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Preparation and reactivity of iridium(III) hydride complexes with pyrazole and imidazole ligands

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Abstract

Pyrazole $IrHCl_2(HRpz)P_2$ [P = PPh_3, P^iPr_3; R = H, 3-Me], bis(pyrazole) $[IrHCl(HRpz)_2(PPh_3)_2]BPh_4$ and imidazole $IrHCl_2(HIm)(PPh_3)_2$ derivatives were prepared by allowing the $IrHCl_2(PPh_3)_3$ complex to react with the appropriate azole in refluxing 1,2-dichloroethane. Nitrile $IrHCl_2(CH_3CN)(PPh_3)_2$ and 2,2′-bipyridine (bpy) $[IrHCl(bpy)(PPh_3)_2]BPh_4$ derivatives were also prepared using $IrHCl_2(PPh_3)_3$ as a precursor. The complexes were characterised spectroscopically (IR and NMR) and a geometry in solution was also established. Protonation with Brønsted acid of pyrazole $IrHCl_2(Hpz)(PPh_3)_2$ and imidazole $IrHCl_2(HIm)(PPh_3)_2$ complexes proceeded with the loss of the azole ligands and the formation of the unstable $IrHCl_2(PPh_3)_2$ derivative. Vinyl $IrCl_2\{CH{=}C(H)R1\}(HRpz)P_2$ and $IrCl_2\{CH{=}C(H)R1\}(HIm)P_2$ (R1 = Ph, *p*-tolyl, $COOCH_3$; P = PPh_3, P^iPr_3) complexes were prepared by allowing hydride-pyrazole $IrHCl_2(HRpz)P_2$ and hydride-imidazole $IrHCl_2(HIm)P_2$ to react with an excess of terminal alkyne in 1,2-dichloroethane. The complexes were characterised spectroscopically and by the X-ray crystal structure determination of the $IrCl_2\{CH{=}C(H)Ph\}(Hpz)(PPh_3)_2$ derivative.

Keywords: Hydride; Pyrazole and imidazole ligands; P ligands; Iridium; Vinyl

1. Introduction

Transition metals hydrides are an important class of compounds which continue to be studied, not only for their chemical and spectroscopic properties, but also because they are involved in many catalytic processes [1,2]. Among the ligands used to stabilise the hydride complexes, π-acceptors such as carbonyl, mono and polydentate phosphine and cyclopentadienyls play a prominent role [1]. Less attention has been devoted to the use of N-donor molecules such as imidazole, pyrazole [3–5] or polypyridyls [6], although the introduction of one or more of these groups in the coordination sphere of the metal may greatly change the properties of the M–H bond. Several studies have been carried out to understand and rationalise the influence of the ancillary ligands on the reactivity of the M–H bond of transition metal polyhydrides and in this context the important role of the N-donor ligands is emerging [1,3–7].

We have interest in the chemistry of classical and non-classical transition metal hydrides and have previously reported the synthesis and the reactivity of several mono and dihydrides of the manganese(I), iron(II) and cobalt(III) triads stabilised by monodentate phosphite ligands [8]. Recently we have also extended these studies with the aim of introducing nitrogen-donor ligands in hydride chemistry and have reported the synthesis and reactivity of mixed-ligand $[MH(N\text{-}N)P_3]^+$ (M = Fe, Ru, Os) hydride complexes with phosphite and polypyridyls [9]. The further extension of these studies to the isoelectronic d^6 iridium(III) has been suggested [10] by the properties of the $IrHCl_2(PPh_3)_3$ complex, in which one triphenylphosphine

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ligand is rather labile and can be easily substituted by several ligands. The $IrHCl_2(PPh_3)_3$ species can therefore be used as a precursor to introduce N-donor molecules into hydride complexes of Ir(III). The results of our studies, which allowed the synthesis and some reactivity of iridium(III) hydrides containing pyrazole, imidazole and 2,2′-bipyridine, are reported here.

2. Experimental

2.1. General comments

All synthetic work was carried out in an appropriate atmosphere (Ar, N_2) using standard Schlenk techniques or a vacuum atmosphere dry-box. Once isolated, the complexes were found to be relatively stable in air, but were stored in an inert atmosphere at −25 °C. All solvents were dried over appropriate drying agents, degassed on a vacuum line, and distilled into vacuum-tight storage flasks. $IrCl_3$ was a Pressure Chemical Co. (USA) product, used as received.

Pyrazole (Hpz), 3-methylpyrazole (H-3-Mepz), imidazole (HIm), 2,2′-bipyridine (bpy) and alkynes RC≡CH (R = Ph, *p*-tolyl, ^{t}Bu, COOMe) were Aldrich products used without further purification. Other reagents were purchased from commercial sources (Aldrich, Fluka) in the highest available purity and used as received. Infrared spectra were recorded on Nicolet Magna 750 FT-IR or Perkin–Elmer Spectrum One spectrophotometers. NMR spectra (^{1}H, ^{31}P, ^{13}C) were obtained on AC200 or AVANCE 300 Bruker spectrometers at temperatures between −90 and +30 °C, unless otherwise noted. ^{1}H and ^{13}C 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, HMQC and HMBC NMR experiments were performed using their standard programs. The SwaN-MR software package [11] was used to treat NMR data. The conductivity of 10^{-3} mol dm^{-3} solutions of the complexes in CH_3NO_2 at 25 °C were measured with a Radiometer CDM 83.

2.2. Synthesis of complexes

The *mer*- and *fac*-$IrHCl_2(PPh_3)_3$, $IrH_2Cl(PPh_3)_3$ and $IrHCl_2(P^iPr_3)_2$ hydrides were prepared following the reported methods [12,13].

2.2.1. $IrHCl_2(HRpz)(PPh_3)_2$ (**1**) and $[IrHCl(HRpz)_2(PPh_3)_2]BPh_4$ (**2**) [R = H (**a**), 3-Me (**b**)]

Method 1. An excess of the appropriate pyrazole (1.44 mmol) was added to a solution of *mer*-$IrHCl_2(PPh_3)_3$ (0.50 g, 0.48 mmol) in 50 mL of 1,2-dichloroethane and the reaction mixture refluxed for 3 h. The solvent was removed under reduced pressure leaving an oil which was treated with ethanol (2 mL). A yellow solid slowly separated out from the resulting solution, which was filtered and crystallised from CH_2Cl_2 and ethanol. The solid is the monopyrazole complex **1** [181 mg, 44% (**1a**), 188 mg, 45% (**1b**)].

An excess of $NaBPh_4$ (0.96 mmol, 0.33 g) in 2 mL of ethanol was added to the mother liquor of the reaction and the solution stirred until a yellow solid separated out, which was filtered and crystallised from CH_2Cl_2 and ethanol. The solid is the bis(pyrazole) complex **2** [191 mg, 33% (**2a**), 202 mg, 34% (**2b**)]. Found: C, 54.88; H, 4.21; Cl, 8.06; N, 3.15. $C_{39}H_{35}Cl_2IrN_2P_2$ (**1a**) requires C, 54.67; H, 4.12; Cl, 8.28; N, 3.27%. Found: C, 55.02; H, 4.36; Cl, 8.31; N, 3.33. $C_{40}H_{37}Cl_2IrN_2P_2$ (**1b**) requires C, 55.17; H, 4.28; Cl, 8.14; N, 3.22%. Found: C, 65.34; H, 5.01; Cl, 2.78; N, 4.69. $C_{66}H_{59}BClIrN_4P_2$ (**2a**) requires C, 65.59; H, 4.92; Cl, 2.93; N, 4.64%. $\Lambda_M = 56.6\ \Omega^{-1}\ mol^{-1}\ cm^2$. Found: C, 65.89; H, 5.10; Cl, 2.66; N, 4.43. $C_{68}H_{63}BClIrN_4P_2$ (**2b**) requires C, 66.04; H, 5.13; Cl, 2.87; N, 4.53%. $\Lambda_M = 58.2\ \Omega^{-1}\ mol^{-1}\ cm^2$.

