

# On the reactivity of $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$ with alkynylsilanes – A new route to vinylidene iridium(I) complexes

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## Abstract

The iridium dinitrogen complex  $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$  (**1**) was found to react with alkynylsilanes  $\text{RC}\equiv\text{CSiR}'_3$  to form the vinylidene iridium(I) complexes  $\text{trans}-[\text{IrCl}\{\text{C}=\text{CR}(\text{SiR}'_3)\}(\text{PPh}_3)_2]$  ( $\text{R/R}' = \text{Ph/Me}$ , **2**;  $\text{Me/Me}$ , **3**;  $\text{Bn/Me}$ , **4**;  $\text{SiMe}_3/\text{Me}$ , **5**;  $\text{SiEt}_3/\text{Et}$ , **6**;  $^i\text{Pr/Me}$ , **7**) and with  $\text{Me}_3\text{SiC}\equiv\text{CC}(\text{O})\text{R}$  to yield the iridium  $\eta^2$ -alkyne complexes  $\text{trans}-[\text{IrCl}\{\eta^2\text{-Me}_3\text{SiC}\equiv\text{CC}(\text{O})\text{R}\}(\text{PPh}_3)_2]$  ( $\text{R} = \text{OEt}$ , **9**;  $\text{Me}$ , **11**). Complex **9** was found to isomerize upon heating or upon UV irradiation yielding the vinylidene complex  $\text{trans}-[\text{IrCl}\{\text{C}=\text{C}(\text{SiMe}_3)\text{CO}_2\text{Et}\}(\text{PPh}_3)_2]$  (**10**). The reaction of **1** with  $\text{Me}_3\text{SiC}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3$  yielded the complex  $\text{trans}-[\text{IrCl}\{\text{C}=\text{C}(\text{SiMe}_3)\text{C}\equiv\text{CSiMe}_3\}(\text{PPh}_3)_2]$  (**8**), whereas with  $\text{MeO}_2\text{CC}\equiv\text{CCO}_2\text{Me}$  the iridacyclopentadiene complex  $[\text{Ir}\{\text{C}_4(\text{CO}_2\text{Me})_4\}\text{Cl}(\text{PPh}_3)_2]$  (**13**) was formed. The complexes were characterized by means of  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectroscopy as well as by IR spectroscopy and microanalysis. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** Iridium; Alkynylsilane; Vinylidene complexes;  $\eta^2$ -Alkyne complexes; Iridacyclopentadiene

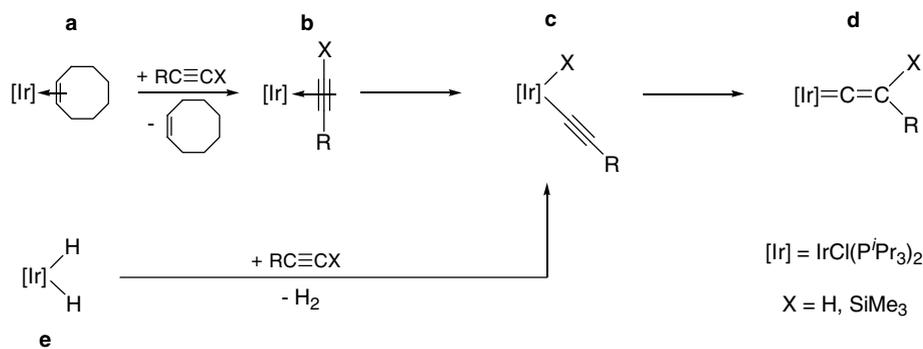
## 1. Introduction

It is well-known that vinylidenes – the thermodynamically less stable isomers of alkynes – can be effectively stabilized via coordination to a transition metal center [1] and that vinylidene transition metal complexes play an important role as intermediates in some homogeneously catalyzed reactions [2]. Square-planar vinylidene iridium(I) complexes  $\text{trans}-[\text{IrCl}(\text{C}=\text{CHR})(\text{P}^i\text{Pr}_3)_2]$  have been firstly prepared by Werner et al. [3] as shown in Scheme 1 ( $\text{X} = \text{H}$ ). The substitution reactions of terminal alkynes  $\text{RC}\equiv\text{CH}$  with the cyclooctene complex **a** (generated in situ from  $[\{\text{IrCl}(\text{C}_8\text{H}_{14})_2\}]_2$  and  $\text{P}^i\text{Pr}_3$  [4]) gave the alkyne complexes **b**, which were found to isomerize via hydrido(alkynyl)iridium(III) complexes **c** yielding the vinylidene complexes **d** [3,5]. Alternatively, the dihydrido-iridium(III) complex **e** underwent, with the reductive elimination of  $\text{H}_2$ , the oxidative addition of terminal alkynes

to provide the intermediate complexes **c**, which isomerized to the vinylidene complexes **d** [6]. Furthermore, alkynylsilanes  $\text{RC}\equiv\text{CSiMe}_3$  were found to react analogously with  $\equiv\text{C}-\text{Si}$  bond activation (Scheme 1,  $\text{X} = \text{SiMe}_3$ ), likely also via type **c** intermediate complexes [7,8]. However, all these reactions proceeded with triisopropylphosphine as co-ligands [3,5–8]. Other phosphines could be used only in special cases. Thus,  $[\text{IrCl}(\text{C}=\text{CH}_2)(\text{PMe}^i\text{Bu}_2)_2]$  was obtained from the reaction of  $[\text{IrCl}(\text{H})_2(\text{PMe}^i\text{Bu}_2)_2]$  with acetylene, but reactions using  $\text{PMePh}_2$ ,  $\text{PMe}_2^i\text{Bu}$ ,  $\text{PMe}_2\text{Ph}$  or  $\text{PPh}_3$  failed [9]. The only complex having  $\text{PPh}_3$  co-ligands  $[\text{IrCl}(\text{C}=\text{CH}_2)(\text{PPh}_3)_2]$  was isolated in the elimination reaction of CO from  $[\text{Ir}(\text{C}\equiv\text{CH})\text{Cl}(\text{H})(\text{CO})(\text{PPh}_3)_2]$  with  $\text{Me}_3\text{NO}$  [9]. Furthermore, some vinylidene type **d** complexes with bifunctional phosphines  $\text{P}(\text{CH}_2\text{CH}_2\text{O}-\text{Me})(^i\text{Pr})_2$  or  $\text{P}(\text{CH}_2\text{CO}_2\text{Me})(^i\text{Pr})_2$  have also been obtained [10].

