Synthesis and Molecular Structure of the First Neutral Transition-Metal Complex Containing a Linear $M{=}C{=}C{=}C{=}C{=}CR_2$ Chain

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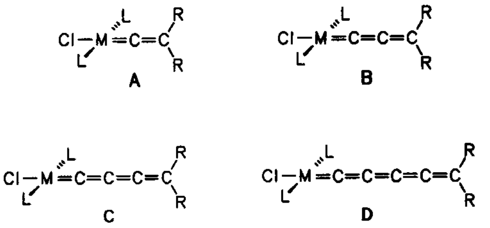
Dedicated to Professor Max Schmidt on the occasion of his 70th birthday

Abstract: The reaction of $[IrH_2Cl(PiPr_3)_2]$ (**2**) with the pentadiyne derivative $HC{\equiv}C{-}C{\equiv}C{-}CPh_2OH$ (**1**) yields the five-coordinate compound $[IrH(C{\equiv}C{-}C{\equiv}CCPh_2OH)Cl(PiPr_3)_2]$ (**3**), which photochemically rearranges to give the vinylidene-substituted isomer *trans*-$[IrCl({=}C{=}CH{-}C{\equiv}CCPh_2OH)(PiPr_3)_2]$ (**4**). On treatment of **3** with pyridine, the octahedral complex $[IrH(C{\equiv}C{-}C{\equiv}CCPh_2OH)Cl(py)(PiPr_3)_2]$ (**5**) is formed. While attempts to eliminate water from **4** (or **5**) failed, the reaction of **3** with one equivalent of trifluorosulfonic acid anhydride and two equivalents of triethylamine led to the formation of *trans*-$[IrCl({=}C{=}C{=}C{=}C{=}CPh_2)(PiPr_3)_2]$ (**6**), which is the first neutral transition-metal complex containing a C_5R_2 ligand. The X-ray structural analysis of **6** reveals a perfect square-planar coordination geometry around the metal centre and an almost linear IrC_5 chain with Ir-C-C and C-C-C bond angles of 174–179°.

Keywords
carbon ligands · diynes · iridium compounds · metallacumulenes

Introduction

Following the discovery that acetylene and terminal alkynes $HC{\equiv}CR$ (R = alkyl or aryl) are smoothly converted to metal-bound vinylidenes upon coordination to rhodium(I) or iridium(I),[1, 2] a large variety of square-planar complexes of type **A** (Scheme 1) have been described.[3] While attempts to rearrange the corresponding alkynyl-substituted rhodium vinylidenes *trans*-$[RhCl({=}C{=}CH{-}C{\equiv}CR)(PiPr_3)_2]$ or *trans*-$[RhCl({=}C{=}C(SiMe_3){-}C{\equiv}CR)(PiPr_3)_2]$ by [1,3]H or [1,3]$SiMe_3$ shifts, respectively, to give compounds of type **C** failed,[4] several allenylidene rhodium(I) and iridium(I) complexes (type **B**) were recently prepared in our laboratory.[5, 6] The synthetic route (originally developed by Selegue)[7] was based on metal-assisted activation of propargylic alcohol derivatives $HC{\equiv}CCR_2OH$ that were initially transformed to vinylidene compounds *trans*-$[MCl({=}C{=}CHCR_2OH)(PiPr_3)_2]$ (M = Rh, Ir) and subsequently, by abstraction of water, to complexes of type **B**.[8]



Scheme 1. M = Rh, Ir; L = $PiPr_3$.