2.2.2. $[IrHCl(HRpz)_2(PPh_3)_2]BPh_4$ (**2**) [R = H (**a**), 3-Me (**b**)]

Method 2. An equimolar amount of CF_3SO_3H (26.5 μL, 0.30 mmol) was added to a solution of $IrH_2Cl(PPh_3)_3$ (0.30 g, 0.30 mmol) in CH_2Cl_2 (10 mL) cooled to −196 °C. The reaction mixture was brought to room temperature, stirred for 1 h and then an excess of pyrazole (1.0 mmol, 68 mg) was added. The solution was stirred for 5 h and then the solvent removed under reduced pressure to give a yellow solid which was treated with ethanol (5 mL) containing an excess of $NaBPh_4$ (0.6 mmol, 0.21 g). A yellow solid slowly separated out from the resulting solution, which was filtered and crystallised from CH_2Cl_2 and ethanol [207 mg, 57% (**2a**), 200 mg, 54% (**2b**)].

2.2.3. $IrHCl_2(Hpz)(P^iPr_3)_2$ (**3**)

An excess of pyrazole (68 mg, 1 mmol) was added to a solution of $IrHCl_2(P^iPr_3)_2$ (0.200 g, 0.34 mmol) in 10 mL of $ClCH_2CH_2Cl$ and the reaction mixture was refluxed for 2 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (2 mL). A yellow solid slowly separated out which was filtered and crystallised from CH_2Cl_2 and ethanol (180 mg, 81%). Found: C, 38.81; H, 7.36; Cl, 10.62; N, 4.35. $C_{21}H_{47}Cl_2IrN_2P_2$ requires C, 38.64; H, 7.26; Cl, 10.86; N, 4.29%.

2.2.4. $IrHCl_2(HIm)(PPh_3)_2$ (**4**)

An excess of imidazole (2 mmol, 136 mg) was added to a solution of $IrHCl_2(PPh_3)_3$ (0.50 g, 0.48 mmol) in 15 mL of 1,2-dichloroethane and the reaction mixture refluxed for 4 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (3 mL). A yellow solid slowly separated out which was filtered and crystallised from CH_2Cl_2 and ethanol (238 mg, 58%). Found: C, 54.90; H, 4.22; Cl, 8.15; N, 3.25. $C_{39}H_{35}Cl_2IrN_2P_2$ requires C, 54.67; H, 4.12; Cl, 8.28; N, 3.27%.

2.2.5. $IrHCl_2(CH_3CN)(PPh_3)_2$ (**5**)

An excess of CH_3CN (3 mmol, 0.16 mL) was added to a solution of $IrHCl_2(PPh_3)_3$ (0.50 g, 0.48 mmol) in 15 mL of 1,2-dichloroethane and the reaction mixture refluxed for

4 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (3 mL). A yellow solid slowly separated out which was filtered and crystallised from CH_2Cl_2 and ethanol (299 mg, 75%). Found: C, 55.18; H, 4.23; Cl, 8.70; N, 1.72. $C_{38}H_{34}Cl_2IrNP_2$ requires C, 55.01; H, 4.13; Cl, 8.55; N, 1.69%.

2.2.6. *[IrHCl(bpy)(PPh$_3$)$_2$]BPh$_4$ (**6**) (bpy = 2,2′-bipyridine)*

In a 50-mL three-necked round-bottomed flask were placed 0.50 g (0.48 mmol) of $IrHCl_2(PPh_3)_3$, 0.22 g (excess, 1.41 mmol) of 2,2′-bipyridine and 15 mL of 1,2-dichloroethane. The resulting solution was refluxed for 3 h and then the solvent was removed under reduced pressure. The brown oil obtained was treated with ethanol (4 mL) containing an excess of $NaBPh_4$ (0.328 g, 0.96 mmol). A yellow-orange solid slowly separated out which was filtered and crystallised from CH_2Cl_2 and ethanol (372 mg, 63%). Found: C, 68.25; H, 4.68; Cl, 2.64; N, 2.25. $C_{70}H_{59}BClIrN_2P_2$ requires C, 68.43; H, 4.84; Cl, 2.89; N, 2.28%. $\Lambda_M = 60.4\ \Omega^{-1}\ mol^{-1}\ cm^2$.

2.2.7. *IrCl$_2${CH=C(H)R1}(Hpz)(PPh$_3$)$_2$ (7) [R1 = Ph (**a**), p-tolyl (**b**), COOCH$_3$ (**c**)]*

An excess of the appropriate alkyne R1C≡CH (1.2 mmol) was added to a solution of the pyrazole $IrHCl_2(Hpz)(PPh_3)_2$ complex (0.2 mmol) in 25 mL of 1,2-dichloroethane and the reaction mixture was refluxed for 3 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (2 mL). A red-orange solid separated out which was filtered and crystallised from CH_2Cl_2 and ethanol [144 mg, 75% (**7a**), 132 mg, 68% (**7b**), 135 mg, 72% (**7c**)]. Found: C, 59.03; H, 4.44; Cl, 7.61; N, 2.80. $C_{47}H_{41}Cl_2IrN_2P_2$ (**7a**) requires C, 58.87; H, 4.31; Cl, 7.39; N, 2.92%. Found: C, 59.34; H, 4.55; Cl, 7.12; N, 2.75. $C_{48}H_{43}Cl_2IrN_2P_2$ (**7b**) requires C, 59.26; H, 4.45; Cl, 7.29; N, 2.88%. Found: C, 54.65; H, 4.26; Cl, 7.41; N, 3.07. $C_{43}H_{39}Cl_2IrN_2O_2P_2$ (**7c**) requires C, 54.89; H, 4.18; Cl, 7.54; N, 2.98%.

2.2.8. *IrCl$_2${CH=C(H)Ph}(H-3-Mepz)(PPh$_3$)$_2$ (**8a**)*

This complex was prepared exactly like the related complexes **7** [134 mg, 69%]. Found: C, 59.05; H, 4.53; Cl, 7.14; N, 2.75. $C_{48}H_{43}Cl_2IrN_2P_2$ requires C, 59.26; H, 4.45; Cl, 7.29; N, 2.88%.

2.2.9. *IrCl$_2${CH=C(H)Ph}(Hpz)(P^i Pr$_3$)$_2$ (**9a**)*

This complex was prepared exactly like the related triphenylphosphine derivative **7**, **8** using $IrHCl_2(Hpz)(P^iPr_3)_2$ (0.12 g, 0.2 mmol) as a precursor (113 mg, 75%). Found: C, 46.35; H, 7.18; Cl, 9.21; N, 3.60. $C_{29}H_{53}Cl_2IrN_2P_2$ requires C, 46.15; H, 7.08; Cl, 9.39; N, 3.71%.

2.2.10. *IrCl$_2${CH=C(H)R1}(HIm)(PPh$_3$)$_2$ (**10**) [R1 = Ph (**a**), p-tolyl (**b**)]*

These complexes were prepared exactly like the related pyrazole complexes **7**, **8** using $IrHCl_2(HIm)(PPh_3)_2$ (0.17 g, 0.2 mmol) as a precursor [134 mg, 70% (**10a**), 132 mg, 68% (**10b**)]. Found: C, 58.99; H, 4.48; Cl, 7.18; N, 2.90. $C_{47}H_{41}Cl_2IrN_2P_2$ (**10a**) requires C, 58.87; H, 4.31; Cl, 7.39; N, 2.92%. Found: C, 59.49; H, 4.50; Cl, 7.38; N, 2.82. $C_{48}H_{43}Cl_2IrN_2P_2$ (**10b**) requires C, 59.26; H, 4.45; Cl, 7.29; N, 2.88%.