As early as 1967 Collman et al. reported the reactions of  $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$  (**1**) with internal alkynes having two electron-withdrawing substituents  $\text{RC}\equiv\text{CR}'$  ( $\text{R}, \text{R}' = \text{CO}_2\text{Me}, \text{Ph}, \dots$ ) to form iridium  $\eta^2$ -alkyne [11] or

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Scheme 1.

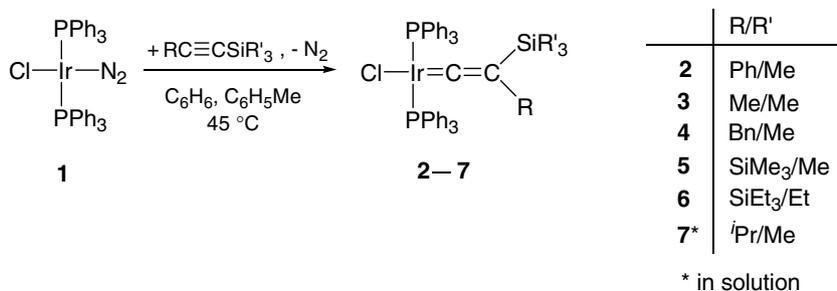
iridacyclopentadiene [12] complexes. Thus, it was shown that the dinitrogen ligand in **1** could be – in principle – substituted by alkynes. However, from the analogous reactions with acetylene and phenylacetylene it was not possible to isolate either the requisite alkyne or vinylidene complexes [9]. Within this paper we describe our investigations on the reactivity of the iridium dinitrogen complex **1** toward trialkylsilyl-substituted alkynes yielding  $\eta^2$ -alkyne complexes and/or, with  $\equiv\text{C}-\text{Si}$  bond activation, square-planar iridium(I) vinylidene complexes having triphenylphosphine co-ligands.

## 2. Results and discussion

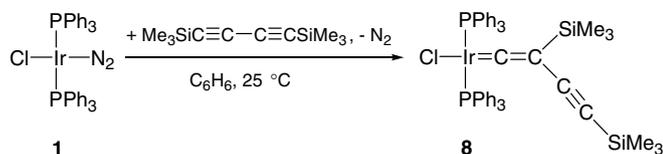
The dinitrogen iridium complex  $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$  (**1**) was found to react with  $\text{RC}\equiv\text{CSiR}'_3$  in benzene or toluene at 45 °C yielding the iridium(I) vinylidene complexes *trans*- $[\text{IrCl}\{\text{C}=\text{C}(\text{SiR}'_3)\}(\text{PPh}_3)_2]$  (**2–7**) (Scheme 2). Monitoring the reactions NMR spectroscopically ( $^{13}\text{C}$ ,  $^{31}\text{P}$ ) revealed that the complexes **2–7** were almost quantitatively formed within 1–6 h. Complexes **2–6** were isolated in yields of 53–78%; complex **7** has been characterized in  $\text{C}_6\text{D}_6$  solution. The vinylidene complexes **2–6** are red-pink or orange, with the exception of **4**, moderately air-sensitive solids, which are well soluble in benzene and methylene chloride and sparingly soluble in methanol, hexane and diethyl ether. They undergo decomposition within 15 min up to 1 h on air but can be stored under argon at –40 °C at least for a few weeks without decomposition. Complex **4** (R = Bn) is air-sensitive in the solid state and it turns brownish within a few minutes.

The identities of the vinylidene complexes were confirmed by microanalyses, IR spectroscopy as well as  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectroscopy. The  $^{13}\text{C}$  NMR resonances for vinylidene  $\alpha$ -carbon atoms are strongly low-field shifted (244–264 ppm) exhibiting  $^2J(\text{P},\text{C})$  coupling constants of 11–13 Hz, whereas the resonances for vinylidene  $\beta$ -carbon atoms were found at 82–103 ppm having  $^3J(\text{P},\text{C})$  coupling constants of 2–4 Hz. The triplet patterns of these two signals give clear evidence for the *trans* configuration of the complexes. In accordance with that in the  $^{31}\text{P}$  NMR spectra singlet resonances at 25–28 ppm were found. The NMR data are consistent with those reported by Werner et al. for analogous complexes with  $\text{P}^i\text{Pr}_3$  ligands ( $^{13}\text{C}$  NMR: 240–255 ppm ( $\text{C}_\alpha$ ); 80–100 ppm ( $\text{C}_\beta$ );  $^{31}\text{P}$  NMR: 29–34 ppm) [7]. The IR spectra of complexes **2–6** revealed bands in the range 1587–1659  $\text{cm}^{-1}$  that were assigned to the  $\text{C}=\text{C}$  stretching vibration. For comparison, in the IR spectra of alkenes  $\text{C}=\text{C}$  stretching vibrations usually appear in the range 1635–1690  $\text{cm}^{-1}$  [13].

Complex **1** was found to react with excess of  $\text{Me}_3\text{SiC}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3$  yielding the vinylidene complex *trans*- $[\text{IrCl}\{\text{C}=\text{C}(\text{SiMe}_3)\text{C}\equiv\text{CSiMe}_3\}(\text{PPh}_3)_2]$  (**8**) (Scheme 3). This complex was isolated in 68% yield as a violet-brown powder that is stable on air in the solid state for about 1 h. The analogous reaction of **1** with only 0.5 equiv. of  $\text{Me}_3\text{SiC}\equiv\text{C}-\text{C}\equiv\text{CSiMe}_3$  did not lead to the formation of a binuclear complex having a bridging bis(vinylidene) ligand  $\mu\text{-}(\text{C}=\text{C}(\text{SiMe}_3)-\text{C}(\text{SiMe}_3)=\text{C}=\text{C})$ . The  $^{13}\text{C}$  NMR spectrum of **8** gave clear evidence for its identity. The low-field shifted resonance for the vinylidene  $\alpha$ -carbon atom was found as triplet at 261.5 ppm ( $^2J(\text{P},\text{C}) =$



Scheme 2.



Scheme 3.

