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Iridium-assisted C≡C bond cleavage of 1-alkyne by water: preparation of new alkyl derivatives

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Alkyl complexes $IrCl_2(\eta^1\text{-}CH_2Ar)(CO)(PPh_3)_2$ (**1**) [Ar = Ph (**a**), *p*-tolyl (**b**)] were prepared by allowing the hydride *mer*- or *fac*-$IrHCl_2(PPh_3)_3$ to react with terminal alkynes ArC≡CH in the presence of water. The complexes were characterized spectroscopically (IR and ^{1}H, ^{31}P, ^{13}C NMR) and by the X-ray crystal structure determination of **1b**. The acyl complex $IrCl_2\{C(O)CH_2C(CH_3)_3\}(PPh_3)_2$ (**2**) was also prepared by reacting *mer*-$IrHCl_2(PPh_3)_3$ with *tert*-butylacetylene $HC{\equiv}CC(CH_3)_3$ in the presence of H_2O. A reaction path for the hydration of terminal alkyne in the presence of the Ir(III) complex leading to the cleavage of the C≡C bond, with the formation of the complexes **1** or **2** is also proposed. Acetylide complexes $IrHCl(C{\equiv}CAr)(PPh_3)_3$ (**3**), $IrHCl(C{\equiv}CAr)(AsPh_3)_3$ (**4**) [Ar = Ph (**a**), *p*-tolyl (**b**)] and $IrHCl(C{\equiv}CPh)\{PPh(OEt)_2\}(PPh_3)_2$ (**5**) were prepared by reacting $IrHCl_2L_3$ (L = PPh_3, $AsPh_3$) or $IrHCl_2\{PPh(OEt)_2\}(PPh_3)_2$ with lithium acetylide. Protonation reaction with Brønsted acids of the acetylide **3** was also studied and led to unstable vinyl derivatives. The stable vinyl $[IrCl\{\eta^2\text{-}CH{=}C(H)COOMe\}L_2]BPh_4$ (**6**,**7**) [L = PPh_3 (**6**), $AsPh_3$ (**7**)] complexes, instead, were prepared by allowing $IrHCl_2L_3$ to react first with $AgCF_3SO_3$ and then with methyl propiolate.

Introduction

Transition metal complexes are known to promote hydration of unactivated alkyne affording species such as aldehydes, ketones, or vinyl alcohol complexes.[1] In some cases the metal-assisted reaction of 1-alkynes with water has been reported to give a C–C triple bond cleavage with the formation of CO and a saturated hydrocarbon with one fewer carbon atom. They are generally present as a carbonyl and η^1-alkyl ligand.[2–4] Among the metal centres, a prominent role is played by those of the iron-group. A mechanistic study on the stoichiometric Ru(II)-assisted C–C fission of phenylacetylene by water involving the participation of a Ru(II)–vinylidene intermediate has also been recently reported.[3a] Less is known for other metal centres and, for the iridium, the formation of an acyl $[Ir]C(CO)CH_2Ph$ derivative by hydrolysis of phenylacetylene was reported in one case with a binuclear complex,[4b] while a carbonyl complex was obtained in the reaction of PhC≡CH with both a metallacyclo complex[4a] and, very recently, with a water-soluble iridium derivative.[4c] However, what is known of the hydrolysis of alkyne is still rather limited and further studies on the influence of the metal centre, the ancillary ligands and the nature of the alkyne on the reaction course and the nature of the final product should therefore be desirable.

We have previously reported some studies on the reactivity of metal complexes of the iron triad and of cobalt with 1-alkynes, which allows the synthesis of the acetylide, vinyl and vinylidene derivatives.[5] We have now extended these investigations to include iridium as a metal centre and found a new example of hydration of terminal alkyne promoted by a transition metal complex which yields both alkyl-carbonyl and acyl derivatives. The results of these studies, which also include the synthesis of both alkynyl and vinyl complexes of Ir(III) and a detailed study on the hydrolysis of the alkyne, are reported here.

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Experimental

General

All synthetic work was carried out under an inert atmosphere (argon) using standard Schlenk techniques or a Vacuum Atmosphere dry-box. Once isolated, the complexes turned out to be quite air-stable and were stored at −25 °C. All solvents used were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. Phosphine $PPh(OEt)_2$ was prepared by the method of Rabinowitz and Pellon.[6] Alkynes RC≡CH (R = Ph, *p*-tolyl, Bu^t or Pr^n, $Si(CH_3)_3$, COOMe) were Aldrich products, used without further purification. Lithium acetylide $Li^+[ArC{\equiv}C]^-$ (Ar = Ph, *p*-tolyl) was prepared by reacting a slight excess of 1-alkyne (22 mmol) with lithium (20 mmol, 0.14 g) in 10 cm^3 of tetrahydrofuran (THF). Oxygen-18-labelled water (95 atom% ^{18}O) was an Aldrich product. Other reagents were purchased from commercial sources in the highest available purity and used as received. Infrared spectra were recorded on Digilab Bio-Rad FTS-40 or Nicolet Magna 750 FT-IR spectrophotometers. NMR spectra (^{1}H, ^{13}C, ^{31}P) were obtained on Bruker AC200 or AVANCE 300 spectrometer at temperatures between −90 and +30 °C, unless otherwise stated. ^{1}H and ^{13}C{^{1}H} (Table 2) spectra are referred to internal tetramethylsilane; ^{31}P{^{1}H} chemical shifts are reported with respect to 85% H_3PO_4, with downfield shifts considered positive. The COSY and HMQC NMR experiments were obtained on the Bruker AVANCE 300 instrument using its standard programs. The SwaN-MR software package[7] was used to treat NMR data. The conductivity of 10^{-3} mol dm^{-3} solutions of the complexes in $MeNO_2$ at 25 °C was measured with a Radiometer CDM 83 instrument.

Synthesis of the complexes

The hydrides *mer*- and *fac*-$IrHCl_2(PPh_3)_3$, *mer*-$IrHCl_2(AsPh_3)_3$ and $IrHCl_2\{PPh(OEt)_2\}(PPh_3)_2$ were prepared following the reported methods.[8]

$IrCl_2(\eta^1\text{-}CH_2Ar)(CO)(PPh_3)_2$ (1) [Ar = Ph (a), *p*-tolyl (b)]

An excess of the appropriate alkyne (0.2 mmol) was added to a solution of *mer*-$IrHCl_2(PPh_3)_3$ (0.100 g, 0.095 mmol) in 10 cm^3 of THF and the reaction mixture was refluxed for 1 h. The solvent was removed under reduced pressurre giving an oil which was triturated with ethanol (5 cm^3). An orange–yellow solid slowly separated out from the resulting solution, which

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was filtered and recrystallized by cooling to −25 °C a saturated solution prepared at room temperature by treating the solid with 10 cm^3 of ethanol and enough CH_2Cl_2 to dissolve it. It can be noted that the addition of an excess of H_2O (0.2 mmol, 36 µL) to the reaction mixture does not change the yield in the products; yield ≥80% (Found: C, 58.45; H, 4.06; Cl, 7.70%. $C_{44}H_{37}Cl_2IrOP_2$ (**1a**) requires C, 58.28; H, 4.11; Cl, 7.82%); $\bar{\nu}_{max}$/cm^{-1} (CO) 2048s (KBr); δ_H (CD_2Cl_2, 293 K) 7.95–6.06 (35H, m, Ph) and 3.55 (2H, t, CH_2, J_{PH} = 6 Hz); δ_P (CD_2Cl_2, 293 K) −15.41 (s). (Found: C, 58.85; H, 4.19; Cl, 7.88%. $C_{45}H_{39}Cl_2IrOP_2$ (**1b**) requires C, 58.69; H, 4.27; Cl, 7.70%); $\bar{\nu}_{max}$/cm^{-1} (CO) 2048s (KBr); δ_H (CD_2Cl_2, 293 K) 7.95–5.80 (m), 6.69, 5.95 (d) (34H, Ph), 3.52 (2H, t, CH_2, J_{PH} = 6 Hz) and 2.23 (3H, s, CH_3); δ_P (CD_2Cl_2, 293 K) −15.68 (s).

$IrCl_2(\eta^1\text{-}CD_2Ph)(CO)(PPh_3)_2$ (1a-d$_2$)

This complex was prepared in the same manner as the related **1a** by adding first an excess of $PhC{\equiv}CH$ (0.2 mmol, 22 µL) and then an excess of D_2O (0.4 mmol, 7.2 µL) to a solution of *mer*-$IrHCl_2(PPh_3)_3$ (0.100 g, 0.095 mmol) in 10 cm^3 of THF. After 1 h of reflux of the resulting solution and the evaporation of the solvent at reduced pressure, the addition of EtOD allowed to separate the solid. Proton and ^{13}C NMR spectra confirm the selective replacement of the methylenic hydrogen atoms of the benzylic group by deuterium.

