ionic species **62a** and **63a** (see Scheme 12). Since in solution the carbyne–metal cations and the trifluoroacetate anion are in equilibrium with the undissociated carbene complexes, the attempts to isolate salt-like products of the composition [IrCl{≡CCH=C(Ph)R}(PiPr₃)₂]CF₃CO₂ failed.

However, the cations can be trapped if the precursors **60** and **61** are disssolved in methanol and one equivalent of NaBPh₄ is added. The isolated solids **62b** and **63b** have been characterized by elemental analysis, conductivity measurements and spectroscopic techniques. The chemical shift of the triplet resonance for the metal-bonded carbon atom, observed in the ¹³C-NMR spectra of **62b** and **63b** in CD₂Cl₂, is quite similar to that of the carbyneosmium(II) [OsHCl₂(≡CCH=CMe₂)(PiPr₃)₂] [29] and also of the carbyneiridium(I) complexes trans-[IrCl(≡CCH₂R)(PiPr₃)₂]BF₄ (R = H, Ph), the latter being prepared by protonation of the iridium(I) vinylidenes trans-[IrCl(=C=CHR)(PiPr₃)₂] with HBF₄ [10].

4. [IrC₄]: the counterparts of pentatetraenes

While the tracks for the metal-assisted conversion of terminal alkynes HC≡CR to vinylidenes and of prop-argylic alcohols HC≡CCR(R′)OH to allenylidenes have already been laid in the late 1970s and early 1980s by Antonova and coworkers [30] and Selegue [18], prior to our work it was not clear, how a :C=C=C=CRR′ ligand can be generated in the coordination sphere of a transition metal. One of the first precursors that we used was the alkynylketone HC≡CC(O)CHPh₂ which in principle could be transformed to the cumulenylidene fragment C₄Ph₂ by elimination of water. However, although the alkynylketone as well as the respective enol acetate HC≡CC(OAc)=CPh₂ react with the dihydrido compound **1** to give the expected functionalized alkynyl(hydrido)- and vinylideneiridium complexes, all attempts to convert these species into the target molecule trans-[IrCl(=C=C=C=CPh₂)(PiPr₃)₂] (**64**) failed.

The key to success was the use of the enol triflate HC≡CC(OTf)=CPh₂ (Tf = CF₃SO₂) which contains a better leaving group at the γ-carbon atom of the substituted alkyne than the related enol acetate. Treating a solution of the starting material **1** and one equivalent of NEt₃ in hexane at −100 °C with the enol triflate led after warming to −30 °C, separation of the ammonium salt [HNEt₃](OTf) and recrystallization of the crude product from acetone to the IrC₄ complex **64**, which was isolated as an olive-green, only moder-
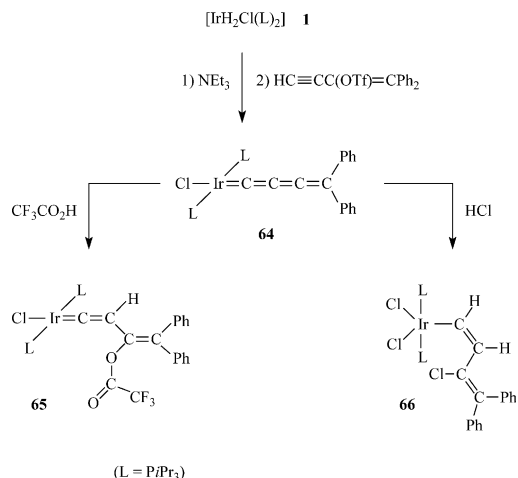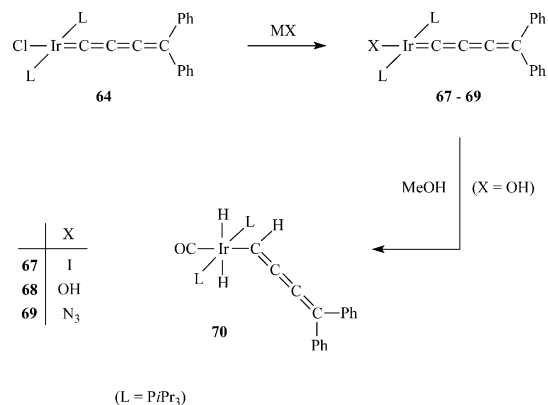
Scheme 13.