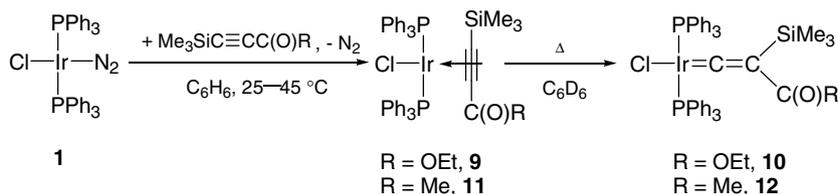
12.0 Hz). The assignment of two high-field shifted resonances at 78.4 and 83.8 ppm, with almost the same  $J(\text{P,C})$  coupling constants of 3.0/3.1 Hz, to the vinylidene  $\beta$ -carbon and the alkyne  $\gamma$ -carbon atoms is equivocal. However, in the analogous complex with  $\text{P}^i\text{Pr}_3$  ligands reported by Werner et al. the corresponding high-field shifted signal at 77.2 ppm was assigned to the vinylidene  $\beta$ -carbon atom, whereas that at 83.1 ppm to the  $\gamma$ -carbon atom [7]. The singlet resonance at 95.0 ppm is unequivocally assigned to the  $\text{C}\equiv\text{CSiMe}_3$  carbon atom of the uncoordinated triple bond. In the case of free diyne the resonances of the  $\text{C}\equiv\text{C}$  triple bond appear at 86.2 and 89.5 ppm. Moreover, the two  $\text{SiMe}_3$  groups were found to be chemically nonequivalent in the  $^{13}\text{C}$  and  $^1\text{H}$  NMR spectra. The *trans* disposition of the phosphine ligands in complex **8** is inferred from the observation of a singlet resonance in the  $^{31}\text{P}$  NMR spectrum at 26.6 ppm. The IR spectrum of **8** reveals two characteristic bands at 1611 and  $2105\text{ cm}^{-1}$  that can be assigned to the  $\text{C}=\text{C}$  and  $\text{C}\equiv\text{C}$  stretching vibrations, respectively. A band due to  $\text{C}\equiv\text{C}$  stretching vibration of uncoordinated ligand appears at  $2066\text{ cm}^{-1}$ .

In contrast to the reactions of the dinitrogen complex **1** with alkynylsilanes bearing electron-donating or weakly electron-withdrawing substituents, the reactions of **1** with  $\text{Me}_3\text{SiC}\equiv\text{CC}(\text{O})\text{R}$  led to the formation of the iridium  $\eta^2$ -alkyne complexes *trans*- $[\text{IrCl}\{\eta^2\text{-Me}_3\text{SiC}\equiv\text{CC}(\text{O})\text{R}\}(\text{PPh}_3)_2]$  ( $\text{R} = \text{OEt}$ , **9**;  $\text{R} = \text{Me}$ , **11**) (Scheme 4). Complexes **9** and **11** were isolated as orange and brownish moderately air-sensitive powders in 60% and 78% yield, respectively. Complex **9** was found to undergo on heating in benzene at  $50\text{ }^\circ\text{C}$  (3 days) or upon UV irradiation (14 h) an isomerization yielding the vinylidene isomer *trans*- $[\text{IrCl}\{\text{C}=\text{C}$

$(\text{SiMe}_3)\text{CO}_2\text{Et}\}(\text{PPh}_3)_2]$  (**10**) with a degree of conversion of about 50% and 95%, respectively. On the other hand, in  $\text{C}_6\text{D}_6$  solution of complex **11** the resonances of the uncoordinated ligand (10–30%) were also found, although the solid substance gave correct analytical data (C, H) and its IR spectrum showed only one stretching vibration ( $1801\text{ cm}^{-1}$ ) assigned to the coordinated ligand. Thus, in solution the alkyne ligand seems to be partially cleaved off. Furthermore, the  $\text{C}_6\text{D}_6$  solutions of **11** turned out to be much less stable. Even at room temperature within one day a partial decomposition took place and isomerization, yielding the requisite vinylidene complex *trans*- $[\text{IrCl}\{\text{C}=\text{C}(\text{SiMe}_3)\text{C}(\text{O})\text{Me}\}(\text{PPh}_3)_2]$  (**12**), occurred only to an extent of about 10% (Scheme 4).

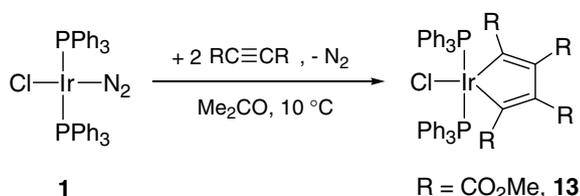
The identities of complexes **9** and **11** were confirmed by microanalyses as well as by IR and NMR spectroscopic measurements. The resonances of alkyne carbon atoms (**9**: 94.9/97.7 ppm; **11**: 103.1/105.8 ppm) show coordination-induced shifts (CIS) of 2.1/1.5 ppm (**9**) and 7.7/2.4 ppm (**11**). The triplet pattern of the signals due to the  $^2J(\text{P,C})$  coupling (1.4–2.1 Hz) and the singlet  $\delta(^{31}\text{P})$  resonances at 19.8 (**9**) and 22.4 ppm (**11**) give evidence for the *trans* configuration. The IR spectra of  $\eta^2$ -alkyne complexes display a band due to the  $\text{C}\equiv\text{C}$  stretching vibration at  $1828$  (**9**) and  $1801\text{ cm}^{-1}$  (**11**). Thus, it is lowered in comparison with uncoordinated alkynes by ca.  $350\text{ cm}^{-1}$ . The  $^{13}\text{C}$  NMR spectra of the vinylidene complexes **10** and **12** show the characteristic triplet resonances for the vinylidene  $\alpha$ - and  $\beta$ -carbon atoms (**10/12**: 263.7/267.9 ppm; 97.2/108.1 ppm) and are analogous to those of the vinylidene complexes **2–7**. Analogously, the above-described triplet pattern and the singlet phosphorus resonances (27.1/26.0 ppm) account for the *trans* configuration of both complexes.