$IrCl_2(\eta^1\text{-}CH_2Ph)(C^{18}O)(PPh_3)_2$ (1a-^{18}O)

This complex was prepared in the same manner as the related **1a-d$_2$** using $H_2{}^{18}O$ (95 atom% ^{18}O) instead of D_2O. $\bar{\nu}_{max}$/cm^{-1} ($C{\equiv}{}^{18}O$) 2005 (KBr).

$IrCl_2\{\eta^1\text{-}C(O)CH_2C(CH_3)_3\}(PPh_3)_2$ (2)

An excess of $Bu^tC{\equiv}CH$ (0.3 mmol, 38 µL) was added to a solution of *mer*-$IrHCl_2(PPh_3)_3$ (0.100 g, 0.095 mmol) in 10 cm^3 of CH_2Cl_2 and the reaction mixture was stirred at room temperature for 40 h. The solvent was removed under reduced pressure to give a red–brown oil which was triturated with ethanol (5 cm^3). A yellow solid separated out from the resulting solution, which was filtered and recrystallized from CH_2Cl_2–ethanol. It can be noted that the addition of an excess of H_2O (0.3 mmol, 5.4 µL) to the reaction mixture does not change either the reaction course, or the yield in the final product; yield ≥70% (Found: C, 56.61; H, 4.78; Cl, 8.18%. $C_{42}H_{41}Cl_2IrOP_2$ requires C, 56.88; H, 4.66; Cl, 8.00%); $\bar{\nu}_{max}$/cm^{-1} (C=O) 1681s (KBr); δ_H (CD_2Cl_2, 293 K) 7.70–6.90 (30H, m, Ph), 2.76 (2H, s, CH_2) and 0.69 (9H, s, CH_3); δ_P (CD_2Cl_2, 293 K) 8.25 (s).

$IrCl_2\{\eta^1\text{-}C(O)CD_2C(CH_3)_3\}(PPh_3)_2$ (2-d$_2$)

This complex was prepared in the same manner as the related **2**, by adding first an excess of $Bu^tC{\equiv}CH$ (0.3 mmol, 38 µL) and then an excess of D_2O (0.4 mmol, 7.2 µL) to a solution of *mer*-$IrHCl_2(PPh_3)_3$ (0.100 g, 0.095 mmol) in 10 cm^3 of THF. The reaction mixture was stirred for 40 h and, after evaporation of the solvent, the solid complex was recovered by stirring the oil obtained with EtOD. The ^1H NMR spectra confirm the selective replacement of the methylenic hydrogen atom of the neopentyl group by deuterium.

$IrCl_2\{\eta^1\text{-}C(^{18}O)CH_2C(CH_3)_3\}(PPh_3)_2$ (2-^{18}O)

This complex was prepared in the same manner as **2** by adding first an excess of $Bu^tC{\equiv}CH$ (0.3 mmol, 38 µL) and then an excess of $H_2{}^{18}O$ (95 atom% ^{18}O) (0.3 mmol, 5.4 µL) to a solution of *mer*-$IrHCl_2(PPh_3)_3$ in 10 cm^3 of CH_2Cl_2. After 40 h of stirring of the reaction mixture and work-up, a yellow solid was obtained. $\bar{\nu}_{max}$/cm^{-1} ($C{=}{}^{18}O$) 1649 (KBr).

Reaction of *mer*- or *fac*-$IrHCl_2(PPh_3)_3$ with phenylacetylene in NMR tube

In a vacuum-atmosphere dry box a sample of *mer*- or *fac*-$IrHCl_2(PPh_3)_3$ (20 mg, 0.019 mmol) was placed in a screw-cap 5-mm NMR tube and 1 cm^3 of the appropriate deuterated solvent (THF-d$_8$, CD_2Cl_2 or C_6D_6) was added. An excess of phenylacetylene (0.04 mmol, 4.5 µL) was added by syringe to the resulting suspension and the NMR tube was transferred into the probe of the spectrometer. Owing to the low solubility of $IrHCl_2(PPh_3)_3$ complex in THF-d$_8$ and C_6D_6, the reaction was carried out at 40 °C preheating the probe to this temperature. To the reaction mixture in the NMR tube was also added in some cases an excess of H_2O, D_2O or $H_2{}^{18}O$ and the reaction was monitored by recording successive spectra.

$IrHCl(C{\equiv}CAr)(PPh_3)_3$ (3) [Ar = Ph (a), *p*-tolyl (b)]

To a solution of *mer*-$IrHCl_2(PPh_3)_3$ (0.100 g, 0.095 mmol) in 10 cm^3 of THF was added an excess of the appropriate $Li^+[ArC{\equiv}C]^-$ (0.38 mmol, 0.19 cm^3 of a 2.0 M solution in THF) and the reaction mixture refluxed for about 1 h. The solvent was removed by evaporation under reduced pressure to give a red–brown oil which was treated with ethanol (5 cm^3). By vigorous stirring of the resulting solution, a red–brown solid slowly separated out, which was filtered and recrystallized from toluene–ethanol; yield ≥75% (Found: C, 66.52; H, 4.68; Cl, 3.35%. $C_{62}H_{51}ClIrP_3$ (**3a**) requires C, 66.69; H, 4.60; Cl, 3.17%); $\bar{\nu}_{max}$/cm^{-1} (IrH) 2168w and (C≡C) 2098m (KBr); δ_H (C_6D_6, 293 K) 7.70–6.85 (50H, m, Ph) and −11.62 (1H, dt, H^-, $^2J_{PH cis}$ = 18 Hz, $^2J_{PH trans}$ = 140 Hz); δ_P (C_6D_6, 293 K) spin syst A_2B, δ_A −4.92, δ_B −22.36, J_{AB} = 15 Hz. (Found: C, 66.78; H, 4.68; Cl, 3.01%. $C_{63}H_{53}ClIrP_3$ (**3b**) requires C, 66.92; H, 4.72; Cl, 3.14%); $\bar{\nu}_{max}$/cm^{-1} (IrH) 2162w and (C≡C) 2099m (KBr); δ_H (C_6D_6, 293 K) 7.70–6.80 (49H, m, Ph), 2.18 (3H, s, CH_3) and −11.61 (1H, dt, H^-, $^2J_{PH cis}$ = 18 Hz, $^2J_{PH trans}$ = 140 Hz); δ_P (C_6D_6, 293 K) spin syst A_2B, δ_A −5.02, δ_B −22.41, J_{AB} = 15 Hz.

$IrHCl(C{\equiv}CAr)(AsPh_3)_3$ (4) [Ar = Ph (a), *p*-tolyl (b)]

These complexes were prepared exactly in the same manner as the related complexes **3** by reacting *mer*-$IrHCl_2(AsPh_3)_3$ with an excess of $Li^+[ArC{\equiv}C]^-$ in THF at reflux for 3 h; yield ≥70% (Found: C, 59.81; H, 4.05; Cl, 2.65%. $C_{62}H_{51}As_3ClIr$ (**4a**) requires C, 59.65; H, 4.12; Cl, 2.84%); $\bar{\nu}_{max}$/cm^{-1} (IrH) 2166w and (C≡C) 2095m (KBr); δ_H (C_6D_6, 293 K) 7.74–6.80 (50H, m, Ph) and −14.18 (1H, s, H^-). (Found: C, 59.70; H, 4.32; Cl, 3.02%. $C_{63}H_{53}As_3ClIr$ (**4b**) requires C, 59.93; H, 4.23; Cl, 2.81%); $\bar{\nu}_{max}$/cm^{-1} (IrH) 2156w and (C≡C) 2098m (KBr); δ_H (CD_2Cl_2, 293 K) 7.60–6.50 (49H, m, Ph), 2.27 (3H, s, CH_3) and −14.73 (1H, s, H^-).