In the present paper we report the synthesis and structural characterization of the first compound of type **D** with M = Ir, which extends the series of metallacumulenes containing $[IrCl(PiPr_3)_2]$ as a molecular unit. We note that the first metal complex with a $M({=}C)_4{=}CR_2$ chain is the octahedral cationic species $[RuCl({=}C{=}C{=}C{=}C{=}CPh_2)(dppe)_2]^+$ (dppe = $Ph_2PCH_2CH_2PPh_2$), which has recently been prepared by Dixneuf et al. from $[RuCl_2(dppe)_2]$ and $HC{\equiv}C{-}C{\equiv}C{-}CPh_2OSiMe_3$.[9] Although our search for the $Ir({=}C)_4{=}CPh_2$ derivative started at almost exactly the same time as that of the Rennes group,[10] we finished second, since i) the established methods for abstraction of water from $L_nM{=}C{=}CHCPh_2OH$ intermediates to afford $L_nM{=}C{=}C{=}CPh_2$ complexes[5–7] could not be employed for the conversion of $L_nIr{=}C{=}CHC{\equiv}CCPh_2OH$ to $L_nIr{=}C{=}C{=}C{=}C{=}CPh_2$ species, and ii) it took us nearly six months to grow suitable single crystals of the title compound.

Results and Discussion

The Stepwise Construction of the IrC_5R_2 Chain: The labile starting material $[IrCl(C_8H_{14})(PiPr_3)_2]$ can be generated in situ from $[IrCl(C_8H_{14})_2]_2$ and four equivalents of $PiPr_3$,[11] and has been used for the preparation of iridium complexes of types **A** and **B**.[2, 6] On treatment of this complex with the 5-hydroxypentadiyne $HC{\equiv}C{-}C{\equiv}CCPh_2OH$ (**1**) insoluble, probably polymeric products were obtained. In contrast, a clean reaction occurred between the dihydridoiridium(III) compound **2**[12] and **1**

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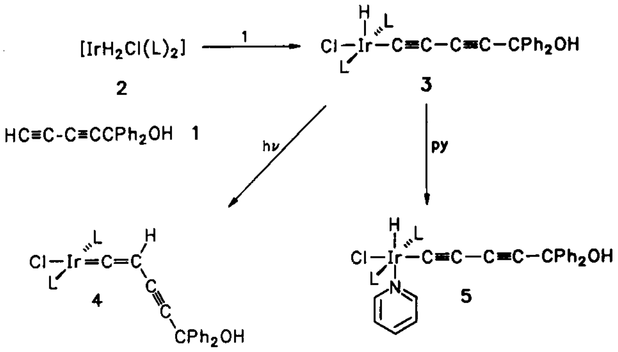
leading to the diynyl(hydrido) complex **3** in approximately 80% yield (Scheme 2). Related five-coordinate iridium(III) derivatives, possibly possessing a square-pyramidal structure with the hydrido ligand in the apical position, have also been obtained from **2** and HC≡CR (R = Ph, CO_2Me).[13] Compound **3** is a dark red solid which is only moderately air-sensitive and in contrast to **1** is remarkably stable in the solid state. Since the IR spectrum displays characteristic bands at $\tilde{\nu} = 3570$, 2240 and 2180 cm^{-1}, which are assigned to the O–H, Ir–H and C≡C stretching frequencies, there is no doubt that during the formation of **3** an oxidative addition of the pentadiyne to the iridium centre has taken place.



Scheme 2. L = $PiPr_3$.

The desired rearrangement of compound **3** to the isomeric vinylidene complex **4** could not be achieved thermally. When solutions of **3** in benzene were warmed to 40–60 °C for several hours, decomposition occurred which led, inter alia, to the carbonyliridium derivative *trans*-$[IrCl(CO)(PiPr_3)_2]$.[14] However, upon irradiation of the diynyl(hydrido) complex **3** in benzene with a UV lamp, a clean, albeit very slow, reaction took place, which after 5 days afforded compound **4** as a red-violet, almost air-stable solid in 63% yield. As with other vinylideneiridium(I) compounds,[2, 13] the ^{13}C NMR spectrum of **4** reveals two triplets at $\delta = 258.67$ and 88.06, which correspond to the α-C and β-C vinylidene carbon atoms. The two signals for the C≡C carbon atoms appear at $\delta = 99.55$ and 56.97, likewise as triplets but with smaller P–C coupling.