The reaction of  $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$  (**1**) with  $\text{MeO}_2\text{CC}\equiv\text{C-CO}_2\text{Me}$  at  $10\text{ }^\circ\text{C}$  in acetone resulted in the formation of the iridacyclopentadiene complex  $[\text{Ir}\{\text{C}_4(\text{CO}_2\text{Me})_4\}\text{Cl}(\text{PPh}_3)_2]$  (**13**) (Scheme 5), which has been already reported by Collman et al. in an analogous reaction at  $45\text{ }^\circ\text{C}$  in thiophene-free benzene [12]. Complex **13** was isolated in 42% yield as air-stable red crystals, which are well soluble in chlorinated solvents and acetone. The spectroscopic data are consistent



	<i>t</i> in h	<b>9</b> : <b>10</b>	<b>11</b> : <b>12</b> : dec.
50 °C	72	53 : 47	50 : 10 : 40
UV	14	5 : 95	-

Scheme 4.



Scheme 5.

with those reported in the literature [12]; the crystal structure has been reported elsewhere [14].

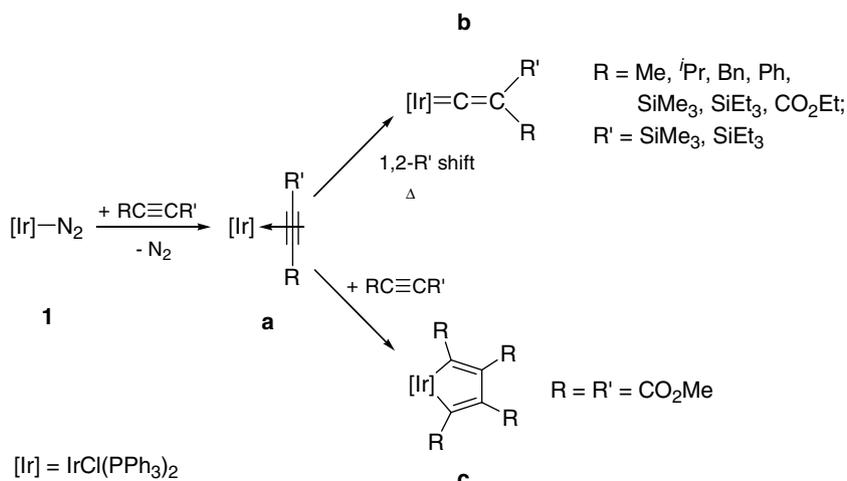
The results presented in this paper are summarized in Scheme 6. Thus, the iridium dinitrogen complex  $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$  (**1**) was found to be a versatile starting material for the preparation of square-planar  $\text{Me}_3\text{Si}$ - or  $\text{Et}_3\text{Si}$ -substituted vinylidene iridium(I) complexes having  $\text{PPh}_3$  co-ligands (Scheme 6, **b**). Most likely, the first step is the substitution of the dinitrogen ligand by an alkyne yielding  $\eta^2$ -alkyne complexes (**a**) as it was proved in the reactions with alkynylsilanes having a strongly electron-withdrawing substituent ( $\text{Me}_3\text{SiC}\equiv\text{CC}(\text{O})\text{R}$ ,  $\text{R} = \text{OEt}$ ,  $\text{Me}$ ). Furthermore, as it was shown by Collman the use of internal alkynes  $\text{RO}_2\text{CC}\equiv\text{CCO}_2\text{R}$  ( $\text{R} = \text{Me}$ ,  $\text{Et}$ ) having two strongly electron-withdrawing substituents led to the formation of type **a** complexes, which were found to react further yielding iridacyclopentadiene complexes **c** [12]. Using alkynylsilanes  $\text{RC}\equiv\text{CR}'$  ( $\text{R}' = \text{SiMe}_3$ ,  $\text{SiEt}_3$ ) having electron-donating ( $\text{R} = \text{Me}$ ,  $i\text{Pr}$ ,  $\text{SiMe}_3$ ,  $\text{SiEt}_3$ ) or weakly electron-withdrawing ( $\text{R} = \text{Bn}$ ,  $\text{Ph}$ ) substituents, the formation of the intermediate type **a** complexes could not be proved experimentally. However, the formation of complexes  $[\text{IrCl}(\eta^2\text{-RC}\equiv\text{CSiMe}_3)(\text{P}^i\text{Pr}_3)_2]$  has been proved NMR spectroscopically in the reactions of  $[\{\text{IrCl}(\text{C}_8\text{H}_{14})_2\}]_2$  with  $\text{P}^i\text{Pr}_3/\text{RC}\equiv\text{CSiMe}_3$  [7]. The silyl shift reactions (**a**  $\rightarrow$  **b**) may proceed via silyl(alkynyl)iridium(III) intermediate complexes; with terminal alkynes ( $\text{P}^i\text{Pr}_3$  co-ligands) the analogous hydrido(alkynyl)irid-

ium(III) complexes (Scheme 1, **c**,  $\text{X} = \text{H}$ ) could be isolated [3,5] and, furthermore, the reaction of  $[\text{IrCl}(\text{C}_8\text{H}_{14})(\text{P}^i\text{Pr}_3)_2]$  and  $\text{HSiMe}_3$  resulted in the formation of hydrido(silyl) complex  $[\text{IrHCl}(\text{SiMe}_3)(\text{P}^i\text{Pr}_3)_2]$  [7]. Overall, the route shown in Scheme 6 is similar to that reported by Werner et al. (Scheme 1) but seems to be restricted to  $\text{C}\text{--}\text{Si}$  bond activation using alkynylsilanes, whereas Werner's route also allows  $\text{C}\text{--}\text{H}$  bond activation in terminal alkynes. Nevertheless, to date the formation of vinylidene complexes according to Scheme 6 is the only way to obtain a broader variety of Werner's type vinylidene iridium complexes, other than with triisopropylphosphine ligands. Although the properties of vinylidene iridium complexes with  $\text{PPh}_3$  ligands are similar to those reported for analogous complexes with  $\text{P}^i\text{Pr}_3$  ligands, the former complexes seem to be less stable.