$IrHCl(C{\equiv}CPh)\{PPh(OEt)_2\}(PPh_3)_2$ (5)

This complex was prepared in the same manner as the related compounds **3** and **4** by refluxing a 10 cm^3 THF solution of $IrHCl_2\{PPh(OEt)_2\}(PPh_3)_2$ (0.100 g, 0.101 mmol) containing an excess of $Li^+[PhC{\equiv}C]^-$ (0.4 mmol, 0.2 cm^3 of a 2.0 M solution in THF) for about 18 h; yield ≥30% (Found: C, 61.85; H, 4.81; Cl, 3.21%. $C_{54}H_{51}ClIrO_2P_3$ requires C, 61.62; H, 4.88; Cl, 3.37%); $\bar{\nu}_{max}$/cm^{-1} (IrH) 2166w and (C≡C) 2099s (KBr); δ_H (CD_2Cl_2, 293 K) 7.60–6.67 (40H, m, Ph), 3.80, 3.61 (4H, m, CH_2), 1.09 (6H, t, CH_3) and −11.78 (1H, dt, H^-, $^2J_{PH}$ = 4 Hz, $^2J_{PH}$ = 18 Hz); δ_P (CD_2Cl_2, 293 K) spin syst AB_2, δ_A 100.23, δ_B −1.97, J_{AB} = 18 Hz.

$[IrCl\{\eta^2\text{-}CH{=}C(H)COOMe\}(PPh_3)_2]BPh_4$ (6)

In a 25-cm^3 three-necked round-bottomed flask were placed a solid sample of *mer*-$IrHCl_2(PPh_3)_3$ (0.150 g, 0.143 mmol) and an equimolar amount of $AgCF_3SO_3$ (0.143 mmol, 0.037 g). Dichloromethane (10 cm^3) was added and the reaction mixture

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stirred for about 24 h in the dark. After filtration to remove the solid AgCl, an equimolar amount of methyl propiolate HC≡CCOOMe was added (0.143 mmol, 13 µL) and the reaction mixture stirred for 24 h. The solvent was removed by evaporation under reduced pressure to give an oil which was treated with ethanol (3 cm^3). The addition of an excess of $NaBPh_4$ (0.3 mmol, 0.103 g) in 2 cm^3 of ethanol to the resulting solution caused the separation of a pale-yellow solid which was filtered and crystallized by slow cooling to −25 °C of its saturated solution prepared at room temperature using a mixture of ethanol and CH_2Cl_2 as solvent; yield ≥55% (Found: C, 66.22; H, 4.69; Cl, 3.24%. $C_{64}H_{55}BClIrO_2P_2$ requires C, 66.46; H, 4.79; Cl, 3.07%); $\bar{\nu}_{max}$/cm^{-1} (CO) 1570m (KBr); δ_H (CD_2Cl_2, 293 K) 7.80–6.80 (50H, m, Ph), 9.47 (1H, dt, $C_\alpha H$, J_{HH} = 15 Hz, J_{PH} = 9 Hz), 6.11 (1H, d, $C_\beta H$, J_{HH} = 15 Hz) and 3.71 (3H, s, CH_3); δ_P (CD_2Cl_2, 293 K) spin syst AB, δ_A −15.2, δ_B −17.8, J_{AB} = 13.8 Hz.

[IrCl{η^2-CH=C(H)COOMe}(AsPh$_3$)$_2$]BPh$_4$ (7)

This complex was prepared exactly in the same manner as the related complex **6** starting from *mer*-IrHCl$_2$(AsPh$_3$)$_3$; yield ≥45% (Found: C, 61.60; H, 4.38; Cl, 3.02%. $C_{64}H_{55}As_2BClIrO_2$ requires C, 61.77; H, 4.45; Cl, 2.85%); $\bar{\nu}_{max}$/cm^{-1} (CO) 1580m (KBr); (CD_2Cl_2, 293 K) 8.00–7.80 (50H, m, Ph), 9.66, 6.02 (2H, d, $C_\alpha H$ and $C_\beta H$, J_{HH} = 16 Hz) and 3.64 (3H, s, CH_3).

X-Ray crystal structure determination of IrCl$_2$(η^1-CH$_2$(*p*-tolyl))(CO)(PPh$_3$)$_2$·3H$_2$O (1b·3H$_2$O).

Suitable crystals were obtained by slow cooling to −20 °C of a saturated solution of the complex in an ethanol–dichloromethane mixture (10 : 1 ratio). The crystals were analysed as obtained and contained three water molecules per iridium atom. A yellow irregular prism single crystal was mounted on a glass fiber and X-ray diffraction data were collected on a Philips PW1100 diffractometer, using graphite monochromated Mo-Kα radiation (λ = 0.71069 Å). Crystal decay resulted negligible. The phase problem was solved by direct methods[9] and refined by full-matrix least squares on all F^2,[10] with the support of the WinGX package.[11] Exctinction effects were accounted for by refining an exctinction parameter as implemented in SHELXL97.[10] Anisotropic displacement parameters were refined for all non carbon atoms, while carbon atoms and carbonyl oxygen were located from Fourier maps and refined isotropically. Hydrogens were introduced in calculated positions. All aromatic rings were constrained to behave as rigid bodies. Three water molecules were found in the asymmetric unit, but the relative hydrogens were not located in the final map. Use of the Cambridge Crystallographic Database[12] facilities was made for structure discussion. The final map was featureless, except for large residues close to the iridium. Data collection and refinement results are summarized in Table 1.

CCDC reference number 207370.

See http://www.rsc.org/suppdata/dt/b3/b303635a/ for crystallographic data in CIF or other electronic format.

Results and discussion

Both *mer*- and *fac*-iridium(III) complexes IrHCl$_2$(PPh$_3$)$_3$ react with terminal alkynes HC≡CAr in THF or CH$_2$Cl$_2$ to give the alkyl-carbonyl derivatives IrCl$_2$(η^1-CH$_2$Ar)(CO)(PPh$_3$)$_2$ (**1**), which were then isolated and characterized (Scheme 1).

$$\textit{mer-}\text{ or }\textit{fac-}\mathrm{IrHCl_2(PPh_3)_3} + \mathrm{HC{\equiv}CAr} + \mathrm{H_2O} \longrightarrow$$

$$\longrightarrow \underset{\mathbf{1}}{\mathrm{IrCl_2(\eta^1\text{-}CH_2Ar)(CO)(PPh_3)_2}} + \mathrm{PPh_3} + \mathrm{H_2}$$

Scheme 1 Ar = Ph (**a**), *p*-tolyl (**b**)

Table 1 Crystal data and structure refinement for IrCl$_2$(η^1-CH$_2$-(*p*-tolyl))(CO)(PPh$_3$)$_2$·3H$_2$O (**1b·3H$_2$O**)

Empirical formula	$C_{45}H_{45}Cl_2IrO_4P_2$
Formula weight	974.85
Temperature/K	293(2)
Wavelength/Å	0.71069
Crystal system	Orthorhombic
Space group	$P2_1ab$
Unit cell dimensions	
a/Å	17.814(3)
b/Å	25.489(5)
c/Å	10.209(2)
V/Å^3	4635(1)
Z	4
D_c/Mg m^{-3}	1.397
Absorption coefficient/mm^{-1}	3.102
F(000)	1952
Crystal size/mm	0.4 × 0.4 × 0.6
Theta range for data collection/°	3–22
Index ranges	$0 \le h \le 18, 0 \le k \le 26, 0 \le l \le 10$
Reflections collected	2958
Independent reflections	2958
Observed independent reflections [$I > 2\sigma(I)$]	1872
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2958/1/175
Goodness-of-fit on F^2	1.041
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0842$, $wR2 = 0.2056$
R indices (all data)	$R1 = 0.1416$, $wR2 = 0.2466$
Absolute structure parameter	−0.01(4)
Extinction coefficient	0.0009(5)
Largest ΔF max., min./e Å^{-3}	2.181, −2.998

The reaction entails the hydrolysis of 1-alkyne with a C≡C bond cleavage and the formation of **1**, in agreement with the reaction shown in Scheme 1. The stoichiometry of this reaction is confirmed by the separation of both complex **1** and free PPh$_3$ from the reaction mixture carried out in "anhydrous" THF or CH$_2$Cl$_2$ as a solvent in about quantitative yield (≥90%). The addition of H$_2$O, in fact, is not necessary for the progress of the reaction, because the traces of H$_2$O present even in highly anhydrous solvents is shown to be enough to afford the final complex **1**. However, that H$_2$O is involved in the metal-mediated hydrolysis of the alkyne, yielding the alkyl-carbonyl derivative **1**, is unambiguously confirmed by the addition of D$_2$O or H$_2$^{18}O to the reaction mixture, which yield either the labelled IrCl$_2$(η^1-CD$_2$Ph)(CO)(PPh$_3$)$_2$ (**1a-d$_2$**) or the IrCl$_2$(η^1-CH$_2$Ph)(C^{18}O)(PPh$_3$)$_2$ (**1a-^{18}O**) complexes, respectively. In the reaction mixture, the presence of free H$_2$ (singlet at 4.6 ppm in CD$_2$Cl$_2$)[13] was also detected by ^{1}H NMR so confirming the proposed stoichiometry for the reaction (Scheme 1).