All attempts to eliminate water from compound **4** to give the metallacumulene **6** failed. Neither treatment of **4** with acidic Al_2O_3 nor with CF_3CO_2H (both routes have been used quite successfully to convert a $M{=}C{=}CHCR_2OH$ into a $M{=}C{=}C{=}CR_2$ unit)[5, 15] yielded the $Ir(=C)_4{=}CPh_2$ derivative. Since the reaction of the alkynyl(hydrido)metal species $[IrH(C\equiv C\text{-}CPh_2OH)Cl(PiPr_3)_2]$ with catalytic amounts of CF_3CO_2H is the method of choice for the preparation of the allenylidene complex *trans*-$[IrCl(=C=C=CR_2)(PiPr_3)_2]$,[6] we then attempted to use the five-coordinate compound **3** directly for the preparation of **6**. It reacted with CF_3CO_2H or the anhydride $(CF_3CO)_2O$, presumably to give the vinylidene complex **4** as the initial product. The latter, as mentioned above, is not stable in the presence of acid, and decomposed without forming **6**.

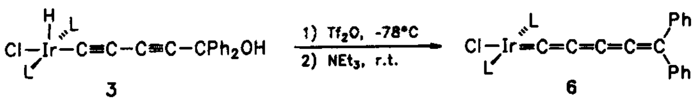
We therefore concluded that we should avoid acidic media and try to perform the desired elimination of HX (X is the non-carbon substituent on the terminal C atom of the chain) under basic conditions. Thus we decided to convert the OH functionality of the C_5 ligand into a corresponding ester unit because otherwise, in the presence of base, deprotonation of the hydroxy group would probably occur.

The idea that tosylate or triflate might be an appropriate leaving group immediately raised the question how the OH substituent of one of the IrC_5 compounds could be transformed to an OTos or OTf (CF_3SO_2O) moiety. From the very beginning, we felt that **4** should not be used as starting material since it is known that vinylidene complexes of type **A** (see Scheme 1) with M = Ir, which like Vaska's compound (*trans*-$[IrCl(CO)(PPh_3)_2]$) behave as Lewis bases, are readily attacked by electrophiles at the *metal centre* and not at another part of the molecule.[16] Attack at the metal should not occur if an iridium(III) precursor, possibly with an octahedral coordination sphere, were used. Therefore, compound **5** was prepared and its reactivity investigated. From previous studies we knew that five-coordinate alkynyl(hydrido)iridium(III) complexes react smoothly with pyridine to give 1:1 adducts. It was therefore not surprising that on treatment of **3** with pyridine a colourless, slightly air-sensitive solid, compound **5**, was formed in approximately 80% yield. All attempts, however, to convert the C_4–CPh_2OH ligand of **5** to a corresponding C_4–CPh_2OTos or C_4–CPh_2OTf unit failed even under mild conditions (in toluene at 0 °C or below) or in the presence of excess pyridine. We assume that the electrophile attacks either the Ir–N or the Ir–C bond and thus initiates the decomposition of the diynyl(hydrido)iridium(III) complex.

Since pyridine failed to facilitate the reaction of the OH group with tosyl chloride or trifluorosulfonic acid anhydride either as the supporting ligand or as the reagent,[17] the next series of experiments was undertaken with triethylamine as base. Although NEt_3 is a much weaker σ donor than pyridine, we considered this, together with the higher volatility of NEt_3, a possible advantage. Preliminary experiments carried out in an NMR tube revealed that solutions of **3** in C_6D_6 slowly decompose upon addition of NEt_3 to yield, inter alia, the vinylidene complex **4**. In spite of this observation, the combination of compound **3** and NEt_3 turned out to be a favourable choice for the synthesis of the metallacumulene **6**. When a solution of the starting material **3** in toluene was treated at −78 °C with one equivalent of Tf_2O a reaction occurred which led to an intermediate of unknown structure. Since the ^{31}P NMR spectrum of this species displays a signal at $\delta = 51$, which is significantly shifted to lower frequencies (ca. 12 ppm) compared with the corresponding resonance in **3**, we assume that the intermediate is not the five-coordinate compound $[IrH(C\equiv C\text{-}C\equiv CCPh_2OTf)Cl(PiPr_3)_2]$.