2.2.11. *IrCl$_2${η^1-C(O)CH$_2$C(CH$_3$)$_3$}(PPh$_3$)$_2$ (**11**)*

An equimolar amount of CF_3SO_3H (10.6 μL, 0.12 mmol) was added to a solution of $IrHCl_2(HIm)(PPh_3)_2$ (0.200 g, 0.23 mmol) in 8 mL of CH_2Cl_2 cooled to −196 °C and the reaction mixture, brought to room temperature, stirred for 1 h. An excess of $(CH_3)_3CC{\equiv}CH$ (0.46 mmol, 58 μL) was added and the solution stirred at room temperature for 24 h. The solvent was removed under reduced pressure to give an oil which was triturated with ethanol (2 mL). A yellow solid slowly separated out which was filtered and crystallised from CH_2Cl_2 and ethanol (78 mg, 38%). Found: C, 57.02; H, 4.78; Cl, 8.12. $C_{42}H_{41}Cl_2IrOP_2$ requires C, 56.88; H, 4.66; Cl, 8.00%.

2.2.12. *Protonation reactions*

The protonation of $IrH_2Cl(PPh_3)_3$, $IrHCl_2(Hpz)(PPh_3)_2$ and $IrHCl_2(HIm)(PPh_3)_2$ complexes was studied in a NMR tube by ^1H and ^{31}P spectra collected between +20 and −80 °C. A typical experiment involved the addition of a CD_2Cl_2 solution (0.5 mL) of the appropriate hydride compound (0.03–0.04 mmol) in a screw-cap 5-mm NMR tube placed in a vacuum-atmosphere dry-box. The tube was sealed, cooled to −80 °C, and then increasing amounts of CF_3SO_3H or HBF_4Et_2O (from 0.5 to 3 equiv.) were added by a microsyringe. The tube was transferred into the instrument's probe pre-cooled to −80 °C and the spectra collected.

2.2.13. *X-ray crystal structure determination of IrCl$_2$-{CH=(CH)Ph}(Hpz)(PPh$_3$)$_2$ (**7a**)*

The data collection was taken on a SIEMENS Smart CCD area-detector diffractometer with graphite-monochromated Mo Kα radiation. Absorption correction were carried out using SADABS [14]. The structure was solved by Patterson methods and refined by a full-matrix least-squares based on F^2 [15]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in idealised positions and refined with isotropic displacement parameters except those bound to the nitrogen atoms of the vinyl ligand, which were located on Fourier maps and refined isotropically. Atomic scattering factors and anomalous dispersion corrections for all atoms were taken from International Tables for X-ray Crystallography [16]. Details of crystal data and structural refinement are given in Table 1. Crystallographic data in CIF format has been deposited at the Cambridge Crystallographic Data Centre, CCDC No. 285382.

Table 1
Crystal data and structure refinement for *trans*-*E*-[$IrCl_2${CH=C(H)Ph}-(Hpz)$(PPh_3)_2$] (**7a**)

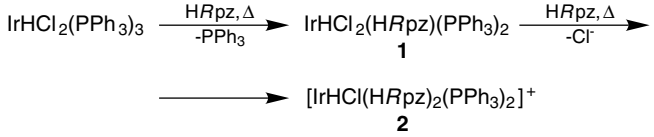
Identification code	$[IrCl_2(pzH)(HC{=}CH{-}Ph)(PPh_3)_2]$
Empirical formula	$C_{47}H_{41}Cl_2IrN_2P_2$
Formula weight	958.86
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	10.3653(9)
b (Å)	14.0417(12)
c (Å)	15.8703(13)
α (°)	81.178(2)
β (°)	72.506(2)
γ (°)	70.040(2)
Volume (Å^3)	2067.4(3)
Z	2
Density (calculated) (Mg/m^3)	1.540
Absorption coefficient (mm^{-1})	3.471
F(000)	956
Crystal size (mm)	$0.35 \times 0.18 \times 0.14$
Θ range for data collection (°)	1.55–28.00
Index ranges	$-13 \leqslant h \leqslant 13$; $-18 \leqslant k \leqslant 17$; $-17 \leqslant l \leqslant 20$
Reflections collected	13060
Independent reflections	9088 [R(int) = 0.0280]
Reflections observed (>2σ)	7332
Data completeness	0.910
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.000000 and 0.806364
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9088/0/495
Goodness-of-fit on F^2	0.899
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0363$ $wR_2 = 0.0626$
R indices (all data)	$R_1 = 0.0503$ $wR_2 = 0.0655$
Largest diff. peak and hole (e Å^{-3})	1.225 and −0.720

3. Results and discussion

3.1. Preparation of the complexes

Both *mer*- and *fac*-iridium(III) $IrHCl_2(PPh_3)_3$ complexes react with both pyrazole and 3-methylpyrazole (HRpz) to give first the $IrHCl_2(HRpz)(PPh_3)_2$ (**1**) complex, which further reacts with pyrazole to yield the final $[IrHCl(HRpz)_2(PPh_3)_2]^+$ (**2**) derivative, as shown in Scheme 1.

The reaction proceeds with the substitution of only one triphenylphosphine in the $IrHCl_2(PPh_3)_3$ precursor to give **1**, which can undergo substitution of the chlorine ligand by the HRpz group to yield the final cationic bis(pyrazole) derivative **2**. Both reactions are very slow at room temperature and need reflux conditions to afford the pyrazole compounds in valuable yield. In every case, mixtures of the two pyrazole derivatives **1** and **2** were always obtained and were easily separated as pure microcrystalline solids and characterised.



Scheme 1. R = H, **a**, 3-Me, **b**.

The bis(pyrazole) $[IrHCl(HRpz)_2(PPh_3)_2]^+$ (**2**) derivative can also be prepared by a different route involving the reaction of the dihydride $IrH_2Cl(PPh_3)_3$ first with triflic acid and then with an excess of pyrazole, as shown in Scheme 2.

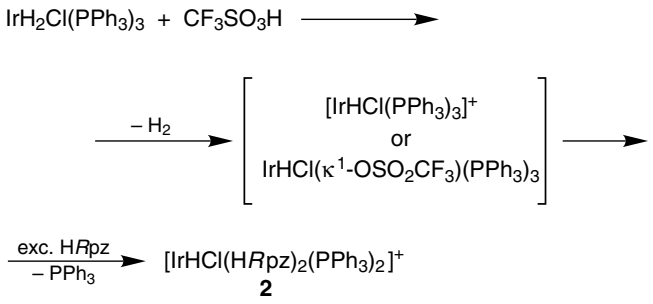
Protonation with triflic acid of $IrH_2Cl(PPh_3)_3$ probably gives the dihydrogen $[IrHCl(\eta^2\text{-}H_2)(PPh_3)_3]^+$ complex which loses the labile η^2-H_2 ligand (^{1}H NMR) [17] yielding either the triflate $IrHCl(\kappa^1\text{-}OSO_2CF_3)(PPh_3)_3$ or the pentacoordinate $[IrHCl(PPh_3)_3]^+$ cation. Reactions of these intermediates with an excess of pyrazole give the bis(pyrazole) $[IrHCl(HRpz)_2(PPh_3)_2]^+$ (**2**) derivatives as the only product formed in high yield. The coordination of one pyrazole to give the $[IrHCl(HRpz)(PPh_3)_3]^+$ intermediate is followed by the substitution of a PPh_3 ligand yielding the final bis(pyrazole) complex **2**.