The alkyl-carbonyl complexes **1** are orange–yellow solids which are stable in the air, diamagnetic, soluble in the more common organic solvents and non-electrolytes. Their formulation is confirmed by analytical and spectroscopic data (Table 2) and by the X-ray crystal structure determination of the IrCl$_2$(η^1-CH$_2$(*p*-tolyl))(CO)(PPh$_3$)$_2$·3H$_2$O (**1b·3H$_2$O**) complex.

Its molecular structure is shown in Fig. 1 along with the labeling scheme. The most relevant geometric parameters are listed in Table 3. The metal coordination is octahedral, with the two triphenylphosphine ligands *trans* to each other, while the CH$_2$(*p*-tolyl) and CO molecules are *cis* to each other. The coordination is completed by two chlorine atoms, and the Ir–Cl bond length is significantly affected by the different *trans* influence of the carbonyl and CH$_2$(*p*-tolyl) groups, the latter inducing a certain weakening of the Ir–Cl2 bond (2.506(9) Å) relative to the Ir–Cl1 one (2.42(1) Å). The geometry of the CO ligand (Ir–C 1.75(6), C–O 1.24(5) Å) apparently deviates from the average values found in literature for hexa-coordinated Ir–CO systems (1.88 and 1.14 Å, respectively), but the observed bond lengths are probably affected by a thermal motion bias. The bonds relating to the coordination of the CH$_2$(*p*-tolyl) group (Ir–C 2.24(5), CH$_2$–C(Ar) 1.62(5) Å) are apparently

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Table 2 $^{13}C\{^1H\}$ NMR Data for selected iridium complexes

Complex	$^{13}C\{^1H\}$ NMR [a,b] δ/ppm J/Hz	Assignment
$IrCl_2(\eta^1\text{-}CH_2Ph)(CO)(PPh_3)_2$ [c] **1a**	160.8 t	C=O
	$J(^{13}C^{31}P) = 7.5$	
	12.8 t	CH_2
	$J(^{13}C^{31}P) = 2$	
$IrCl_2(\eta^1\text{-}CH_2(p\text{-tolyl}))(CO)(PPh_3)_2$ **1b**	160.9 t	C=O
	$J(^{13}C^{31}P) = 7.5$	
	21.0 s	CH_3
	12.7 t	CH_2
	$J(^{13}C^{31}P) = 2$	
$IrCl_2\{C(O)CH_2C(CH_3)_3\}(PPh_3)_2$ **2**	176.7 t	C=O
	$J(^{13}C^{31}P) = 3$	
	65.9 s	CH_2
	33.7 s	$C(CH_3)_3$
	28.6 s	CH_3
$IrHCl(C\equiv CPh)(PPh_3)_3$ **3a**	110.8 br	C_β
	96.1 dt	C_α
	$J(^{13}C^{31}P)_{cis} = 11$	
	$J(^{13}C^{31}P)_{trans} = 14$	
$IrHCl(C\equiv CPh)(AsPh_3)_3$ **4a**	113.2 s	C_β
	88.2 s	C_α
$IrHCl(C\equiv CPh)\{PPh(OEt)_2\}(PPh_3)_2$ **5**	114.6 s	C_β
	92.4 m, br	C_α
	66.2 d	CH_2
	16.4 s	CH_3
$[IrCl\{\eta^2\text{-}CH{=}C(H)COOMe\}(PPh_3)_2]BPh_4$ **6**	164.5 s	C=O
	135.9 s, br	C_α
	128.5 s	C_β
	51.3 s	CH_3
$[IrCl\{\eta^2\text{-}CH{=}C(H)COOMe\}(AsPh_3)_2]BPh_4$ **7**	163.9 s	C=O
	136.1 s	C_α
	128.1 s	C_β
	51.0 s	CH_3

[a] In CD_2Cl_2 at 25 °C, unless otherwise noted. [b] Phenyl carbon resonances are omitted. [c] In C_6D_6.

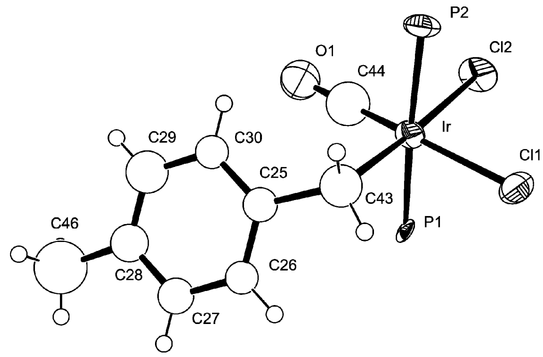

Fig. 1 Perspective view and labeling of the molecular structure of $IrCl_2(\eta^1\text{-}CH_2(p\text{-tolyl}))(CO)(PPh_3)_2$ (**1b**). Phenyl groups of triphenylphosphine are omitted for clarity. Thermal ellipsoids and spheres are represented at the 50% probability level.

Table 3 Selected bond lengths (Å) and angles (°) for $IrCl_2(\eta^1\text{-}CH_2\text{-}(p\text{-tolyl}))(CO)(PPh_3)_2$ (**1b**)

Ir–C44	1.75(6)	C44–Ir–C43	102(2)
Ir–C43	2.24(5)	C44–Ir–P1	83(2)
Ir–P1	2.37(1)	C43–Ir–P1	94(1)
Ir–P2	2.42(1)	C44–Ir–P2	99(2)
Ir–Cl1	2.42(1)	C43–Ir–P2	88(1)
Ir–Cl2	2.506(9)	P1–Ir–P2	177.0(4)
C43–C25	1.62(5)	C44–Ir–Cl1	168(2)
O1–C44	1.24(5)	C43–Ir–Cl1	87(1)
C28–C46	1.58(6)	P1–Ir–Cl1	88.5(4)
		P2–Ir–Cl1	89.7(4)
		C44–Ir–Cl2	77(2)
		C43–Ir–Cl2	176(1)
		P1–Ir–Cl2	89.4(4)
		P2–Ir–Cl2	88.4(4)
		Cl1–Ir–Cl2	94.2(4)
		C25–C43–Ir	113(3)
		O1–C44–Ir	169(5)

weaker with respect to those observed for a related Ir(III)–CH_2Ar complex: Ir–C 2.102(3)–2.125(3) Å, CH_2–C(Ar) 1.496(5) Å, in a pentacoordinated dibenzyl(bis(diphenylphosphinomethyl(dimethyl)silyl)amino-*P*,*P′*,*N*)iridium derivative[14] (structure determined at −40 °C). The intramolecular geometry for $IrCl_2(\eta^1\text{-}CH_2(p\text{-tolyl}))(CO)(PPh_3)_2$ is characterized by a *syn* orientation of the CH_2(*p*-tolyl) group with respect to the carbonyl ligand (C44–Ir–C43–C25 21°, C25 ⋯ C44 3.21 Å), with the C43–C25 bond almost eclipsed with respect to the Ir–C44–O1 vector. The CH_2(*p*-tolyl) ligand is in fact sterically confined between the bulky triphenylphosphine groups and the equatorial orientation of the aryl ring on the carbonyl side is the least hindered by intramolecular non-bonded interactions. Accordingly, the carbonyl is displaced from the CH_2(*p*-tolyl) group, causing the widening of the C43–Ir–C44 angles (102(2)°) and the compression of the C44–Ir–Cl2 (77(2)°) angles. The two triphenylphosphine ligands eclipse each other (torsion C31–P2–P1–C7 6.6°).

The IR spectra of compounds **1** show a strong band at 2048 cm^{-1}, attributed to the ν_{CO} of the carbonyl ligand. In the labelled compound $IrCl_2(\eta^1\text{-}CH_2Ph)(C\equiv{}^{18}O)(PPh_3)_2$ (**1a-^{18}O**) the $\nu_{C^{18}O}$ falls at 2006 cm^{-1} with $\Delta\nu$ of 42 cm^{-1}, which is in good agreement with the value calculated[15] ($\Delta\nu = 47$ cm^{-1}) from the change in reduced mass.