Addition of *one* equivalent of NEt_3 to the solution of the species generated in situ in toluene did not lead (by ^{31}P NMR) to a detectable reaction. If, however, *two* equivalents of the amine were added, a change of colour from dark red to brown took place and, after chromatographic workup, copper-brown crystals of analytical composition $C_{35}H_{52}ClIrP_2$ (corresponding to **6**) were isolated in 80% yield. The product was readily soluble in dichloromethane or benzene, moderately soluble in saturated hydrocarbons and decomposed in polar solvents such as methanol or nitromethane. It is interesting to note that solutions of **6** displayed different colours (from yellow through rose to violet) depending on the solvent and the concentration. In the solid state, compound **6** was remarkably stable. It decomposed, however, in the presence of impurities which were sometimes also present in the crude reaction product and could have been formed from **3**, Tf_2O and NEt_3 in a side reaction. The impurities must be removed by column chromatography with neutral alumina at −78 °C because a similar procedure at room temperature (even with fluorosil or dehydroxygenated silica as adsorbants) led to rapid decomposition.

The IR and NMR spectroscopic data for **6** are in good agreement with the structure proposed in Scheme 3. In analogy to the cationic ruthenium complex prepared by Dixneuf et al.,[9a] the IR spectrum displays two bands at 1960 and 1856 cm^{-1} which are assigned to the C–C–C stretching frequencies of the metallacumulene unit. In the ^{13}C NMR spectrum, the five carbon atoms of the IrC_5 chain give rise to five signals between $\delta = 245-133$, which, owing to P–C coupling, are all split into symmetrical triplets. The proposed assignment noted in the Experimental Section is based on the absolute magnitudes of the P–C coupling constants, which are assumed to decrease from α-C to ε-C along the chain. The ^{31}P NMR spectrum of **6** displays a single resonance (at $\delta = 14.4$ in C_6D_6); this indicates that the two phosphine ligands are equivalent and in a *trans* arrangement.



Scheme 3. L = P*i*Pr_3.

Molecular Structure of Complex 6: The single-crystal X-ray structure analysis confirms (see Fig. 1) that the coordination geometry about the iridium(I) centre is square-planar with the chloride and the C_5 ligand disposed *trans* to one another and that the Ir=C=C=C=C=C moiety is almost linear. There are two crystallographically independent molecules in the unit cell with nearly identical bond lengths and angles (Table 1).

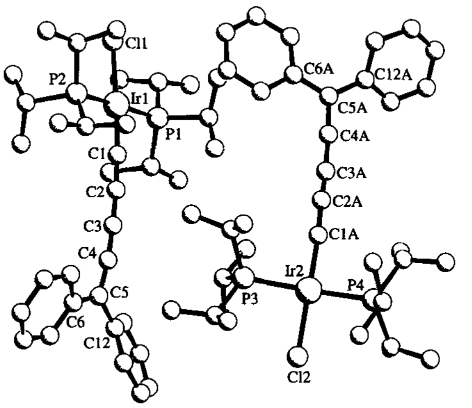


Fig. 1. Arrangement of the two independent molecules of compound **6** in the unit cell (SCHAKAL diagram).

Table 1. Selected intramolecular bond lengths (Å) and bond angles (°) in complex 6 with esds (there are two independent molecules (molecule 1)[molecule 2] in the unit cell).