Hydride-pyrazole complexes can also be prepared with triisopropylphosphine using the $IrHCl_2(P^iPr_3)_2$ species as a precursor. Reaction of this pentacoordinate iridium complex with an excess of pyrazole proceeds to exclusively give the neutral $IrHCl_2(Hpz)(P^iPr_3)_2$ (**3**) complex, which was isolated in good yield and characterised (Scheme 3).

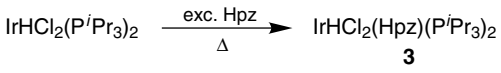
In contrast with the results obtained with the triphenylphosphine $IrHCl_2(PPh_3)_3$ complex, the related triisopropylphosphine derivative does not give the formation of any bis(pyrazole) complex like **2**. The use of a long reaction time produces only some decomposition, decreasing the yield of **3**.

Imidazole also reacts with the $IrHCl_2(PPh_3)_3$ precursor in refluxing 1,2-dichloroethane to give the hydride-imidazole $IrHCl_2(HIm)(PPh_3)_2$ (**4**) derivative (Scheme 4).

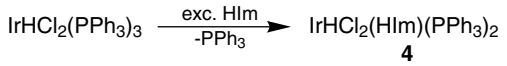
The reaction was extensively studied under different conditions and shows that only one PPh_3 ligand can be easily



Scheme 2. R = H, **a**, 3-Me, **b**.



Scheme 3.



Scheme 4.

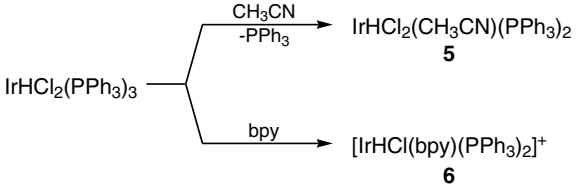
substituted yielding the monoimidazole derivative **4** as the only obtained product.

Mononuclear iridium(III) complexes with pyrazole are known [7,18] and were obtained either by oxidative addition of dihydrogen to the iridium(I) $Ir(CO)(HRpz)(PPh_3)_2$ to give $IrH_2(CO)(HRpz)(PPh_3)_2$ derivatives [18], or by replacing acetone with pyrazole in the $[IrH_2\{(CH_3)_2CO\}_2(PPh_3)_2]BF_4$ precursor giving the $[IrH_2(Hpz)\{(CH_3)_2CO\}(PPh_3)_2]^+$ and $[IrH_2(Hpz)_2(PPh_3)_2]^+$ cations [7a,7b]. More rare are the imidazole complexes [19] which involve the pentakis(amino) $[Ir(NH_3)_5(HIm)]^{3+}$ cation and the tetrachloroiridate $[H_2Im][IrCl_4(HIm)_2]$ derivatives. The use of $IrHCl_2(PPh_3)_3$ and $IrHCl_2(P^iPr_3)_2$ as precursors allows a new series of both pyrazole and imidazole complexes of iridium(III) to be easily prepared.

The facile substitution of the triphenylphosphine in the $IrHCl_2(PPh_3)_3$ complex prompted us to study the reaction with other N-donor molecules such as CH_3CN and 2,2′-bipyridine (bpy). The results show that $IrHCl_2(PPh_3)_3$ reacts with either CH_3CN or bpy to give the new mixed-ligand $IrHCl_2(CH_3CN)(PPh_3)_2$ (**5**) and $[IrHCl(bpy)(PPh_3)_2]^+$ (**6**) complexes, which were isolated in good yields and characterised (Scheme 5).

Acetonitrile replaces a PPh_3 in $IrHCl_2(PPh_3)_3$ to give the mono-substituted complex **5**, while bpy replaces both the PPh_3 and the Cl^- ligands yielding the cationic bipyridine complex **6**.

The new mixed-ligand hydride **1**–**6** complexes with N-donor molecules and phosphine were separated as a yellow or orange solid stable in air and in the solution of the most common organic solvents where they behave either as non-electrolyte (**1**, **3**, **4**, **5**) or as 1:1 electrolyte (**2**, **6**) compounds. Analytical and spectroscopic data (IR and NMR, Tables 2 and 3) support the proposed formulations. The infrared spectra of the pyrazole complexes **1**–**3** show a medium-intensity band at 3322–3282 cm^{-1} attributed to the ν_{NH} of the pyrazole ligand. A medium-intensity band is also present at 2266–2144 cm^{-1} for **1** and **3** and is attributed to the ν_{IrH} of the hydride ligand. Strong support for the presence of these ligands, however, comes from the proton NMR spectra, which show a slightly broad signal at 12.45–10.27 ppm of the NH proton of the HRpz group and a



Scheme 5. bpy = 2,2′-bipyridine.

sharp triplet between −19.70 and −23.50 ppm of the hydride ligand. In the spectra the signals of the CH protons of the pyrazole are also present and their attribution (Table 2) is supported by the multiplicity of the signals, by COSY experiments and by a comparison with literature data [5,6,20–22]. The ^{13}C spectra of both the mono- (**1**, **3**) and bis(pyrazole) (**2**) complexes (Table 3) confirm the presence of the HRpz ligand and allow us, through HMQC and HMBC experiments, to assign all the carbon atoms of the pyrazole.

In the temperature range between +20 and −80 °C the $^{31}P\{^1H\}$ NMR spectra of the monopyrazole $IrHCl_2(HRpz)(PPh_3)_2$ (**1**) complex appear as a sharp singlet suggesting the magnetic equivalence of the two phosphine ligands. Furthermore, the far-IR spectra of complex **1** show only one medium-intensity band at 316 (**1a**) and at 322 (**3**) cm^{-1}, attributable to ν_{IrCl} of the two chloride ligands in a mutually *trans* arrangement. On the basis of these data, a geometry of type I (Chart 1) can reasonably be proposed for the mono-pyrazole $IrHCl_2(HRpz)(PPh_3)_2$ (**1**) derivatives.

Instead, the NMR data do not allow us to unambiguously assign a geometry to the cationic bis(pyrazole) $[IrHCl(HRpz)_2P_2]^+$ (**2**) derivatives. The ^1H NMR spectra show only one NH signal and only one set of pyrazole CH resonances, in agreement with the magnetic equivalence of the two HRpz ligands. The ^{13}C NMR spectra confirm this equivalence showing only one set of signals for the pyrazole carbon atom. In the temperature range between +20 and −80 °C the $^{31}P\{^1H\}$ NMR spectra appear as a sharp singlet suggesting the magnetic equivalence of the two PPh_3 ligands. On the basis of these data, however, we cannot decide between geometries II and III for the bis(pyrazole) $[IrHCl(HRpz)_2P_2]^+$ (**2**) derivatives.

The IR spectra of the imidazole $IrHCl_2(HIm)(PPh_3)_2$ (**4**) complex show the ν_{NH} at 3424 cm^{-1} and the ν_{IrH} at 2168 cm^{-1}. The ^1H NMR spectrum (Table 2) confirms the presence of both the HIm and hydride ligands, showing the characteristic NH proton signal of HIm at 8.87 ppm, while a triplet at −20.68 ppm is attributed to the hydride ligand.

In the temperature range between +20 and −80 °C the $^{31}P\{^1H\}$ NMR spectra of complex **3** appear as a sharp singlet, in agreement with the presence of two magnetically equivalent phosphine ligands. Taking into account that the far-IR spectra show only one ν_{IrCl} band at 318 cm^{-1}, a structure of type-IV (Chart 2) can reasonably be proposed for the imidazole **4** complex.