The NMR data of $IrCl_2(\eta^1\text{-}CH_2Ar)(CO)(PPh_3)_2$ **1** derivatives agree with their formulation and with the presence in solution of a geometry **I** like those of the solid state. In fact, the ^1H NMR spectra show, beside the signals of the phenyl protons of the PPh_3 ligands, a triplet at 3.55 ppm for **1a** and at 3.52 ppm for **1b** attributed to the methylene protons of the alkyl CH_2Ar ligand. In the spectra of **1b** a singlet at 2.18 ppm of the *p*-tolyl

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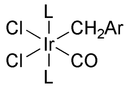
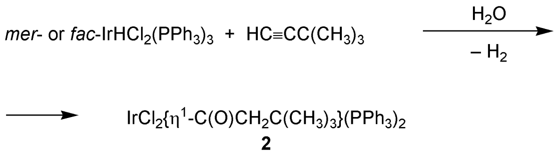
substituent was also observed. The ^{13}C spectra of complexes **1** (Table 2) confirm the presence of CO and CH_2Ar ligands, showing a triplet at 160.8 (**1a**) and 160.9 (**1b**) ppm of the carbonyl carbon atom and a triplet at 12.8 (**1a**) and 12.7 (**1b**) ppm of the methylene CH_2Ar group. A ^{1}H, ^{13}C HMQC experiment clearly correlates this latter signal with the proton triplet at 3.55 ppm of the Ir–CH_2–Ar group, in agreement with the proposed assignment. In the temperature range between +20 and −80 °C, the $^{31}P\{^1H\}$ NMR spectra of **1** appear as a sharp singlet suggesting the magnetic equivalence of the two phosphine ligands. On the basis of these data a *cis–trans* structure **I** (Fig. 2) can be proposed.



I
cis-trans

Fig. 2

The iridium complex *mer*- or *fac*-$IrHCl_2(PPh_3)_3$ also reacts with *tert*-butylacetylene, $HC{\equiv}CC(CH_3)_3$ to give a yellow solid which does not result to be the expected carbonyl-alkyl derivative like **1**, but an acyl complex of the $IrCl_2\{\eta^1\text{-}C(O)CH_2C(CH_3)_3\}(PPh_3)_2$ type (**2**), as shown in Scheme 2.

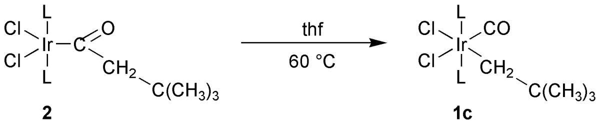


Scheme 2

The reaction with *tert*-butylacetylene involves also in this case the hydrolysis of the alkyne promoted by the traces of water present in the solvent to give the acyl complex **2**. This is confirmed by the red shift of the ν_{CO} observed in the labelled $IrCl_2\{\eta^1\text{-}C(^{18}O)CH_2C(CH_3)_3\}(PPh_3)_2$ (**2-^{18}O**) complex, prepared by adding $H_2{}^{18}O$ to the reaction mixture, and by the preparation of $IrCl_2\{\eta^1\text{-}C(O)CD_2C(CH_3)_3\}(PPh_3)_2$ (**2-d$_2$**) in the reaction with D_2O. The formulation of **2** as an acyl complex is supported by IR and NMR spectroscopic data. The IR spectrum shows a medium intensity band at 1681 cm^{-1} attributed to the ν_{CO} of the $C(O)CH_2C(CH_3)_3$ group. This band shifts to 1649 cm^{-1} in the labelled **2-^{18}O** complex ($\Delta\nu = 32$ cm^{-1}), according to the proposed attribution. The ^{1}H NMR spectra of **2** exhibits a singlet at 2.76 ppm, attributed to the CH_2 protons and a singlet at 0.69 of the CH_3 protons of the neopentyl $CH_2C(CH_3)_3$ moiety. However, strong support for the presence of the acyl ligand comes from the ^{13}C spectrum, which shows a triplet at 176.7 ppm due to the carbonyl carbon atom and three singlets at 65.9, 33.7 and 28.6 ppm attributed to the CH_2, $C(CH_3)_3$ and CH_3 carbon atoms of the neopentyl group, respectively. APT NMR studies confirmed the proposed attribution, whereas a ^{1}H, ^{13}C HMQC NMR experiment clearly correlates the proton singlets at 2.76 and at 0.69 ppm with the $^{13}C\{^1H\}$ signals at 65.9 and at 28.6 ppm of the CH_2 and CH_3 groups of the neopentyl, in agreement with the proposed formulation.

In the temperature range between +20 and −80 °C the ^{31}P spectrum appears as a sharp singlet suggesting the magnetic equivalence of the two phosphine ligands. The spectroscopic data, however, do not give conclusive information on the geometry of the complexes, which contain five ligands, but may reach the octahedral structure through an agostic interaction between the iridium centre and a C–H bond of a methyl substituent of the acyl ligand, or of the phenyl groups of the PPh_3 ligands.

A complex containing an acyl C(O)R ligand may be considered as a precursor of the derivative containing both the carbonyl and the alkyl ligand as in the $IrCl_2(CO)(\eta^1\text{-}CH_2Ar)(PPh_3)_2$ (**1**) complexes obtained in the reaction of $IrHCl_2(PPh_3)_3$ with arylalkynes. We have therefore studied the behaviour of complex **2** in solution by NMR spectra and observed that while at room temperature it is very stable, at 60 °C it slowly reacts to give a new species whose spectra indicate it to be the alkyl-carbonyl $IrCl_2\{\eta^1\text{-}CH_2C(CH_3)_3\}(CO)(PPh_3)_2$ (**1c**) derivative formed by CO deinsertion of the acyl ligand (Scheme 3).



Scheme 3

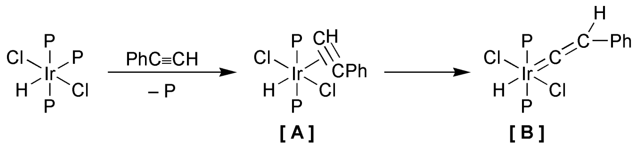
The proton NMR spectra of a solution of **2** in THF-d$_8$ show the disappearance of the two singlets at 2.76 and at 0.69 ppm of the $C(O)CH_2C(CH_3)_3$ group and the appearance of one triplet at 2.49 ppm and one singlet at 0.46 ppm attributable to the $\eta^1\text{-}CH_2C(CH_3)_3$ ligand of the alkyl compound **1c**. Also in the $^{31}P\{^1H\}$ NMR spectra a new singlet at −13.00 ppm appears, concurrent with the disappearance of the signal of **2**.

Unfortunately, this reaction is too slow as compared with the decomposition that takes place at 60 °C to allow the carbonyl $IrCl_2\{\eta^1\text{-}CH_2C(CH_3)_3\}(CO)(PPh_3)_2$ (**1c**) to be prepared in pure form. However, a comparison of its ^{1}H and ^{31}P NMR data with those of the related complexes **1a** and **1b** strongly supports the proposed formulation for this species.

We have also tested other acetylenes such as $CH_3CH_2CH_2C{\equiv}CH$, $(CH_3)_3SiC{\equiv}CH$ and $HC{\equiv}CCO_2R$ in the reaction with $IrHCl_2(PPh_3)_3$, but neither alkyl- nor acyl-derivatives were obtained. The reaction seems to proceed with color change of the reaction mixture, but the NMR spectra do not reveal the presence of the hypothesized species and only intractable oils were separated from the reaction.

Although the number of tested acetylenes is limited, these results seem to indicate that the hydratation of alkynes containing aryl substituents proceeds with a complete cleavage of the C≡C bond affording both CO and the alkyl CH_2Ar groups, each behaving as a ligand. With alkyl- or silyl-substituents, instead, the hydratation of RC≡CH acetylenes does not give isolable products, except with the *tert*-butyl substituent which has the property to stabilize an acyl–iridium derivative of the type $IrCl_2\{C(O)CH_2C(CH_3)_3\}(PPh_3)_2$ **2**.