Ir–Cl	2.347(1)	[2.353(1)]	C2–C3	1.296(6)	[1.279(6)]
Ir–P1	2.340(1)	[2.344(1)]	C3–C4	1.259(6)	[1.249(6)]
Ir–P2	2.344(1)	[2.348(1)]	C4–C5	1.344(6)	[1.343(6)]
Ir–C1	1.834(5)	[1.821(5)]	C5–C6	1.479(6)	[1.475(6)]
C1–C2	1.261(6)	[1.278(6)]	C5–C12	1.475(6)	[1.480(6)]
Cl-Ir-C1	177.4(1)	[172.2(2)]	C1-C2-C3	175.8(5)	[175.6(5)]
P1-Ir-P2	177.69(4)	[172.73(4)]	C2-C3-C4	177.1(5)	[178.9(6)]
Cl-Ir-P1	91.10(4)	[90.95(4)]	C3-C4-C5	174.8(5)	[177.6(6)]
Cl-Ir-P2	90.98(4)	[91.74(4)]	C4-C5-C6	118.3(4)	[119.2(4)]
P1-Ir-C1	88.9(1)	[88.7(1)]	C4-C5-C12	119.8(4)	[117.9(4)]
P2-Ir-C1	89.0(1)	[89.5(1)]	C6-C5-C12	121.9(3)	[122.9(4)]
Ir-C1-C2	176.8(4)	[173.8(5)]			

The most notable structural parameter is the Ir–C1 bond length of 1.834(5) Å (or 1.821(5) Å), which is significantly shorter than an Ir–C single bond[18] but somewhat longer than in the related vinylidene complex *trans*-$[IrCl(=C=CHCO_2Me)(PiPr_3)_2]$ (1.764(6) Å).[2b, 13] Nearly identical M–C bond lengths are found in $[Ir(=C=CH_2)(\kappa^3(N,P,P)\text{-}N(SiMe_2CH_2PPh_2)_2)]$ (1.806(4) Å)[19] and in the ruthenium allenylidene $[RuCl_2(=C=C=CPh_2)(\kappa(P)\text{-}iPr_2PCH_2CO_2Me)(\kappa^2(P,O)\text{-}iPr_2PCH_2CO_2Me)]$ (1.84(1) Å).[15b] In Dixneuf's complex with the RuC_5 chain, the Ru–C bond length is 1.891(9) Å;[9a] the difference with **6** probably results from the cationic nature of the molecule. The C–C bond lengths in the chain alternate between 1.26 Å (average for C1–C2 and C3–C4) and 1.32 Å (average for C2–C3 and C4–C5) and thus indicate that, besides the usual bonding formulation **E**, a second resonance structure **E'** has to be taken into consideration.

(L = P*i*Pr_3)

The Ir-C-C and C-C-C bond angles of the IrC_5 unit are between 174° and 179°; this implies a small bending of the chain (see the SCHAKAL diagram, Fig. 1). The Ir–Cl and Ir–P bond lengths are similar to those found in *trans*-$[IrCl(=C=CHCO_2Me)(PiPr_3)_2]$[2b, 13] and need no further comment.

Conclusion

The work presented in this paper, complementary to recent investigations by Dixneuf et al., has shown that synthetic routes can be developed which lead to metallacumulenes of hitherto unknown chain length. The most useful precursors for the preparation of complexes containing an $M(=C)_4=CR_2$ assembly seem to be pentadiyne derivatives $HC\equiv C-C\equiv CCR_2OR'$ (R' = H in the present work, $SiMe_3$ in refs. [9, 20]) from which, assisted by the transition metal, the two fragments H and OR' are eliminated stepwise to give the cumulene unit. While the strategy of the Rennes group uses an *electrophile* to cleave the C–$OSiMe_3$ bond, our method works under *basic* conditions, which are necessary if the metal centre in either the starting material or the reaction product behaves as a Lewis base.