### 3. Experimental

#### 3.1. General comments

All reactions were carried out under argon using standard Schlenk techniques. Diethyl ether, benzene and toluene were distilled from sodium benzophenone ketyl. *n*-Hexane and *n*-pentane were dried over  $\text{LiAlH}_4$ . Methanol was dried over  $\text{Mg}$  and distilled from  $\text{NaBH}_4/\text{Na}_2[\text{Fe}(\text{pc})] \cdot 5.5\text{THF}$  ( $\text{H}_2\text{pc} = \text{phthalocyanine}$ ).  $[\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2]$  (**1**) [15] and  $\text{BnC}\equiv\text{CSiMe}_3$  [16] were prepared in accordance with the procedures in the literature. All other compounds were commercially available and used as received.  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra were recorded on Varian Gemini 200, VXR 400 and Unity 500 spectrometers. Chemical shifts are relative to  $\text{C}_6\text{H}_6$  ( $\delta$  7.15),  $\text{CH}_2\text{Cl}_2$  ( $\delta$  5.32) and  $\text{C}_6\text{D}_6$  ( $\delta$  128.0),  $\text{CD}_2\text{Cl}_2$  ( $\delta$  53.8) as internal references.  $\delta(^{31}\text{P})$  is relative to external  $\text{H}_3\text{PO}_4$  (85%). Microanalyses (C, H, N) were performed by the University of Halle microanalytical laboratory using CHNS-932 (LECO) and Vario EL (elementar Analysensysteme) elemental analyzers. IR spectra were recorded on a Mattson Galaxy 5000



Scheme 6.

FT-IR spectrometer using CsBr or KBr pellets. To run experiments in NMR tubes, they were charged under argon with educts and solvents by means of syringes and then closed by melting. Reactions were performed in a shaking machine with automatic temperature regulation. In appropriate time intervals NMR spectra were recorded to monitor the reactions.

### 3.2. Syntheses

3.2.1. *trans*-[IrCl{C=CR(SiR'<sub>3</sub>)}(PPh<sub>3</sub>)<sub>2</sub>] (R/R' = Ph/Me, **2**; R/R' = Me/Me, **3**; R/R' = SiMe<sub>3</sub>/Me, **5**; R/R' = SiEt<sub>3</sub>/Et, **6**)

To a yellow suspension of [IrCl(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (**1**) (65 mg, 0.083 mmol) in benzene (**2**, **3**) or toluene (**5**, **6**) (2 ml), the corresponding alkynylsilane RC≡CSiR'<sub>3</sub> (2:1–2.5:1) was added at room temperature with stirring. The reaction mixture was warmed up to about 45 °C and then stirred for a few hours until a clear solution formed and a change of colour from yellow to red-violet (**2**, **3**) or red-orange (**5**, **6**) occurred (4–6 h). The solvent volume was reduced by evaporation in vacuo to ca. 1 ml and freshly distilled methanol (3:1) was added. Solvents were then evaporated in vacuo up to 1–2 ml. The red-pink (**2**, **3**)/orange (**5**, **6**) precipitate formed was subsequently filtered off, washed with methanol (5 ml) at –10 °C and dried in vacuo for 1 h.

(**2**) Yield: 60 mg (78%). Anal. Calc. for IrClP<sub>2</sub>SiC<sub>47</sub>H<sub>44</sub> (926.57): C, 60.93; H, 4.79. Found: C, 59.72; H, 5.22%.  $\nu(\text{C}=\text{C})$  1587(s) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  –0.04 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 6.76/6.89 ('t'/'t',<sup>1</sup> 1H/2H, *p*-H/*m*-H of Ph), 6.97–7.00/7.91–7.96 (m/m, 18H/13H, *p*-H, *m*-H of PPh<sub>3</sub>/*o*-H of PPh<sub>3</sub>, *o*-H of Ph). <sup>13</sup>C NMR (100 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.8 (s, Si(CH<sub>3</sub>)<sub>3</sub>), 101.6 (m, Ir=C=C), 121.9 (s, *i*-C of Ph), 124.2 (s, *p*-C of Ph), 127.5 (s, *o*-C or *m*-C of Ph, the other one is overlapped with C<sub>6</sub>D<sub>6</sub>/PPh<sub>3</sub>), 128.1 ('t', *m*-C of PPh<sub>3</sub>), 130.2 (s, *p*-C of PPh<sub>3</sub>), 132.7 ('t', *i*-C of PPh<sub>3</sub>), 135.8 ('t', *o*-C of PPh<sub>3</sub>), 263.5 (t, <sup>2</sup>J(P,C) = 12.9 Hz, Ir=C). <sup>31</sup>P NMR (81 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  25.1 (s).

(**3**) Yield: 40 mg (56%). Anal. Calc. for IrClP<sub>2</sub>SiC<sub>42</sub>H<sub>42</sub> (864.50): C, 58.35; H, 4.90. Found: C, 57.98; H, 5.32%.  $\nu(\text{C}=\text{C})$  1652(w) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  –0.29 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 1.55 (t, 3H, <sup>5</sup>J(P,H) = 2.1 Hz, CH<sub>3</sub>), 7.01–7.10/7.93–7.98 (m/m, 18H/12H, *p*-H, *m*-H/*o*-H of PPh<sub>3</sub>). <sup>13</sup>C NMR (125.7 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  –6.1 (s, CH<sub>3</sub>), –1.3 (s, Si(CH<sub>3</sub>)<sub>3</sub>), 88.4 (t, <sup>3</sup>J(P,C) = 3.6 Hz, Ir=C=C), 127.9 ('t', *m*-C of PPh<sub>3</sub>), 129.9 (s, *p*-C of PPh<sub>3</sub>), 133.4 ('t', *i*-C of PPh<sub>3</sub>), 135.9 ('t', *o*-C of PPh<sub>3</sub>), 257.9 (t, <sup>2</sup>J(P,C) = 13.1 Hz, Ir=C). <sup>31</sup>P NMR (81 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  25.8 (s).