The hydrolysis of terminal alkynes yielding **1** and **2** was studied extensively in order to obtain information useful to propose a mechanism for the reaction. Treating both *mer*- and *fac*-$IrHCl_2(PPh_3)_3$ in CD_2Cl_2 or THF-d$_8$ solution with phenylacetylene in a NMR tube one can observe the slow formation of **1a** and free PPh_3. The addition of H_2O increases the reaction rate but does not change the profile of the spectra of the reaction mixture which shows the appearance of the signal of free PPh_3 immediately after the addition of PhC≡CH whose signal slowly disappears. The lability of the PPh_3 ligand in $IrHCl_2(PPh_3)_3$, which was observed also in other reactions,[8f,16] may suggest that the first step of the reaction is the substitution of PPh_3 with the alkyne giving an η^2-PhC≡CH intermediate **[A]** (Scheme 4). A tautomerization of the π-coordinate alkyne on the iridium centre could then take place giving a vinylidene derivative **[B]**. This tautomerization is expected on the basis



Scheme 4

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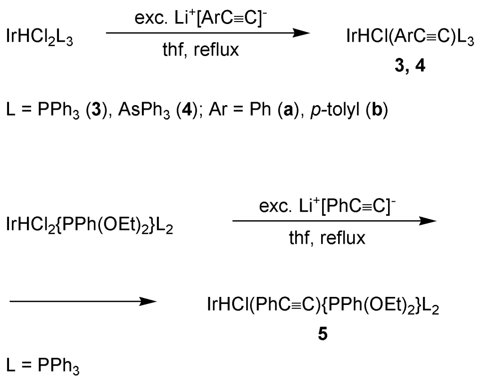
of the large number of precedents[17,18] involving d^6 metal complexes and should occur *via* a 1,2-hydrogen shift mechanism. We therefore attempted to detect this intermediate by monitoring the reaction course by NMR spectra (^{1}H, ^{13}C, ^{31}P), but did not observe any signal attributable to a vinylidene ligand. In fact, the absence of the characteristic carbene carbon signal[17] between 350 and 280 ppm in the ^{13}C NMR spectrum seems to exclude the presence of any vinylidene species, at least in detectable amounts. Therefore, the only new signals that appear in the spectrum of the reaction mixture, *i.e.* a singlet at 3.64 ppm for ^{1}H and a singlet at 114.1 ppm for ^{13}C, may be tentatively attributed to the CH resonances (APT NMR experiment) of an η^2-PhC≡CH ligand formed in the initial step of the reaction. However, the failure to detect the vinylidene intermediate does not mean that [Ir]=C=C(H)Ph species can be ruled out, because its further reaction with H_2O to give the final product can be faster than its formation, making its concentration undetectable.

Stable and isolable vinylidene complexes of iridium are well known[17a,19] but are generally tetracoordinate complexes of Ir(I), with stable species of Ir(III) still unknown. This agrees with our difficulty to detect a Ir(III) vinylidene intermediate. Nevertheless, our results with D_2O and $H_2{}^{18}O$ which give **2-d$_2$** and **2-^{18}O**, respectively, and the isolation, with HC≡CC(CH_3)$_3$, of acyl-complex **2** prompt us to propose a pathway similar to those recently proposed by Bianchini *et al.*[3a] for the hydrolysis of terminal alkyne giving **1**, which involves a [Ir]–vinylidene complex **[B]** as the key intermediate.[20] This mechanism involves the attack of H_2O on the vinylidene **[B]** C_α carbon atom to give an hydroxycarbene[21,22] $IrHCl_2P_2[C(OH)CH_2Ar]$ intermediate **[C]**, which can eliminate H_2 yielding the unsaturated acyl derivative $IrCl_2P_2[C(O)CH_2Ar]$ **[D]**. From this acyl intermediate, the formation of the final alkyl-carbonyl complex **1** can be readily explained by CO deinsertion of the acyl ligand.

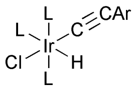
Vinyl and acetylide complexes

In parallel to the studies with terminal alkynes, we have also tested the behaviour of *mer*-$IrHCl_2(PPh_3)_3$ towards $Li^+[ArC{\equiv}C]^-$ and found that the reaction proceeds to give the alkynyl IrHCl(ArC≡C)(PPh_3)$_3$ (**3**) derivatives (Scheme 5). The related mixed-ligand $IrHCl_2\{PPh(OEt)_2\}(PPh_3)_2$ compound, as well as the arsino $IrHCl_2(AsPh_3)_3$ complex also react with $Li^+[ArC{\equiv}C]^-$ to give the alkynyl IrHCl(ArC≡C){PPh(OEt)$_2$}-(PPh_3)$_2$ (**5**) and IrHCl(ArC≡C)($AsPh_3$)$_3$ (**4**) derivatives which were isolated and characterized.



Scheme 5

The complexes **3**–**5** are red–brown solids which are stable in the air, diamagnetic, moderately soluble in the more common organic solvents and non-electrolytes. The analytical and spectroscopic data support the proposed formulation. The IR spectra show a medium-intensity band at 2095–2099 cm^{-1} attributed to the $\nu_{C\equiv C}$ of the acetylide ligand.[23] In the spectra a weak absorption at 2168–2156 cm^{-1} also appears due to the ν_{IrH} of the hydride ligand. Support for the presence of the hydride comes from the proton spectra which show, in the case of the phosphine complexes **3** and **5**, one doublet of triplets in the characteristic low-frequency region at −11.62 (**3a**), at −11.61 (**3b**) and at −11.78 (**5**) ppm. Taking into account that the ^{31}P spectra are A_2B or AB_2 multiplets, the hydride pattern can be easily simulated using the appropriate A_2BX or AB_2X (X = H) model, with the parameters reported in the Experimental section. The high value of 140 Hz found for one of the two J_{PH} in complexes **3a** and **3b** also suggest that the hydride ligand is in a mutually *trans* position with one phosphine and in *cis* with the other two, as in a type-**II** geometry (Fig. 3). The presence of the acetylide ligand in the complexes is also confirmed by the ^{13}C spectra (Table 2) which show the C_α and C_β carbon atoms of the C≡CPh group of **3a** at 96.1 and at 110.6 ppm, respectively. The C_α appears as one doublet of triplets due to the coupling with the phosphorus nuclei of the phosphine and the comparable values observed for the two $J(^{13}C^{31}P)$ of 11 and 14 Hz, respectively, agrees with a type-**II** geometry for the complex.



II

Fig. 3

In the related mixed-ligand compound **5** the values of the two J_{PH} suggest a mutually *cis* position of the hydride with all the phosphines. Unfortunately, the broad multiplet that appears at 92.4 ppm in the ^{13}C NMR spectrum for the C_α carbon atom of the C≡CPh ligand does not allow to determine the $^2J(^{13}CP)$ value and this prevents the unambiguous assignment of a geometry for the complex.

The ^{1}H NMR spectra of the arsino-complexes IrHCl-(ArC≡C)($AsPh_3$)$_3$ (**4**) show the hydride signal as a singlet at −14.18 (**4a**) and at −14.73 (**4b**) ppm, whereas in the ^{13}C spectrum of **4a** the C_α and C_β carbon resonances of the acetylide ligand appear at 82.2 and at 113.2 ppm, respectively. These data support the proposed formulation but, also in this case, do not allow structural information to be obtained in solution.

Studies on the properties of the acetylide complexes **3**–**5** indicate that they are robust complexes, whose substitution reactions with several ligands (phosphine, CO, Cl^-, *etc.*) are slow even in reflux conditions. Protonation reactions with Brønsted acids were also studied in order to test whether the proton attack takes place on the acetylide ligand to yield a [Ir]=C=C(H)Ar vinylidene complex, or on the hydride to give a dihydrogen [Ir]–(η^2-H_2) derivative. The reaction was studied at different temperatures in a NMR tube by adding progressive amounts of $HBF_4{\cdot}Et_2O$ to **3a** in CD_2Cl_2 and the spectra show that the disappearance of the hydride ligand was already observed at −80 °C. However, neither signals attributable to an η^2-H_2 complex formed by the protonation of the hydride, nor due to free H_2 were detected in the spectra of the protonated solution. Furthermore, even after the addition of an excess of $HBF_4{\cdot}Et_2O$, the formation of a vinylidene complex was not detected by ^{1}H and ^{13}C spectra. Instead, two doublets of multiplets at 8.38 and 5.53 ppm, respectively, appear in the proton spectra, which strongly suggest the formation of a vinyl complex.[24] The protonation reaction seems therefore to take place on the acetylide ligand, giving a coordinated terminal alkyne which can react with the hydride to yield the final vinyl complex (Scheme 6).

This vinyl complex is, unfortunately, thermally unstable and decomposed already at −10 °C, preventing its separation to the solid state.

These results prompted us to attempt a different method to prepare stable vinyl complexes and the reactions sequence reported in Scheme 7 does allow this synthesis to be achieved.