As far as the properties of the title compound are concerned, we were surprised at how stable the molecule is, both in the solid state and in solution (with the exception of some polar solvents). This was unexpected, since compared with ruthenium in the octahedral $Ru(=C)_4=CR_2$ complexes[9a, 20] the four-coordinate iridium in **6** is much more poorly shielded, and thus aggregation or oligomerization seemed conceivable. We feel that the stability of **6** (and other possible $Ir(=C)_4=CR_2$ derivatives) is promising, insofar as organometallic compounds containing a carbon-rich conjugated or cumulated chain are currently attracting interest either for their material properties or as polymer precursors.[21] In this regard it is still a challenge to obtain complexes of type **C** in addition to those of type **A**, **B** and **D** (see Scheme 1) because it would then be possible to compare the chemical and physical properties of these metallacumulenes with those of a series of *bimetallic* systems of general composition $[L_nMC_xM'L'_{n'}]$ ($x = 2-8$) which have recently been prepared by Gladysz and coworkers.[22, 23]

Experimental Section

All experiments were carried out under an atmosphere of argon by Schlenk tube techniques. The starting materials **1** [24] and **2** [12b] were prepared as described in the literature. For the chromatographic workup, neutral Al_2O_3 of activity grade V was used. NMR spectra were recorded on a Bruker AC200, IR spectra on a Perkin–Elmer 1420 instrument. Abbreviations used: s, singlet; d, doublet; t, triplet; vt, virtual triplet; m, multiplet. Melting points were measured by DTA.

[IrH(C≡C–C≡CCPh$_2$OH)Cl(P*i*Pr$_3$)$_2$] (**3**): To a solution of **2** (200 mg, 0.364 mmol) in 10 mL of pentane a suspension of **1** (93 mg, 0.40 mmol) in 10 mL of pentane was added dropwise at 0 °C. An immediate change of colour from orange-yellow to red occurred and a gas (H_2) was evolved. The reaction mixture was concentrated in vacuo to approximately 2 mL and then stored at −78 °C. Dark red crystals precipitated and were filtered out, washed repeatedly with pentane (0 °C) and again recrystallized from pentane (40– −78 °C); yield 222 mg (78 %); M.p. 92 °C (decomp.); IR ($CHCl_3$): $\tilde{\nu}$ = 3570 (OH), 2240 (IrH), 2180, 2020 (C≡C) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 7.33 (m, 10H, C_6H_5), 3.10 (m, 6H, PC*H*CH$_3$), 1.34 (dvt, *N* = 14.6, *J*(H,H) = 6.6 Hz, 18H, PCHC*H*$_3$), 1.31 (dvt, *N* = 14.5, *J*(H,H) = 6.6 Hz, 18H, PCHC*H*$_3$), −42.49 (t, *J*(P,H) = 11.6 Hz, 1H, Ir*H*), no OH signal observed; ^{13}C NMR ($CDCl_3$): δ = 145.96, 127.83, 127.12, 125.94 (all s, *C*$_6$H$_5$), 89.86 (t, *J*(P,C) = 1.2 Hz, *C*≡C–CPh$_2$OH), 82.65 (t, *J*(P,C) = 11.3 Hz, Ir*C*≡C), 76.68 (t, *J*(P,C) = 1.8 Hz, IrC≡*C*), 72.56 and 65.67 (both s, C≡*C*–CPh$_2$OH and *C*Ph$_2$OH), 23.12 (vt, *N* = 27.3 Hz, P*C*HCH$_3$), 19.77 and 19.42 (both s, PCH*C*H$_3$); ^{31}P NMR ($CDCl_3$): δ = 39.4 (s); $C_{35}H_{54}ClIrOP_2$ (780.4): calcd C 53.87, H 6.98; found: C 53.97, H 7.13.