(**5**) Yield: 48 mg (62%). Anal. Calc. for IrClP<sub>2</sub>Si<sub>2</sub>C<sub>44</sub>H<sub>48</sub> (922.64): C, 57.28; H, 5.24. Found: C, 57.38; H, 5.39%.  $\nu(\text{C}=\text{C})$  1639 (s, br) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  –0.06 (s, 18H, Si(CH<sub>3</sub>)<sub>3</sub>), 7.02–7.15/7.96–8.00 (m/m,

18H/12H, *m*-H, *p*-H/*o*-H of PPh<sub>3</sub>). <sup>13</sup>C NMR (125.7 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  1.8 (s, Si(CH<sub>3</sub>)<sub>3</sub>), 84.2 (t, <sup>3</sup>J(P,C) = 2.0 Hz, Ir=C=C), 128.0 ('t', *m*-C of PPh<sub>3</sub>), 129.9 (s, *p*-C of PPh<sub>3</sub>), 134.0 ('t', *i*-C of PPh<sub>3</sub>), 136.0 ('t', *o*-C of PPh<sub>3</sub>), 246.7 (t, <sup>2</sup>J(P,C) = 10.9 Hz, Ir=C). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>, 81 MHz):  $\delta$  28.0 (s).

(**6**) Yield: 49 mg (58%). Anal. Calc. for IrClP<sub>2</sub>Si<sub>2</sub>C<sub>50</sub>H<sub>60</sub> (1006.80): C, 59.65; H, 6.01. Found: C, 59.96; H, 6.16%.  $\nu(\text{C}=\text{C})$  1615(s) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.47 (q, 12H, <sup>3</sup>J(H,H) = 8.0 Hz, Si(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 1.05 (t, 18H, <sup>3</sup>J(H,H) = 8.0 Hz, Si(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 7.06/7.13/7.95–8.00 ('t'/'t'/m, 6H/12H/12H, *p*-H/*m*-H/*o*-H of PPh<sub>3</sub>). <sup>13</sup>C NMR (125.7 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  7.1 (s, Si(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 9.3 (s, Si(CH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>), 82.7 (s, br, Ir=C=C), 128.0 ('t', *m*-C of PPh<sub>3</sub>), 129.8 (s, *p*-C of PPh<sub>3</sub>), 134.1 ('t', *i*-C of PPh<sub>3</sub>), 136.1 ('t', *o*-C of PPh<sub>3</sub>), 244.2 (t, <sup>2</sup>J(P,C) = 11.0 Hz, Ir=C). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>, 81 MHz):  $\delta$  27.1 (s).

3.2.2. *trans*-[IrCl{C=C*Bn*(SiMe<sub>3</sub>)}(PPh<sub>3</sub>)<sub>2</sub>] (**4**)

To a yellow suspension of [IrCl(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (**1**) (70 mg, 0.090 mmol) in benzene (3 ml) 1-(trimethylsilyl)-3-phenylprop-1-yne (26 mg, 0.14 mmol) was added with stirring. The reaction mixture was warmed up to about 40 °C and then stirred for a few hours until a clear solution formed and a change of colour to deep red occurred (1–3 h). The solvent was then removed by evaporation in vacuo to dryness and freshly distilled hexane (5 ml) was added. A red-pink precipitate was filtered off, washed with hexane (10 ml) at –10 °C and dried in vacuo for 1 h. Yield: 45 mg (53%).  $\nu(\text{C}=\text{C})$  1659 (m, br) cm<sup>-1</sup>. <sup>1</sup>H NMR (500 MHz CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  –0.58 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 3.22 (s, 2H, CH<sub>2</sub>), 6.70/6.90/6.96 ('d'/'t'/'t', 2H/2H/1H, *o*-H/*m*-H/*p*-H of Ph), 7.36–7.42/7.67–7.71 (m/m, 18H/12H, *m*-H, *p*-H/*o*-H of PPh<sub>3</sub>). <sup>13</sup>C NMR (CD<sub>2</sub>Cl<sub>2</sub>, 125.7 MHz):  $\delta$  –0.8 (s, Si(CH<sub>3</sub>)<sub>3</sub>), 16.8 (s, CH<sub>2</sub>), 95.5 (t, <sup>3</sup>J(P,C) = 3.6 Hz, Ir=C=C), 125.8 (s, *p*-C of Ph), 127.7/129.2 (s/s, *m*-C and *o*-C of Ph), 128.2 ('t', *m*-C of PPh<sub>3</sub>), 130.3 (s, *p*-C of PPh<sub>3</sub>), 133.3 ('t', *i*-C of PPh<sub>3</sub>), 135.8 ('t', *o*-C of PPh<sub>3</sub>), 142.6 (s, *i*-C of Ph), 256.1 (t, <sup>2</sup>J(P,C) = 12.6 Hz, Ir=C). <sup>31</sup>P NMR (CD<sub>2</sub>Cl<sub>2</sub>, 81 MHz):  $\delta$  25.2 (s).

3.2.3. Formation of *trans*-[IrCl{C=C*i*Pr(SiMe<sub>3</sub>)}(PPh<sub>3</sub>)<sub>2</sub>] (**7**)

In an NMR tube [IrCl(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (**1**) (30 mg, 0.038 mmol) and 3-methyl-1-(trimethylsilyl)but-1-yne (13 mg, 0.09 mmol) were reacted in C<sub>6</sub>D<sub>6</sub> (1 ml) at room temperature for a few hours until a yellow suspension turned to a deep red solution. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  –0.04 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 0.62 (d, 6H, <sup>3</sup>J(H,H) = 6.7 Hz, CH<sub>3</sub>), 2.47 (m, 1H, CH), 7.02–7.12/7.95–8.00 (m/m, 18H/12H, *m*-H, *p*-H/*o*-H of PPh<sub>3</sub>). <sup>13</sup>C NMR (125.7 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.8 (s, Si(CH<sub>3</sub>)<sub>3</sub>), 14.6 (s, CH), 25.0 (s, CH<sub>3</sub>), 102.4 (t, <sup>3</sup>J(P,C) = 3.1 Hz, Ir=C=C), 128.1 ('t', *m*-C of PPh<sub>3</sub>), 129.9 (s, *p*-C of PPh<sub>3</sub>), 133.6 ('t', *i*-C of PPh<sub>3</sub>), 136.0 ('t', *o*-C of PPh<sub>3</sub>), 258.0 (t, <sup>2</sup>J(P,C) = 12.4 Hz, Ir=C). <sup>31</sup>P NMR (81 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  25.0 (s).

<sup>1</sup> Here and in the following 't' denotes pseudotriplet, 'd' pseudodoublet.