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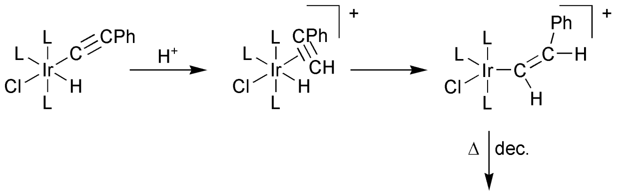
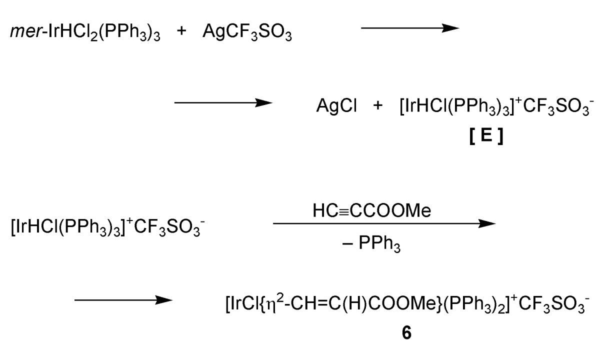


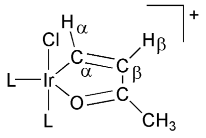
Scheme 6



Scheme 7

Because the reaction of *mer*-$IrHCl_2(PPh_3)_3$ with terminal alkyne does not give the insertion into the Ir–H bond yielding the vinyl species, but the hydrolysis of the ArC≡CH group giving **1**, we prepared the new hydride **[E]** by reacting $IrHCl_2(PPh_3)_3$ with $AgCF_3SO_3$. This complex (tentatively formulated as $[IrHCl(PPh_3)_3]^+CF_3SO_3^-$) was not isolated, but was treated in solution with terminal alkyne and, while with phenylacetylene only intractable products were obtained, with methyl propiolate a yellow solid was isolated after precipitation with $NaBPh_4$ and work-up, whose analytical and spectroscopic data indicated to be the chelate vinyl complex **6**. The related arsino derivative $[IrCl\{\eta^2\text{-}CH{=}C(H)COOMe\}(AsPh_3)_2]BPh_4$ (**7**) was also obtained by reacting $IrHCl_2(AsPh_3)_3$ first with $AgCF_3SO_3$ and then with HC≡CCOOMe. These vinyl complexes **6**, **7** were formed through the insertion of methyl propiolate into the Ir–H bond of the hydride **[E]** and probably involved an initial coordination of the alkyne on the metal. The O-coordination of the carbonyl group to give the chelate vinyl ligand is followed by the dissociation of one PPh_3 ligand yielding a final pentacoordinate species.

Complexes **6** and **7** are yellow solids which are stable in the air and in solution of polar organic solvents, where they behave as 1 : 1 electrolytes.[25] Support for the presence of a chelate O-bonded vinyl ligand comes from the IR spectra which show the ν_{CO} as a medium-intensity band at a relatively low frequency[26] of 1570–1580 cm^{-1}. The ^1H NMR spectrum of the phosphine complex **6** shows, beside the signals of the phenyl protons, one doublet of triplets at 9.47 ppm attributed to the H_α proton and a doublet at 6.11 ppm due to the H_β proton of the $C_\alpha H_\alpha{=}C_\beta(H_\beta)COOMe$ vinyl ligand. A singlet at 3.71 ppm of the methyl protons was also observed. Homodecoupling experiments and a ^1H COSY spectrum confirmed the proposed attribution. A value of 15 Hz for $^3J_{HH}$ was also observed and, although it is somewhat high for a *cis* arrangement of the two vinyl protons,[26,27] the IR spectra support the presence of the chelate (**III**) vinyl ligand (Fig. 4). The ^{13}C spectra of **6** confirm the presence of the $CH{=}C(H)COOCH_3$ ligand showing a singlet at 164.5 ppm of the carbonyl carbon atom, a singlet at 51.3 ppm of the methyl group, while the C_α and C_β vinyl carbons appear at 135.9 and 128.5 ppm, respectively. A $^1H,^{13}C$ HMQC experiment allowed us to correlate the vinyl C_α and C_β carbon signals to the proton multiplets at 9.47 and 6.11 ppm, in agreement with the proposed formulation. In the temperature range between +30 and −80 °C the $^{31}P\{^1H\}$ NMR spectrum of **6** appears as an AB multiplet indicating the magnetic inequivalence of the two phosphine ligands. On the basis of the spectroscopic data alone we cannot unambiguously assign a geometry to our derivative **6**, although type **III** is plausible and can be proposed.



III

Fig. 4

The proton NMR spectra of the arsino complex $[IrCl\{\eta^2\text{-}CH{=}C(H)COOMe\}(AsPh_3)_2]BPh_4$ (**7**) show two doublets at 9.66 and 6.02 ppm with $^3J_{HH}$ of 16 Hz attributed to the two vinyl protons H_α and H_β, respectively, of the vinyl group. The ^{13}C spectra confirm the presence of the η^2-ligand showing the characteristic signals of the C_α and C_β vinyl carbon atoms at 136.1 and at 128.1 ppm and those of the carbonyl and of the methyl group at 163.9 and 51.0 ppm, respectively. These data, therefore, support the proposed formulation for the arsinovinyl derivative.

Conclusions

In this contribution we have reported a new example of hydrolysis of terminal alkynes promoted by Ir(III) hydride complexes which gives, depending on the nature of the alkyne, an alkyl-carbonyl $IrCl_2(\eta^1\text{-}CH_2Ar)(CO)(PPh_3)_2$ or an acyl $IrCl_2\{\eta^1\text{-}C(O)CH_2C(CH_3)_3\}(PPh_3)_2$ derivative. The structural characterization of an alkyl-carbonyl iridium complex is also described. Furthermore, the synthesis of new alkynyl $IrHCl(ArC{\equiv}C)L_3$ and chelate $[IrCl\{\eta^2\text{-}CH{=}C(H)COOMe\}L_2]BPh_4$ (L = PPh_3, $AsPh_3$) vinyl derivatives was achieved using *mer*-$IrHCl_2L_3$ as a precursor.

References and notes

1 (*a*) J. Halpern, B. R. James and A. L. W. Kemp, *J. Am. Chem. Soc.*, 1966, **88**, 5142; (*b*) N. X. Hu, Y. Aso, T. Otsubo and F. Ogura, *Tetrahedron Lett.*, 1986, **27**, 6099; (*c*) W. D. Harman, J. C. Dobson and H. Taube, *J. Am. Chem. Soc.*, 1989, **111**, 3061; (*d*) T. M. M. Khan, S. B. Halligudi and S. Shukla, *J. Mol. Catal.*, 1990, **58**, 299; (*e*) W. Hiscox and P. W. Jennings, *Organometallics*, 1990, **9**, 1997; (*f*) Y. Fukuda and K. Utimoto, *J. Org. Chem.*, 1991, **56**, 3729; (*g*) J. Blum, H. Huminer and H. Alper, *J. Mol. Catal.*, 1992, **75**, 153; (*h*) I. K. Meier and J. A. Marsella, *J. Mol. Catal.*, 1993, **78**, 31; (*i*) M. Tokunaga, T. Suzuki, N. Koga, T. Fukushima, A. Horiuchi and Y. Wakatsuki, *J. Am. Chem. Soc.*, 2001, **123**, 11917.

2 (*a*) O. M. Abu Salah and M. I. Bruce, *J. Chem. Soc., Dalton Trans.*, 1974, 2302; (*b*) M. I. Bruce and A. G. Swincer, *Aust. J. Chem.*, 1980, **33**, 1471; (*c*) B. P. Sullivan, R. S. Smythe, E. M. Kober and T. J. Meyer, *J. Am. Chem. Soc.*, 1982, **104**, 4701; (*d*) C. Mountassir, T. Ben Hadda and H. Le Bozec, *J. Organomet. Chem.*, 1990, **388**, C13; (*e*) S. Davies, J. P. McNally and A. J. Smallbridge, *Adv. Organomet. Chem.*, 1990, **30**, 30; (*f*) W. Knaup and H. Werner, *J. Organomet. Chem.*, 1991, **411**, 471.

3 (*a*) C. Bianchini, J. A. Casares, M. Peruzzini, A. Romerosa and F. Zanobini, *J. Am. Chem. Soc.*, 1996, **118**, 4585; (*b*) M. L. Buil, M. A. Esteruelas, A. M. López and E. Oñate, *Organometallics*, 1997, **16**, 3169.