Scheme 14.

ately air-sensitive solid in 77% yield (Scheme 13). The X-ray crystal structure analysis confirmed that the unsaturated IrC$_4$ chain is nearly linear and deviates only weakly at the metal-bonded carbon atom from the ideal value of 180°. The lengths of the two internal C=C double bonds are almost identical (1.283(8) and 1.275(8) Å), whereas the terminal C=C bond is slightly longer (1.339(8) Å) [9].

Similarly to the iridium allenylidenes **30** and **31**, the butatrienylidene complex **64** also reacts with CF$_3$CO$_2$H and HCl in unpolar solvents such as benzene. In the case of the trifluoroacetic acid, the attack of the electrophile is directed to the C$_\beta$–C$_\gamma$ bond of the IrC$_4$ chain and affords the substituted vinylvinylidene derivative **65** in 87% yield. Treatment of **65** with a second equivalent of CF$_3$CO$_2$H leads to a mixture of products which could not be separated by fractional crystallization or chromatographic techniques.

In contrast to the reaction of **64** with CF$_3$CO$_2$H, the reaction of **64** with HCl proceeds in the molar ratio of 1:2 and gives the five-coordinate, thermally very stable dichloroiridium(III) complex **66** (see Scheme 13). Owing to the twofold addition of HCl, the butatrienylidene unit is transformed to a butadienyl ligand which is σ-bonded to the metal center. From a mechanistic point of view, we assume that in the initial step of the reaction a vinylvinylidene compound *trans*-[IrCl{=C=CH–C(Cl)=CPh$_2$}(PiPr$_3$)$_2$], structurally analogous to **65**, is generated which subsequently reacts with a second molecule of HCl by attack at the Ir=C bond. Support for the formation of the supposed intermediate is provided by the ^{13}C-NMR spectra of the reacting system which show the appearance and disappearance of two triplets having nearly the same chemical shifts and coupling constants as the isolated species **65**.

The IrC$_4$ complex **64** undergoes salt metathesis reactions with KI, KOH and NaN$_3$ to afford the substitution products **67–69** (Scheme 14), of which the hydroxo derivative, in agreement with our earlier findings, behaves as a Broensted base. It does not only react with phenol to give *trans*-[Ir(OPh)(=C=C=C=CPh$_2$)(PiPr$_3$)$_2$] but also initiates the fragmentation of methanol into CO and three hydrogen atoms. Two of these are coordinated as hydrides to the metal center of the octahedral iridium(III) compound **70**, while the third is bonded to the α-carbon atom of the C$_4$ chain, thus converting the butatrienylidene to a butatrienyl ligand [31].