### 3.2.4. *trans*-[IrCl{≡C=C(SiMe<sub>3</sub>)C≡CSiMe<sub>3</sub>}(PPh<sub>3</sub>)<sub>2</sub>] (**8**)

[IrCl(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (**1**) (40 mg, 0.051 mmol) and 1,4-bis(trimethylsilyl)buta-1,3-diyne (19 mg, 0.10 mmol) were suspended in benzene (1 ml). After 1 day of stirring a deep red solution formed. The solvent was removed in vacuo up to dryness. The violet-brown crude product was washed with pentane at –10 °C and dried in vacuo for 1 h. Yield: 33 mg (68%).  $\nu(\text{C}\equiv\text{C})$  2105 (m),  $\nu(\text{C}=\text{C})$  1611 (w) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  –0.26/0.23 (s/s, 9H/9H, Si(CH<sub>3</sub>)<sub>3</sub>), 7.02–7.15/7.91–7.96 (m/m, 18H/12H, *m*-H, *p*-H/*o*-H of PPh<sub>3</sub>). <sup>13</sup>C NMR (125.7 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  –1.4/1.1 (s/s, Si(CH<sub>3</sub>)<sub>3</sub>), 78.4/83.8 (t/t, *J*(P,C) = 3.0/3.1 Hz, Ir=C=C and =C(SiMe<sub>3</sub>)C=C), 95.0 (s, ≡CSiMe<sub>3</sub>), 128.3 (‘t’, *m*-C of PPh<sub>3</sub>), 130.1 (s, *p*-C of PPh<sub>3</sub>), 132.2 (‘t’, *i*-C of PPh<sub>3</sub>), 135.8 (‘t’, *o*-C of PPh<sub>3</sub>), 261.5 (t, <sup>2</sup>*J*(P,C) = 12.0 Hz, Ir=C). <sup>31</sup>P NMR (81 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  26.6 (s). For comparison Me<sub>3</sub>SiC≡C–C≡CSiMe<sub>3</sub>:  $\nu(\text{C}\equiv\text{C})$  2066 cm<sup>-1</sup>. <sup>13</sup>C NMR (125.7 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  –0.65 (s, Si(CH<sub>3</sub>)<sub>3</sub>), 86.2/89.5 (s/s, C≡C).

### 3.2.5. *trans*-[IrCl{η<sup>2</sup>-Me<sub>3</sub>SiC≡CCO<sub>2</sub>Et}(PPh<sub>3</sub>)<sub>2</sub>] (**9**)

To a suspension of [IrCl(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (**1**) (70 mg, 0.090 mmol) in benzene (2 ml) ethyl 3-(trimethylsilyl)propynoate (31 mg, 0.18 mmol) was added at room temperature with stirring. The reaction mixture was warmed up to about 45 °C and stirred for a few hours. After 15 min an orange-brown clear solution formed. After 1–2 h a change of colour to red-brownish occurred. The work-up procedure is analogous to that described in Section 3.2.1. Orange powder. Yield: 50 mg (60%). Anal. Calc. for IrClP<sub>2</sub>SiO<sub>2</sub>C<sub>44</sub>H<sub>44</sub> (922.52): C, 57.29; H, 4.81. Found: C, 56.89; H, 4.73%.  $\nu(\text{C}\equiv\text{C})$  1828(m) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.08 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 0.89 (t, 3H, <sup>3</sup>*J*(H,H) = 7.0 Hz, CH<sub>3</sub>), 3.68 (q, 2H, <sup>3</sup>*J*(H,H) = 7.0 Hz, CH<sub>2</sub>), 7.01–7.11/7.91–7.98 (m/m, 18H/12H, *m*-H, *p*-H/*o*-H of PPh<sub>3</sub>). <sup>13</sup>C NMR (125.7 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  –0.9 (s, Si(CH<sub>3</sub>)<sub>3</sub>), 14.2 (s, CH<sub>2</sub>CH<sub>3</sub>), 59.8 (s, CH<sub>2</sub>), 94.9/97.7 (t/t, <sup>2</sup>*J*(P,C) = 2.1/2.1 Hz, C≡C), 127.9 (‘t’, *m*-C of PPh<sub>3</sub>), 129.8 (s, *p*-C of PPh<sub>3</sub>), 131.9 (‘t’, *i*-C of PPh<sub>3</sub>), 136.0 (‘t’, *o*-C of PPh<sub>3</sub>), 150.7 (s, C=O). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>, 81 MHz):  $\delta$  19.8 (s). For comparison Me<sub>3</sub>SiC≡CCO<sub>2</sub>Et:  $\nu(\text{C}\equiv\text{C})$  2180 cm<sup>-1</sup>. <sup>13</sup>C NMR (125.7 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  –1.1 (s, Si(CH<sub>3</sub>)<sub>3</sub>), 13.8 (s, CH<sub>3</sub>), 61.6 (s, CH<sub>2</sub>), 92.8/96.2 (s/s, C≡C), 153.0 (s, C=O).

### 3.2.6. *trans*-[IrCl{η<sup>2</sup>-Me<sub>3</sub>SiC≡CC(O)Me}(PPh<sub>3</sub>)<sub>2</sub>] (**11**)

To a yellow suspension of [IrCl(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (**1**) (62 mg, 0.079 mmol) in benzene (2 ml) 4-(trimethylsilyl)but-3-yn-2-one (35 mg, 0.25 mmol) was added at room temperature with stirring. After 6 h an orange-brown solution formed. The work-up procedure is analogous to that described in Section 3.2.2. Brownish powder. Yield: 55 mg (78%). Anal. Calc. for IrClP<sub>2</sub>SiOC<sub>43</sub>H<sub>42</sub> (892.51): C, 57.87; H, 4.74. Found: C, 58.28; H, 5.24%.  $\nu(\text{C}\equiv\text{C})$  1801(m) cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  0.08 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 1.62 (s, 3H, CH<sub>3</sub>), 6.97–7.09/7.94–7.98 (m/m, 18H/12H, *m*-H, *p*-

*H*/*o*-H of PPh<sub>3</sub>). <sup>13</sup>C NMR (125.7 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  –0.4 (s, Si(CH<sub>3</sub>)<sub>3</sub>), 30.1 (s, CH<sub>3</sub>), 103.1/105.8 (t/s(br), <sup>2</sup>*J*(P,C) = 1.4 Hz/not observed, C≡C), 127.9 (‘t’, *m*-C of PPh<sub>3</sub>), 129.8 (s, *p*-C of PPh<sub>3</sub>), 131.8 (‘t’, *i*-C of PPh<sub>3</sub>), 136.1 (‘t’, *o*-C of PPh<sub>3</sub>), 180.8 (C=O). <sup>31</sup>P NMR (C<sub>6</sub>D<sub>6</sub>, 81 MHz):  $\delta$  22.4 (s). For comparison Me<sub>3</sub>SiC≡CC(O)Me:  $\nu(\text{C}\equiv\text{C})$  2151 cm<sup>-1</sup>. <sup>13</sup>C NMR (125.7 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  –1.0 (s, Si(CH<sub>3</sub>)<sub>3</sub>), 32.0 (s, CH<sub>3</sub>), 95.4/103.4 (s/s, C≡C), 182.8 (s, C=O).