4 (*a*) J. M. O'Connor and L. Pu, *J. Am. Chem. Soc.*, 1990, **112**, 9013; (*b*) M. V. Jiménez, E. Sola, A. P. Martínez, F. J. Lahoz and L. A. Oro, *Organometallics*, 1999, **18**, 1125; (*c*) C. S. Chin, D. Chong, B. Maeng, J. Ryu, H. Kim, L. Kim and H. Lee, *Organometallics*, 2002, **21**, 1739.

5 (*a*) G. Albertin, P. Amendola, S. Antoniutti, S. Iannelli, G. Pelizzi and E. Bordignon, *Organometallics*, 1991, **10**, 2876; (*b*) G. Albertin, S. Antoniutti, E. Del Ministro and E. Bordignon, *J. Chem. Soc., Dalton Trans.*, 1992, 3203; (*c*) G. Albertin, S. Antoniutti and E. Bordignon, *J. Chem. Soc., Dalton Trans.*, 1995, 719; (*d*) G. Albertin, S. Antoniutti, E. Bordignon, F. Cazzaro, S. Iannelli and G. Pelizzi, *Organometallics*, 1995, **4**, 4114; (*e*) G. Albertin, S. Antoniutti, A. Bacchi, E. Bordignon and G. Pelizzi, *Organometallics*, 1995, **14**, 4126; (*f*) G. Albertin, S. Antoniutti, M. Bettiol, E. Bordignon and F. Busatto, *Organometallics*, 1997, **16**, 4959; (*g*) G. Albertin, S. Antoniutti, E. Bordignon and D. Bresolin, *J. Organomet. Chem.*, 2000, **609**, 10.

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6 R. Rabinowitz and J. Pellon, *J. Org. Chem.*, 1961, **26**, 4623.

7 G. Balacco, *J. Chem. Inf. Comput. Sci.*, 1994, **34**, 1235.

8 (*a*) S. Park, A. J. Lough and R. H. Morris, *Inorg. Chem.*, 1996, **35**, 3001; (*b*) L. Vaska, *J. Am. Chem. Soc.*, 1961, **83**, 751; (*c*) R. G. Hayter, *J. Am. Chem. Soc.*, 1961, **83**, 1259; (*d*) N. Ahmad, S. D. Robinson and M. F. Uttley, *J. Chem. Soc., Dalton Trans.*, 1972, 843; (*e*) G. L. Geoffroy and R. Pierantozzi, *J. Am. Chem. Soc.*, 1976, **98**, 8054; (*f*) G. Albertin, S. Antoniutti, E. Bordignon and F. Menegazzo, *J. Chem. Soc., Dalton Trans.*, 2000, 1181.

9 SIR97: A New Program for Solving and Refining Crystal Structures: A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 1999, **32**, 115.

10 G. M. Sheldrick, SHELXL97: Program for Structure Refinement; University of Goettingen, Germany, 1997.

11 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.

12 F. H. Allen, O. Kennard and R. Taylor, *Acc. Chem. Res.*, 1983, **16**, 146.

13 R. H. Crabtree, M. Lavin and L. Bonneviot, *J. Am. Chem. Soc.*, 1986, **108**, 4032.

14 M. D. Fryzuk, P. A. MacNeil, R. L. Massey and R. G. Ball, *J. Organomet. Chem.*, 1989, **368**, 231.

15 D. M. P. Mingos, in *Comprehensive Organometallic Chemistry*, ed. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon Press, Oxford, UK, 1982, vol. 3, p. 1.

16 G. Albertin *et al.* manuscript in preparation.

17 (*a*) M. I. Bruce, *Chem. Rev.*, 1991, **91**, 197; (*b*) C. Bianchini, M. Peruzzini, A. Vacca and F. Zanobini, *Organometallics*, 1991, **10**, 3697; (*c*) M. D. Fryzuk, L. Huang, N. T. McManus, P. Paglia, S. J. Rettig and G. S. White, *Organometallics*, 1992, **11**, 2979; (*d*) J. R. Lumprey and J. P. Selegue, *J. Am. Chem. Soc.*, 1992, **114**, 5518; (*e*) I. de los Rios, M. Jimenez-Tenorio, M. C. Puerta and P. Valerga, *J. Am. Chem. Soc.*, 1997, **119**, 6529; (*f*) M. I. Bruce, B. C. Hall, N. N. Zaitseva, B. W. Skeldon and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1998, 1793; (*g*) C. Bruneau and P. H. Dixneuf, *Acc. Chem. Res.*, 1999, **32**, 311.

18 (*a*) J. Silvestre and R. Hoffmann, *Helv. Chim. Acta*, 1985, **68**, 1461; (*b*) Y. Wakatsuki, N. Koga, H. Yamazaki and K. Morokuma, *J. Am. Chem. Soc.*, 1994, **116**, 8105.

19 (*a*) F. J. Garcia Alonso, A. Höhn, J. Wolf, H. Otto and H. Werner, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 406; (*b*) A. Höhn, H. Otto, M. Dziallas and H. Werner, *J. Chem. Soc., Chem. Commun.*, 1987, 852; (*c*) H. Werner, A. Höhn and M. Schulz, *J. Chem. Soc., Dalton Trans.*, 1991, 777; (*d*) H. Werner, R. W. Lass, O. Gevert and J. Wolf, *Organometallics*, 1997, **16**, 4077; (*e*) K. Ilg and H. Werner, *Organometallics*, 2001, **20**, 3782.

20 A cationic vinylidene intermediate may also be formed by protonation of the coordinate alkyne in $IrHCl_2(\eta^2\text{-}PhC{\equiv}CH)(PPh_3)_2$ **[A]** to give a formal Ir(V) cationic vinyl species $[IrHCl_2\{CH{=}C(H)Ph\}(PPh_3)_2]^+$ which can undergo the Caulton-type[20a] reaction to give the vinylidene $[IrCl_2\{{=}C{=}C(H)Ph\}(PPh_3)_2]^+$ and H_2. Reaction of this intermediate with OH^- or with H_2O followed by deprotonation can then give the acyl complex **[D]**: (*a*) M. Olivan, E. Clot, O. Eisenstein and K. G. Caulton, *Organometallics*, 1998, **17**, 3091.

21 Hydroxycarbene metal complexes are generally unstable and thermally degrade to give acyl derivatives *via* HCl-elimination when chloride ligands are present in the complex framework.[21a] Deprotonation of hydroxycarbene complexes with weak bases, giving formyl derivatives, was also observed.[21b] (*a*) K. R. Grundy and J. Jenkins, *J. Organomet. Chem.*, 1984, **265**, 77; (*b*) M. A. Lilga and J. A. Ibers, *Organometallics*, 1985, **4**, 590.

22 For hydroxycarbene metal complexes, see: (*a*) R. A. M. Robertson, A. D. Poole, M. J. Payne and D. J. Cole-Hamilton, *J. Chem. Soc., Dalton Trans.*, 2000, 1817; (*b*) C. P. Casey, C. J. Czerwinski and R. K. Hayashi, *J. Am. Chem. Soc.*, 1995, **117**, 4189; (*c*) D. S. Barrett, C. Glidewell and D. J. Cole-Hamilton, *J. Chem. Soc., Chem. Commun.*, 1988, 1079; (*d*) V. Guerchais and C. Lapinte, *J. Chem. Soc., Chem. Commun.*, 1986, 663; (*e*) D. S. Barrett and D. J. Cole-Hamilton, *J. Organomet. Chem.*, 1986, **306**, C41; (*f*) W. E. Buhro, A. Wong, J. H. Merrifield, G.-Y. Lin, A. C. Constable and J. A. Gladysz, *Organometallics*, 1983, **2**, 1852; (*g*) E. O. Fischer and A. Riedel, *Chem. Ber.*, 1968, **101**, 156.

23 J. Manna, K. D. John and M. D. Hopkins, *Adv. Organomet. Chem.*, 1995, **38**, 79.

24 For vinyl complexes see: refs. 5*a*,*c* and (*a*) C. Bianchini, P. Barbaro, A. Meli, M. Peruzzini, A. Vacca and F. Vizza, *Organometallics*, 1993, **12**, 2505; (*b*) C. Bohanna, M. A. Esteruelas, F. J. Lahoz, E. Oñate and L. A. Oro, *Organometallics*, 1995, **14**, 4685.

25 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.

26 G. Albertin, S. Antoniutti and E. Bordignon, *J. Chem. Soc., Dalton Trans.*, 1995, 719 and references therein.

27 (*a*) B. Chamberlain and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1991, 2067; (*b*) J. M. Bray and R. J. Mawby, *J. Chem. Soc., Dalton Trans.*, 1989, 589.