A related structure (V) with both the phosphine and the chloride ligands each in a mutually *trans* position can also be proposed for the acetonitrile $IrHCl_2(CH_3CN)(PPh_3)_2$ (**5**) complex. The far-IR shows, in fact, only one ν_{IrCl} absorption at 323 cm^{-1} indicating the mutually *trans* position of the two chloride ligands, while only one singlet at −0.43 ppm is observed in the $^{31}P\{^1H\}$ spectra, in agreement with the magnetic equivalence of the two phosphorus nuclei. The IR spectra show a medium-intensity band at

Table 2
Selected IR and NMR spectroscopic data for iridium complexes

	Compound	IR[a] ν (cm^{-1})	Assgnt	^1H NMR[b] δ (J, Hz)	Assgnt	Spin system	$^{31}P\{^1H\}$NMR[b,c] δ (J, Hz)
1a	$IrHCl_2(Hpz)(PPh_3)_2$	3309 m 2203 m 316 m	ν_{NH} ν_{IrH} ν_{IrCl}	10.86 s, br 6.89 d 5.80 d 5.32 t −20.94 t $J_{PH} = 14$	NH H5 pz H3 pz H4 pz IrH	A_2	10.19 s
1b	$IrHCl_2(H\text{-}3\text{-}Mepz)(PPh_3)_2$	3322 m 2144 m	ν_{NH} ν_{IrH}	10.27 s, br 7.07 s, br 5.52 s, br 1.81 s −20.85 t $J_{PH} = 14$	NH H5 pz H4 pz CH_3 IrH	A_2	7.84 s
2a	$[IrHCl(Hpz)_2(PPh_3)_2]BPh_4$	3322 w 334 m	ν_{NH} ν_{IrCl}	11.70 s, br 7.27 s, br 7.01 d 5.85 t −19.70 t $J_{PH} = 18$	NH H5 pz H3 pz H4 pz IrH	A_2	−7.75 s
2b	$[IrHCl(H\text{-}3\text{-}Mepz)_2(PPh_3)_2]BPh_4$	3282 m	ν_{NH}	11.11 s, br 6.07 s, br 5.63 s, br 1.93 s −19.73 t $J_{PH} = 18$	NH H5 pz H4 pz CH_3 IrH	A_2	−8.59 s
3	$IrHCl_2(Hpz)(P^iPr_3)_2$	3285 s 2266 s 322 m	ν_{NH} ν_{IrH} ν_{IrCl}	12.45 s, br 8.36 s, br 7.68 s, br 6.48 t 2.77 m 1.11 m −23.50 t $J_{PH} = 14$	NH H5 pz H3 pz H4 pz CH phos CH_3 IrH	A_2	2.90 s
4	$IrHCl_2(HIm)(PPh_3)_2$	3424 m 2168 m 318 m	ν_{NH} ν_{IrH} ν_{IrCl}	8.87 s, br 7.19 s 6.93 d 6.37 d −20.68 t $J_{PH} = 14$	NH H2 Im H4 Im H5 Im IrH	A_2	10.10 s
5	$IrHCl_2(CH_3CN)(PPh_3)_2$	2203 m 323 m	ν_{CN} ν_{IrCl}	1.24 s −21.23 t $J_{PH} = 14$	CH_3 IrH	A_2	−0.43 s
6	$[IrHCl(bpy)(PPh_3)_2]BPh_4$	2235 w	ν_{IrH}	ABX spin syst δ_X −19.15 $J_{AX} = J_{BX}$ =18	IrH	AB	δ_A 2.0 δ_B −6.40 $J_{AB} = 16$
7a	$IrCl_2\{CH{=}C(H)Ph\}(Hpz)(PPh_3)_2$	3314 m 324 m	ν_{NH} ν_{IrCl}	11.26 s, br 9.30 dt $J_{HH} = 16.5$ $J_{PH} = 2.0$ 5.95 d $J_{HH} = 16.5$ 7.63 s, br 7.04 s, br 5.90 t	NH CHα CHβ H5 pz H3 pz H4 pz	A_2	−15.17 s
7b	$IrCl_2\{CH{=}C(H)\text{-}p\text{-}tolyl\}(Hpz)(PPh_3)_2$	3315 m	ν_{NH}	11.25 s, br 9.15 dt $J_{HH} = 16.5$	NH CHα	A_2	−15.76 s

(*continued on next page*)

Table 2 (*continued*)

	Compound	IR[a] ν (cm^{-1})	Assgnt	^1H NMR[b] δ (J, Hz)	Assgnt	Spin system	$^{31}P\{^1H\}$NMR[b,c] δ (J, Hz)
				$J_{PH} = 2.0$			
				5.87 d	CHβ		
				$J_{HH} = 16.5$			
				7.61 s, br	H5 pz		
				7.02 d	H3 pz		
				5.89 t	H4 pz		
				2.26 s	CH_3		
7c	$IrCl_2\{CH{=}C(H)COOMe\}(Hpz)(PPh_3)_2$	3300 m	ν_{NH}	11.13 s, br	NH	A_2	−13.97 s
		1696 s	ν_{CO}	10.90 dt	CHα		
				$J_{HH} = 16.0$			
				$J_{PH} = 2.0$			
				5.60 d	CHβ		
				$J_{HH} = 16.0$			
				7.64 s, br	H5 pz		
				7.03 s, br	H3 pz		
				5.89 t	H4 pz		
				3.48 s	CH_3		
8a	$IrCl_2\{CH{=}C(H)Ph\}(H\text{-}3\text{-}Mepz)(PPh_3)_2$	3311 m	ν_{NH}	10.57 s, br	NH	A_2	−16.08 s
				9.34 dt	CHα		
				$J_{HH} = 16.5$			
				$J_{PH} = 2.0$			
				5.94 d	CHβ		
				$J_{HH} = 16.5$			
				7.47 s, br	H5 pz		
				5.58 s, br	H4 pz		
				1.89 s	CH_3		
9a	$IrCl_2\{CH{=}C(H)Ph\}(Hpz)(P^iPr_3)_2$	3267 s	ν_{NH}	12.20 br	NH	A_2	6.33 s
				8.59 dt	CHα		
				$J_{HH} = 12.0$			
				$J_{PH} \leqslant 0.5$			
				8.23 d	H5 pz		
				7.63 d	H3 pz		
				6.42 t	H4 pz		
				5.97 d	CHβ		
				$J_{HH} = 12.0$			
				2.74 m	CH phos		
				1.27 m	CH_3		
10a	$IrCl_2\{CH{=}C(H)Ph\}(HIm)(PPh_3)_2$	3402 m	ν_{NH}	9.31 dt	CHα	A_2	−14.59 s
		321 m	ν_{IrCl}	$J_{HH} = 16.5$			
				$J_{PH} = 3.8$			
				8.84 s	NH		
				5.88 d	CHβ		
				$J_{HH} = 16.5$			
				7.58 d	H2 Im		
				7.21 t	H4 Im		
				6.41 dt	H5 Im		
10b	$IrCl_2\{CH{=}C(H)p\text{-}tolyl\}(HIm)(PPh_3)_2$	3404 m	ν_{NH}	9.17 dt	CHα	A_2	−14.79 s
				$J_{HH} = 16.5$			
				$J_{PH} = 3.8$			
				8.91 s, br	NH		
				5.84 d	CHβ		
				$J_{HH} = 16.5$			
				7.62 d	H2 Im		
				7.25 t	H4 Im		
				6.39 dt	H5 Im		
				2.27 s	CH_3		

[a] In KBr pellets.
[b] In CD_2Cl_2 at 25 °C, unless otherwise noted.
[c] Positive shift downfield from 85% H_3PO_4.