Quite remarkably, the azido complex **69** as well as the methyliridium(I) counterpart **71** react with CO by migratory insertion (Scheme 15). In contrast to the allenylidene derivatives **30** and **31**, which upon treatment with CH$_3$Li yield a mixture of products, the reaction of **64** with methyllithium in pentane at −78 °C gives almost exclusively the extremely air-sensitive complex **71** [31]. Diagnostic for the metal-bonded CH$_3$ group is a triplet at δ 1.56 in the ^{1}H-NMR
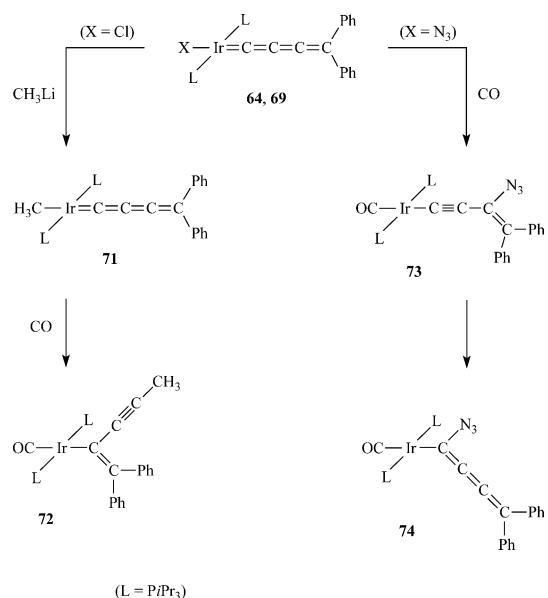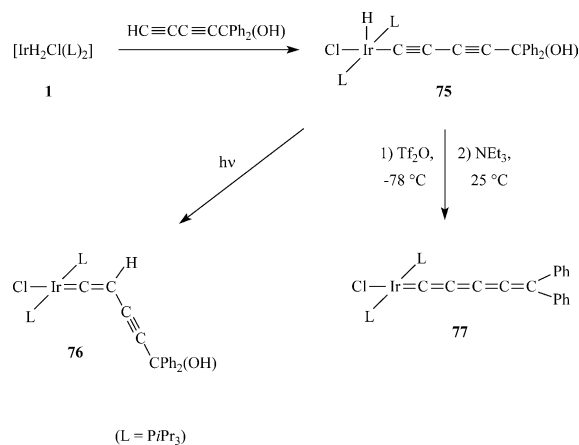

Scheme 15.

spectrum, the position of which is similar to that of the vinylidene analogue **12** (see Scheme 4).

Treating the in situ generated compound **71** with CO leads to the formation of the carbonyliridium(I) complex **72** which, however, does not have the supposed composition *trans*-[Ir{C(CH$_3$)=C=C=CPh$_2$}(CO)-(PiPr$_3$)$_2$]. An alkynyl-substituted vinyl derivative is obtained instead, the molecular structure of which has been confirmed crystallographically [31]. Due to steric constrains, caused by the bulky PiPr$_3$ ligands and the CH$_3$C≡C–C=CPh$_2$ unit, the coordination geometry around the metal is distorted square-planar with bond angles P–Ir–P and C–Ir–C of, respectively, 167.64(4) and 174.89(18)°. The two phosphines are *trans* to each other with an eclipsed conformation along the P–Ir–P axis. The distance between iridium and the vinyl carbon atom is significantly longer than in **64** but comparable to that in **13**.

The migratory insertion reaction of the azidoiridium(I) species **69** with CO affords in the first step the functionalized alkynyl complex **73** (Scheme 15), which after chromatographic workup can be isolated as a yellow, moderately air-sensitive solid in good yield. However, when we attempted to further purify **73** by recrystallization we observed that in solution a slow rearrangement of the initially formed product takes place. The conversion to the isomer **74** is completed after stirring a solution of **73** in benzene for 36 h at room temperature. In contrast to **73**, the IR spectrum of **74** displays an intense ν(C=C=C) band at 1992 cm^{-1}, that is at a similar position as found for **70**. It is interesting to note that the postulated allenyliridium(I) compound *trans*-[Ir{C(N$_3$)=C=CPh$_2$}(CO)(PiPr$_3$)$_2$], generated from **40** (see Scheme 8) and related to **74**, is extremely labile and rapidly looses dinitrogen to give **42** [19]. Under the same conditions, the butatrienyl complex **74** is exceedingly stable and reacts neither under UV irradiation nor in refluxing benzene by elimination of N$_2$.