***trans*-[IrCl(=C=CH–C≡CCPh$_2$OH)(P*i*Pr$_3$)$_2$]** (**4**): A solution of **3** (60 mg, 0.08 mmol) in 0.5 mL of benzene was irradiated in an NMR tube at room temperature (water cooling) with a mercury lamp (Osram HBO 500 W) for 5 d. The solvent was removed, the residue was dissolved in 2 mL of toluene and the solution was chromatographed on Al_2O_3 at −78 °C. A dark red fraction was eluted and dried in vacuo. The residue was recrystallized from pentane (40–78 °C) to give red-violet crystals which were filtered, washed with small quantities of pentane (−20 °C) and dried; yield 38 mg (63 %); M.p. 76 °C (decomp.); IR (C_6H_6): $\tilde{\nu}$ = 3380 (OH), 2180 (C≡C), 1610 (C=C) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 7.50 (m, 10H, C$_6$*H*$_5$), 2.91 (m, 6H, PC*H*CH$_3$), 1.31 (dvt, *N* = 13.8, *J*(H,H) = 6.7 Hz, 36H, PCHC*H*$_3$), −3.34 (t, *J*(P,H) = 2.4 Hz, 1H, Ir=C=CH), no OH signal observed; ^{13}C NMR (C_6D_6): δ = 258.67 (t, *J*(P,C) = 12.9 Hz, Ir=*C*), 147.14 (s, *ipso*-C of C_6H_5), 99.55 (t, *J*(P,C) = 1.5 Hz, C≡*C*–CPh$_2$OH), 88.06 (t, *J*(P,C) = 3.2 Hz, Ir=C=*C*), 75.05 (s, *C*Ph$_2$OH), 56.97 (t, *J*(P,C) = 2.8 Hz, *C*≡C–CPh$_2$OH), 22.97 (vt, *N* = 26.8 Hz, P*C*HCH$_3$), 19.98 (s, PCH*C*H$_3$); in $CDCl_3$ signals of *ortho*-, *meta*- and *para*-carbon atoms of C_6H_5 observed at δ = 127.95, 127.3 and 126.2 (all s); ^{31}P NMR ($CDCl_3$): δ = 33.1 (s); $C_{35}H_{54}ClIrOP_2$ (780.4): calcd C 53.87, H 6.98; found: C 54.33, H 7.20.

[IrH(C≡C–C≡CCPh$_2$OH)Cl(py)(P*i*Pr$_3$)$_2$] (**5**): A suspension of **3** (69 mg, 0.09 mmol) in 5 mL of pentane was treated with excess pyridine (ca. 0.1 mL) at room temperature. Almost immediately, a dark grey precipitate was formed. The solvent was removed, the residue was dissolved in 2 mL of toluene, and the solution was chromatographed on Al_2O_3. A pale yellow fraction was eluted with toluene and concentrated to ca. 2 mL in vacuo. After 2 mL of hexane was added, the solution was stored at −78 °C for 12 h. A colourless microcrystalline solid was formed, which was separated from the mother liquor, washed repeatedly with pentane (−20 °C) and dried; yield 60 mg (79 %); M.p. 138 °C (decomp.); IR (KBr): $\tilde{\nu}$ = 3610 (OH), 2280 (IrH), 2188, 2043 (C≡C) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ = 9.89 (m, 2H, NC$_5$*H*$_5$), 7.68 and 7.24 (both m, 13H, C$_6$*H*$_5$ and C$_5$*H*$_5$), 2.88 (m, 6H, PC*H*CH$_3$), 1.12 (dvt, *N* = 13.3, *J*(H,H) = 6.7 Hz, 36H, PCHC*H*$_3$), −21.99 (t, *J*(P,H) = 15.1 Hz, 1H, Ir*H*), no OH signal observed; ^{31}P NMR ($CDCl_3$): δ = 9.95 (s); $C_{40}H_{59}ClIrNOP_2$ (859.5): calcd C 55.90, H 6.92, N 1.63; found: C 55.99, H 6.78, N 1.38.