Table 3
^{13}C NMR data for selected iridium complexes

	Compound	^{13}C NMR[a] δ (J, Hz)	Assgnt
1b	$IrHCl_2(H\text{-}3\text{-}Mepz)(PPh_3)_2$	138–127 m	Ph
		138.7 s	C3
		136.8 s	C5
		105.6 s	C4
		11.1 s	CH_3
2a	$[IrHCl(Hpz)_2(PPh_3)_2]BPh_4$	165–122 m	Ph
		144.4 s	C5
		131.5 s	C3
		108.8 s	C4
4	$IrHCl_2(HIm)(PPh_3)_2$	137–127 m	Ph
		134.2 s	C2 Im
		125.8 s	C4 Im
		114.5 s	C5 Im
7a	$IrCl_2\{CH{=}C(H)Ph\}(Hpz)(PPh_3)_2$	141–124 m	Ph
		137.2 t	Cβ
		139.2 s	C5 pz
		124.5 s	C3 pz
		113.4 t	Cα[b]
		$J_{CP} = 10$	
		107.2 s	C4 pz
8a	$IrCl_2\{CH{=}C(H)Ph\}(H\text{-}3\text{-}Mepz)(PPh_3)_2$	141–124 m	Ph
		139.5 s	C5 pz
		137.0 t	Cβ
		134.7 s	C3 pz
		$J_{CP} = 4$	
		113.6 t	Cα
		$J_{CP} = 10$	
		106.6 s	C4 pz
		11.1 s	CH_3
10a	$IrCl_2\{CH{=}C(H)Ph\}(HIm)(PPh_3)_2$	141–127 m	Ph
		137.3 t	Cβ
		$J_{CP} = 4.2$	
		111.5 t	Cα
		$J_{CP} = 10.6$	
		137.0 s	C2 Im
		128.3 s	C4 Im
		115.0 s	C5 Im

[a] In CD_2Cl_2 at 25 °C, unless otherwise noted.
[b] $J_{CH} = 140$ Hz.

2203 cm^{-1} attributed to ν_{CN} of the nitrile ligand, while no absorption attributable to ν_{IrH} of the hydride was observed. The presence of both the nitrile and the hydride ligands, however, is confirmed by the proton NMR spectra, which show a singlet at 1.24 ppm of the methyl group of CH_3CN and a triplet at −21.23 ppm of the hydride ligand.

The $^{31}P\{^1H\}$ NMR spectra of the 2,2′-bipyridine $[IrHCl(bpy)(PPh_3)_2]BPh_4$ (**6**) complex is an AB multiplet, in agreement with the magnetic inequivalence of the two phosphine ligands. As a result, the hydride signal appear in the proton spectra as an ABX (X = ^1H) multiplet which can be simulated with the parameters reported in Table 2. The same value of 18 Hz found for the two J_{PH} suggests that both the phosphines should be in a mutually *cis* position with respect to the hydride ligand. On the basis of these data, a geometry of the VI type can reasonably be proposed for the bipyridine **6** derivative (Chart 3).

3.2. Reactivity

Reactivity studies of the new hydride containing N-donor ligands has been undertaken toward both protonation and insertion reactions, with the aim to test how the introduction of nitrogenous ligands changes the properties of hydride complexes.

Neutral pyrazole $IrHCl_2(HRpz)(PPh_3)_2$ (**1**) and imidazole $IrHCl_2(HIm)(PPh_3)_2$ (**4**) complexes react with Brønsted acids such as CF_3SO_3H or $HBF_4 \cdot Et_2O$ to give a pale-yellow solution from which no stable compound was isolated. The reaction, however, was studied by NMR spectroscopy between +20 and −80 °C and the results show that the addition of acid at −80 °C caused a variation in the proton spectra, with the disappearance of the hydride triplet near −20 ppm of the precursors **1** and **4** and the appearance of a new triplet near −16 ppm. T_1 measurements at −80 °C on this new signal give values of about 120 ms which are comparable with those of the precursors (between 140 and 120 ms) thus excluding the formation of a dihydrogen [Ir]-η^2-H_2 complex [23]. The addition of acid

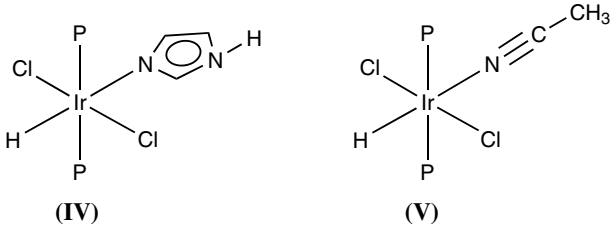


Chart 2.

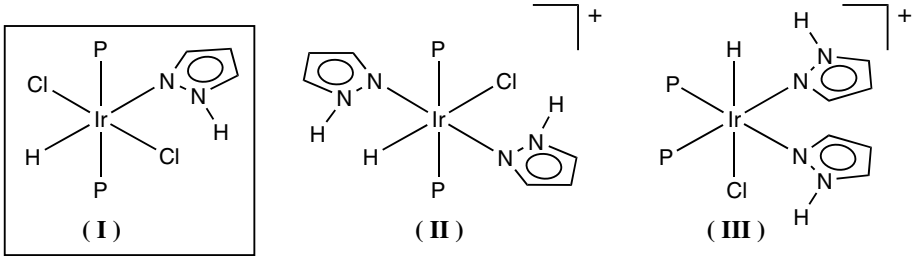
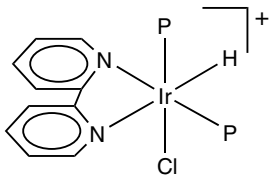


Chart 1.



(VI)

Chart 3.

to $IrHCl_2(HRpz)(PPh_3)_2$ also causes the disappearance of the signals of the coordinate Hpz and the concurrent appearance of new signals, attributable to the pyrazole and imidazole species. These results suggest that the protonation of pyrazole and imidazole complexes **1**, **4** proceeds to the azolic nitrogen atom of the N-donor ligand, resulting in the loss of the same ligand and the formation of the pentacoordinate $IrHCl_2(PPh_3)_2$ species, as shown in Scheme 6.

Support for this hypothesis comes from the reversibility of the reaction which gives the starting **1**, **4** complexes through the addition of base (NEt_3) to the solution of the protonated compounds. Unfortunately, the pentacoordinate $IrHCl_2(PPh_3)_2$ species is unstable and cannot be isolated in the solid state. However, chemical and spectroscopic data strongly support the reaction of Scheme 6 for the protonation of the pyrazole **1** and imidazole **4** complexes.

Aryldiazonium cations ArN_2^+ do not react with the **1**–**6** hydrides containing nitrogenous ligands and the starting complexes can be recovered unchanged after several hours of reaction (Scheme 7).

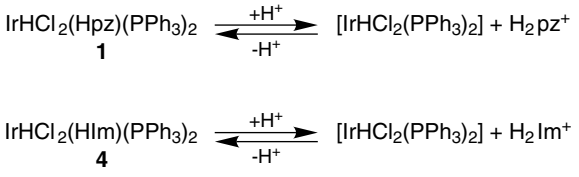
This unreactivity is somewhat unexpected because the comparable $IrHCl_2L(PPh_3)_2$ [$L = P(OEt)_3$ and $PPh(OEt)_2$] complexes [24] do react with aryldiazonium cations to give the corresponding [Ir]-HN=NAr aryldiazene derivatives. The introduction of a N-donor ligand such as pyrazole, imidazole or CH_3CN into the coordination sphere of $[IrHCl_2(PPh_3)_2]$ hydridic fragment changes the properties of the corresponding Ir–H bond, making it unreactive toward the insertion of an ArN_2^+ group.

Terminal alkynes such as R1C≡CH (R1 = Ph, *p*-tolyl, $COOCH_3$), instead, react with pyrazole and imidazole complexes in refluxing 1,2-dichloroethane to give the corresponding vinyl [Ir]-CH=C(H)R1 (**7**–**10**) derivatives, which were isolated and characterised (Scheme 8).