### 3.2.7. Isomerization of **9** to *trans*-[IrCl{≡C=C(SiMe<sub>3</sub>)-CO<sub>2</sub>Et}(PPh<sub>3</sub>)<sub>2</sub>] (**10**)

In an NMR tube **9** (20 mg) was dissolved in C<sub>6</sub>D<sub>6</sub> (1 ml). The solution was then warmed up to about 50 °C and kept for a few days at that temperature. After three days the ratio **9**:**10** was found to be 53:47%. The analogous reaction was performed with UV irradiation (150 W Heraeus TQ 150 Z1). After 14 h **9** was almost quantitatively rearranged to **10** (>95%).

<sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  –0.10 (s, 9H, Si(CH<sub>3</sub>)<sub>3</sub>), 0.96 (t, 3H, <sup>3</sup>*J*(H,H) = 7.0 Hz, CH<sub>3</sub>), 3.88 (q, 2H, <sup>3</sup>*J*(H,H) = 7.0 Hz, CH<sub>2</sub>), 7.03–7.10/7.95–8.00 (m/m, 18H/12H, *p*-H, *m*-H/*o*-H of PPh<sub>3</sub>). <sup>13</sup>C NMR (125.7 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  –0.4 (s, Si(CH<sub>3</sub>)<sub>3</sub>), 14.8 (s, CH<sub>3</sub>), 59.3 (s, CH<sub>2</sub>), 97.2 (t, <sup>3</sup>*J*(P,C) = 2.7 Hz, Ir=C=C), 128.3 (‘t’, *m*-C of PPh<sub>3</sub>), 130.3 (s, *p*-C of PPh<sub>3</sub>), 132.2 (‘t’, *i*-C of PPh<sub>3</sub>), 135.8 (‘t’, *o*-C of PPh<sub>3</sub>), 151.0 (C=O), 263.7 (t, <sup>2</sup>*J*(P,C) = 11.8 Hz, Ir=C). <sup>31</sup>P NMR (81 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  27.1 (s).

### 3.2.8. Isomerization of **11** to *trans*-[IrCl{≡C=C(SiMe<sub>3</sub>)-C(O)Me}(PPh<sub>3</sub>)<sub>2</sub>] (**12**)

In an NMR tube [IrCl(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (**1**) (41 mg, 0.053 mmol) and 4-(trimethylsilyl)but-3-yn-2-one (15 mg, 0.11 mmol) were reacted in C<sub>6</sub>D<sub>6</sub> (1 ml) for 2 days at room temperature. After a few hours a yellow suspension turned to a brown solution. The <sup>31</sup>P NMR spectrum after 1 day revealed a mixture of **11**, **12** and decomposition products (**d**) in an approximate ratio **11**:**12**:**d** = 80:10:10%. Performing the reaction at 50 °C resulted in further decomposition of **11** within three days (**11**:**12**:**d** = 50:10:40%). <sup>13</sup>C NMR (125.7 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  30.5 (s, CH<sub>3</sub>), 108.1 (t, <sup>3</sup>*J*(P,C) = 2.1 Hz, Ir=C=C), 181.9 (s, C=O), 267.9 (t, <sup>2</sup>*J*(P,C) = 11.6 Hz, Ir=C), other resonances are overlapped with those of **11** and decomposition products. <sup>31</sup>P NMR (81 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  26.0 (s).

### 3.2.9. *trans*-[Ir{C<sub>4</sub>(CO<sub>2</sub>Me)<sub>4</sub>}Cl(PPh<sub>3</sub>)<sub>2</sub>] (**13**)

To a suspension of [IrCl(N<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>] (**1**) (110 mg, 0.141 mmol) in acetone (2–3 ml) dimethyl but-2-ynedioate (41 mg, 0.29 mmol) was added at 10 °C with stirring. After 10–15 min an orange-red clear solution formed. The solvent was evaporated in vacuo to ca. 1 ml. Methanol (ca. 5 ml) and chloroform (ca. 5 ml) was then added. The solution was stored for a few days at –40 °C. Within that time red crystals formed that were filtered off, washed with pentane (10 ml) and dried in vacuo for 1 h. Yield: 62 mg (42%). Anal. Calc.

for  $\text{IrClP}_2\text{O}_8\text{C}_{48}\text{H}_{42}$  (1036.47): C, 55.62; H, 4.08. Found: C, 56.03; H, 3.43%.  $\nu(\text{C}=\text{C})$  1547(w), 1504(w)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  3.14/3.35 (s/s, 6H/6H,  $2 \times \text{CH}_3/2 \times \text{CH}_3$ ), 7.34–7.38/7.41–7.45/7.56 (m/m/br, 12H/6H/12H, *m-H/p-H/o-H* of  $\text{PPh}_3$ ).  $^{13}\text{C}$  NMR (100.6 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  51.1/51.2 (s/s,  $2 \times \text{CH}_3/2 \times \text{CH}_3$ ), 128.2 ('t', *m-C* of  $\text{PPh}_3$ ), 130.8 (s, *p-C* of  $\text{PPh}_3$ ), 135.3 ('t', *o-C* of  $\text{PPh}_3$ ), 141.6/151.5 ('t'/s, *i-C* of  $\text{PPh}_3$  and  $\text{C}=\text{C}$ , two of three signals were observed), 165.0/168.6 (s/s,  $2 \times \text{C}=\text{O}$ ).  $^{31}\text{P}$  NMR (81 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  21.4 (s).

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