***trans*-[IrCl(=C=C=C=C=CPh$_2$)(P*i*Pr$_3$)$_2$]** (**6**): A stirred solution of **3** (100 mg, 0.13 mmol) in 10 mL of toluene was treated at −78 °C with trifluoromethanesulfonic acid anhydride (22 µL, 0.13 mmol). The reaction mixture was warmed to room temperature and NEt_3 (36 µL, 0.26 mmol) was added. After the solution had been stirred for 10 min, it was concentrated to approximately 2 mL and the concentrate was chromatographed at −78 °C on Al_2O_3. With toluene, a brown fraction was eluted from which the solvent was removed in vacuo. The residue was recrystallized from pentane (40– −78 °C) to give copper-brown crystals which were filtered, washed with small quantities of pentane (−20 °C) and dried; yield 78 mg (80 %); M.p. 132 °C (decomp.); IR (hexane): $\tilde{\nu}$ = 1960, 1856 (C=C=C) cm^{-1}; ^{1}H NMR (C_6D_6): δ = 8.33, 7.74 and 6.60 (all m, 10H, C$_6$*H*$_5$), 3.12 (m, 6H, PC*H*CH$_3$), 1.37 (dvt, *N* = 13.7, *J*(H,H) = 6.6 Hz, 36H, PCHC*H*$_3$); ^{13}C NMR (C_6D_6): δ = 245.45 (t, *J*(P,C) = 4.0 Hz, Ir=C=*C*), 209.61 (t, *J*(P,C) = 3.2 Hz, *C*=CPh$_2$), 186.70 (t, *J*(P,C) = 13.9 Hz, Ir=*C*), 161.74 (t, *J*(P,C) = 1.5 Hz, *C*Ph$_2$), 139.57 (t, *J*(P,C) = 1.5 Hz, *ipso*-C of C_6H_5), 133.70 (t, *J*(P,C) = 3.3 Hz, Ir=C=C=*C*), 131.15, 127.28 and 123.24 (all s, *C*$_6$H$_5$), 23.64 (vt, *N* = 26.4 Hz, P*C*HCH$_3$), 20.57 (s, PCH*C*H$_3$); ^{31}P NMR (C_6D_6): δ = 14.4 (s); $C_{35}H_{52}ClIrP_2$ (762.4): calcd C 55.14, H 6.88; found: C 55.41, H 7.25.

X-Ray Structural Analysis of 6: Single crystals were grown from hexane. Crystal data (from 23 reflections, $10° < \theta < 12°$): triclinic, space group $P\bar{1}$ (No. 2); $a = 11.236(2)$ Å, $b = 11.548(2)$ Å, $c = 28.708(3)$ Å, $\alpha = 98.24(1)°$, $\beta = 93.67(1)°$, $\gamma = 94.88(1)°$, $V = 3662(1)$ Å^3, $Z = 4$, $d_{\mathrm{calcd}} = 1.34$ g cm^{-3}, $\mu(\mathrm{Mo}_{K\alpha}) = 38.1$ cm^{-1}; crystal size 0.05 × 0.30 × 0.50 mm; Enraf–Nonius CAD4 diffractometer, $\mathrm{Mo}_{K\alpha}$ radiation (0.70930 Å), graphite monochromator, zirconium filter (factor 16.4); $T = 293$ K; ω/θ scan, max $2\theta = 44°$; 8538 reflections measured, 7408 independent reflections, 6522 regarded as being observed $[F_0 > 3\sigma(F_0)]$; intensity data were corrected for Lorentz and polarization effects, empirical absorption correction (ψ-scan method) was applied, minimum transmission was 52.4 %. The structure was solved by direct methods (SHELXS-86); atomic coordinates and anisotropic thermal parameters of the non-hydrogen atoms were refined by full-matrix least squares (703 parameters, unit weights, Enraf–Nonius SDP) [25]. The positions of all hydrogen atoms were calculated according to an ideal geometry (C–H distance 0.95 Å) and were included in the structure factor calculation in the last refinement cycle. There are two independent molecules in the unit cell which differ slightly in respect of bond lengths and bond angles (Table 1). $R = 0.023$, $R_w = 0.026$; reflex/parameter ratio 9.28; residual electron density $+0.51/-0.41$ eÅ^{-3} [26].

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