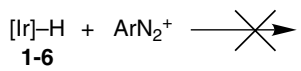
The reaction with alkyne was studied extensively and the results show that the insertion reaction is very slow at room temperature and needs reflux conditions in 1,2-dichloroethane to yield the final vinyl complex in reasonable quantities. With the *tert*-butylacetylene, however, the reaction is so slow that only traces of the vinyl complex were obtained. The reactivity studies also show that only with the neutral complexes the reaction proceeds, while with the cationic $[IrHCl(HRpz)_2(PPh_3)_2]^+$ (**2**) and $[IrHCl(bpy)(PPh_3)_2]^+$ (**6**) derivatives no vinyl complex was obtained. In these cases, the hydride precursors were recovered unchanged after several hours of reflux with an excess of acetylene. This unreactivity may be explained by taking into account that the mechanism proposed [25] for the insertion of alkyne into the Ir–H bond usually requires a vacant *cis* site to accommodate the alkyne. Whereas in the neutral complexes **1**, **4** one of the two chlorides is labile (see Scheme 1) and can be replaced by the alkyne, allowing the coordination of R1C≡CH prior the insertion, in the cationic **2**, **6** no ligand is probably labile, thus preventing the coordination of the alkyne and therefore the insertion.

The need of an open coordination site for the insertion of alkyne into the Ir–H bond prompted us to also study the reactivity of the pentacoordinate $IrHCl_2(PPh_3)_2$ obtained from the protonation reaction of pyrazole and imidazole complexes **1**, **4** with alkyne. The reaction was carried out by adding first an equimolar amount of $HBF_4 \cdot Et_2O$ and then an excess of terminal alkyne to the starting $IrHCl_2(HRpz)(PPh_3)_2$ and $IrHCl_2(HIm)(PPh_3)_2$ complexes. Surprisingly, no vinyl complex was isolated from the reaction, which gives a yellow-orange solid characterised as the alkyl-carbonyl $IrCl_2(\eta^1\text{-}CH_2C_6H_5)(CO)(PPh_3)_2$ derivative [10] in the case of phenylacetylene. With *tert*-butylacetylene, instead, the acyl $IrCl_2\{\eta^1\text{-}C(O)CH_2C(CH_3)_3\}(PPh_3)_2$ complex [10] was obtained, as shown in Scheme 9.

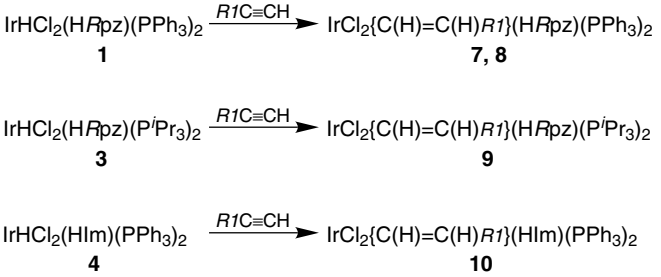
The reaction proceeds with the hydrolysis of the coordinate alkyne to give the alkyl-carbonyl **12** or the acyl **11** derivatives and these results are the same as those we previously obtained [10] from the reaction of $IrHCl_2(PPh_3)_3$ with alkynes. As in the previous cases, the traces of water present in the solvent are enough to afford the final complexes. The hydrolysis of the alkyne with C≡C bond



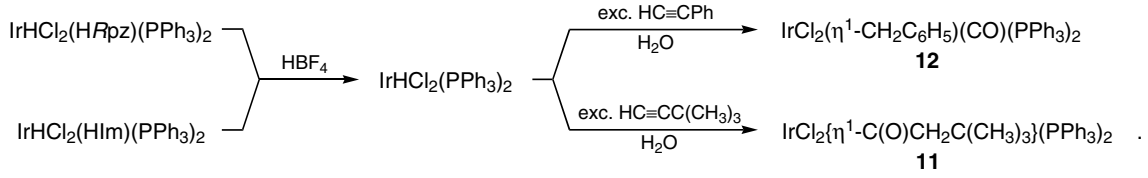
Scheme 6.



Scheme 7.



Scheme 8. R1 = Ph, **a**; *p*-tolyl, **b**; CH_3COO, **c**.



Scheme 9.

cleavage and formation of alkyl or acyl complexes in the reaction of pentacoordinate $IrHCl_2(PPh_3)_2$ species is therefore not surprising taking into account the behaviour of the hexacoordinate $IrHCl_2(PPh_3)_3$ complex containing one labile PPh_3 ligand [10]. In both cases the reaction with alkyne probably gives the $IrHCl_2(\eta^1\text{-}R1C{\equiv}CH)(PPh_3)_2$ intermediate which results to be the first step of the hydrolysis affording the final **12** or **11** derivatives.

The vinyl complexes $IrCl_2\{CH{=}C(H)R1\}(HRpz)P_2$ (**7–9**) (P = PPh_3, P^iPr_3) and $IrCl_2\{CH{=}C(H)R1\}$ (HIm)-$(PPh_3)_2$ (**10**) are red-brown solids stable in air and in a solution of the most common organic solvents, where they behave as non-electrolytes. Their characterisation is supported by analytical and spectroscopic data (Tables 2 and 3) and by the crystal structure determination of the $IrCl_2\{CH{=}C(H)Ph\}(Hpz)(PPh_3)_2$ (**7a**) derivative.

The solid-state structure of *trans-E*-[$IrCl_2\{CH{=}C(H)$-Ph}(Hpz)$(PPh_3)_2$] (**7a**) was determined by single-crystal X-ray crystallographic analysis (Table 1). ORTEP plot, including the atom-numbering scheme, of the complex is shown in Fig. 1. Selected bond lengths and bond angles of the complex are listed in Table 4. The iridium atom is coordinated by two triphenylphosphine ligands, two chlorine atoms, one pyrazolyl ligand and a phenylvinyl ligand in an octahedral fashion. The geometry of the complex can be rationalised as a distorted octahedron with the two phosphorus atoms of the triphenylphosphine ligands occupying the apical positions, in relative *trans* positions [P(1)–Ir–P(2) = 171.09(4)°]. The equatorial plane is formed by the two chlorine atoms mutually *trans* disposed [Cl(1)–Ir–Cl(2) = 172.59(4)°] and the carbon atom of the styryl ligand and the nitrogen atom of a pyrazolyl ligand also in relative *trans* positions [C(1)–Ir–N(1) = 177.30(17)°]. These *trans* angle values show some distortion in the defined as equatorial plane since the chlorine atoms are deviated in the direction of the pyrazolyl ligand and the phosphorous atoms are deviated in the direction of the styrene ligand.

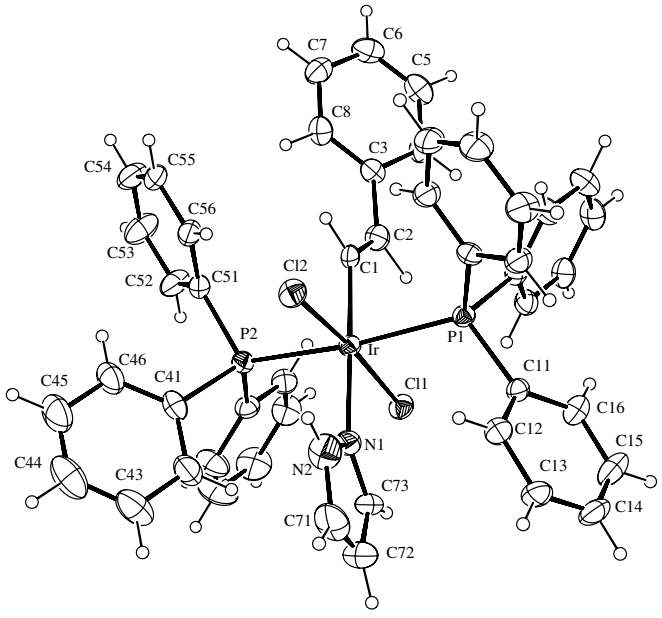


Fig. 1. Molecular structure of *trans-E*-[$IrCl_2\{CH{=}C(H)Ph\}(HPz)(PPh_3)_2$] (**7a**).