5. [IrC$_5$]: the presently last member of the [IrC$_n$] family

The synthesis of the wanted product *trans*-[IrCl(=C=C=C=C=CPh$_2$)(PiPr$_3$)$_2$] (**77**) created an equal challenge as that of the IrC$_4$ counterpart. While attempts to prepare the diynyl(hydrido) complex **75** using the intermediate generated from [IrCl(C$_8$H$_{14}$)$_2$]$_2$ and PiPr$_3$ as precursor failed, the dihydridoiridium(III) species **1** reacts with the unsaturated alcohol HC≡CC≡CCPh$_2$(OH) in pentane at 0 °C to give **75** as a dark red, slightly air-sensitive solid in 78% isolated yield (Scheme 16). The IR spectrum of **75** displays characteristic absorptions at 3570, 2240 and 2180 cm^{-1}, which are assigned to the ν(OH), ν(IrH) and ν(C≡C) vibrational modes.

Scheme 16.

Upon UV irradiation in benzene, a slow rearrangement of **75** to the red–violet vinylidene isomer **76** takes place. Although **75** and **76** are near relatives to the IrC$_3$ compounds **27** and **29** (see Scheme 7), both of which react with traces of trifluoroacetic acid to give the iridiacumulene **30**, all attempts to eliminate water from **75** or **76** using CF$_3$CO$_2$H or acidic Al$_2$O$_3$ as abstracting reagents remained unsuccessful. Since we observed in the course of these studies that **75** (and even more **76**) decompose in the presence of acids, we reasoned that in order to achieve elimination of H$_2$O acidic substrates have to be avoided.

The successful route to obtain the IrC$_5$ complex **77** is somewhat similar to that used for the IrC$_4$ analogue **64** (see Scheme 13). Treatment of a solution of **75** in toluene at −78 °C with an equimolar amount of (CF$_3$SO$_2$)$_2$O followed, after warming to room temperature, by the addition of two equivalents of NEt$_3$ afforded a dark reaction mixture from which copper-brown crystals with the analytical composition corresponding to **77** could be isolated in 80% yield [32]. The IrC$_5$ compound (being the second representative of MC$_5$ cumulenes [33]) is thermally quite stable and decomposes at 132 °C. We note that solutions of **77** display different colors from yellow through rose to violet depending on the solvent and the concentration. Characteristic spectroscopic features of **77** are the five ^{13}C-NMR signals for the carbon atoms of the IrC$_5$ chain which appear between δ 245–133 and, owing to ^{13}C–^{31}P coupling, are all split into symmetrical triplets.

The X-ray crystal structure analysis confirmed that **77** is indeed a metallacumulene [32]. The coordination geometry around iridium is square-planar with two *trans*-disposed phosphine ligands and an almost linear IrC$_5$ chain. The Ir–C bond length is 1.834(5) Å (or 1.821(5) Å in the second independent molecule present in the unit cell) and thus slightly longer than in the IrC$_4$ counterpart **64** (1.818(6) Å). The shortest metal–carbon distance in the [IrC$_n$] family is found for the IrC$_2$

complex **3** (1.764(6) Å) which is in agreement with the assumption that vinylidenes are the best π-acceptor ligands in the :$C(=C)_n RR'$ series [24].

6. Outlook

In this account, preparative routes to iridiacumulenes with backbones as shown in Scheme 1 have been presented. Although we are still at the beginning to learn what the potential of these compounds is, possibly as materials with non-linear optical properties or as precursors for metal-containing copolymers, it is quite obvious that the reactivity of complexes of the general composition $[M\{=C(=C)_n RR'\}(L)_n]$ toward both electrophilic and nucleophilic substrates is worth to be investigated. From a recent DFT study using the model system $[Cr\{=C(=C)_n H_2\}(CO)_5]$ ($n = 1$–8), Sgamellotti and coworkers concluded that the dissociation energies for the metal–cumulenylidene bond is essentially independent of the chain length [34]. Owing to these calculations it appears that there is no thermodynamic upper limit regarding the cumulene chain lengths which means that the synthetic difficulties experienced in the preparation of metal complexes of the type $[M\{=C(=C)_n RR'\}(L)_n]$ with chains longer than three carbon atoms are mainly due to the high reactivity of these species.

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