The pyrazolyl ligand is situated almost in the defined as equatorial plane [dihedral angle 4.0(4)°]. This disposition allows intramolecular hydrogen bonds between the coordinated chlorine atoms and the *ortho* atoms of the ring, N(2) and C(73) (see Table 5). The styryl ligand, however, is deviated from the equatorial plane showing more twisting freedom along the Ir–C(1) and C(2)–C3(3) bonds. The carbon atom labelled as C(2) lies only 0.165(6) Å out of the plane defined as equatorial for the complex, but the donor carbon atom labelled as C(1) lies 0.547(8) Å out of the plane of the benzene ring. The benzene ring plane forms a dihedral angle of 36.6(1)° with the defined as equatorial plane for the complex.

Distances and angles into the ligands are as expected since values of 1.309(6) Å for C(1)–C(2) and of 1.485(6) Å for C(2)–C(3) are characteristic for a styryl ligand as well as the sp^2 nature of the C(1) and C(2) atoms [26]. The two substituents at the double bond of the styrene ligand are in *trans* positions (*E*-isomer) as is usual for these kinds of complexes, although some *cis* compounds (*Z*-isomer) could be found [27].

The phenyl rings at the phosphine ligands are in a staggered disposition with each other as is seen by the torsion angle values close to 60° of C–P–P–C (see Table 4), showing no distortion at this stage.

The IR spectra of all the vinyl complexes **7–10** show a medium-intensity band at 3402–3267 cm^{-1} attributed to the ν_{NH} of the HRpz or HIm ligand. In the spectra of the $IrCl_2\{CH{=}C(H)COOCH_3\}(Hpz)(PPh_3)_2$ (**7c**) complex a strong band at 1696 cm^{-1} is also present, due to ν_{CO} of the $COOCH_3$ substituent.

The ^1H NMR spectra show, beside the signals of the N- and P-donor ligands, a doublet of triplets between 10.90 and 8.59 ppm attributed to the Hα proton of the vinyl ligand. The Hβ proton signal, instead, appear as a doublet between 5.97 and 5.60 ppm and these attributions are

Table 4
Bond lengths (Å) and angles (°) for $[IrCl_2\{CH{=}C(H)Ph\}(Hpz)(PPh_3)_2]$ (**7a**)

Lengths			
Ir–C(1)	2.042(4)	Ir–N(1)	2.192(4)
Ir–Cl(1)	2.3534(10)	Ir–Cl(2)	2.3841(10)
Ir–P(2)	2.3865(12)	Ir–P(1)	2.3986(11)
P(1)–C(21)	1.830(4)	P(1)–C(11)	1.832(4)
P(1)–C(31)	1.857(4)	P(2)–C(61)	1.834(4)
P(2)–C(41)	1.848(4)	P(2)–C(51)	1.852(5)
C(1)–C(2)	1.309(6)	C(2)–C(3)	1.485(6)
C(3)–C(8)	1.378(6)	C(3)–C(4)	1.386(6)
C(4)–C(5)	1.379(6)	C(5)–C(6)	1.370(7)
C(6)–C(7)	1.372(6)	C(7)–C(8)	1.368(6)
N(1)–C(73)	1.322(5)	N(1)–N(2)	1.356(5)
N(2)–C(71)	1.362(7)	C(71)–C(72)	1.340(8)
Angles			
C(1)–Ir–N(1)	177.30(17)	C(1)–Ir–Cl(1)	96.54(13)
N(1)–Ir–Cl(1)	86.07(10)	C(1)–Ir–Cl(2)	90.86(13)
N(1)–Ir–Cl(2)	86.54(10)	Cl(1)–Ir–Cl(2)	172.59(4)
C(1)–Ir–P(2)	85.93(11)	N(1)–Ir–P(2)	94.70(10)
Cl(1)–Ir–P(2)	91.76(4)	Cl(2)–Ir–P(2)	88.33(4)
C(1)–Ir–P(1)	85.77(11)	N(1)–Ir–P(1)	93.74(10)
Cl(1)–Ir–P(1)	85.98(4)	Cl(2)–Ir–P(1)	95.02(4)
P(2)–Ir–P(1)	171.09(4)	C(2)–C(1)–Ir	134.1(4)
N(2)–N(1)–Ir	124.7(3)	N(1)–N(2)–C(71)	110.0(5)
C(72)–C(71)–N(2)	107.1(6)	N(1)–C(73)–C(72)	110.3(5)
Torsion angles			
Ir–C(1)–C(2)–C(3)	−176.9(3)	C(11)–P(1)–P(2)–C(51)	−179.5(2)
C(21)–P(1)–P(2)–C(51)	56.8(2)	C(31)–P(1)–P(2)–C(51)	−59.5(2)
C(11)–P(1)–P(2)–C(61)	−65.6(2)	C(21)–P(1)–P(2)–C(61)	170.7(2)
C(31)–P(1)–P(2)–C(61)	54.5(2)	C(11)–P(1)–P(2)–C(41)	60.0(2)
C(21)–P(1)–P(2)–C(41)	−63.7(2)	C(31)–P(1)–P(2)–C(41)	−180.0(2)

Table 5
Hydrogen bonds parameters for $[IrCl_2\{CH{=}C(H)Ph\}(Hpz)(PPh_3)_2]$ (**7a**) (Å, °)

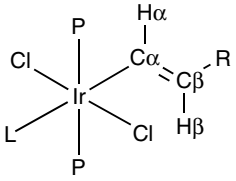
D–H...A	*d*(D–H)	*d*(H...A)	*d*(D...A)	∠(DHA)
N(2)–H(21)...Cl(2)	0.86	2.57	3.094(5)	120.4
C(73)–H(73)...Cl(1)	0.93	2.66	3.162(5)	115.0
C(12)–H(12)...N(2)	0.93	2.60	3.280(6)	130.2
C(32)–H(32)...Cl(1)	0.93	2.56	3.327(4)	140.6
C(42)–H(42)...N(1)	0.93	2.55	3.213(6)	128.6
C(56)–H(56)...Cl(2)	0.93	2.66	3.485(5)	148.3
C(54)–H(54)...Cl(1′)	0.93	2.71	3.439(5)	136.0
C(71)–H(71)...Cl(2″)	0.93	2.82	3.597(6)	141.6
C(8)–H(8)...Cg	0.93	3.03	3.833(4)	145.4

Cg stands for the centroid of the benzene ring labeled as C(51)–C(56). Symmetry transformations used to generate equivalent atoms: ′: $x+1, y, z$; ″: $1-x, 1-y, -z$.

confirmed by a COSY experiment. Taking into account that the $^{31}P\{^1H\}$ NMR indicate the magnetic equivalence of the two phosphine ligands showing a sharp singlet between −16.08 and 6.33 ppm, the vinyl Hα proton signal can be easily simulated using an ABX_2 ($A = {}^1H\alpha$, $B = {}^1H\beta$, $X_2 = {}^{31}P$) model with J_{AB} near 16 Hz and J_{AX} of about 2 Hz. The values of the coupling constant J_{HH} of 16 Hz also suggest [28] a *trans* arrangement of the two vinyl protons, as observed in the solid state.

The ^{13}C NMR spectra (Table 3) confirm the presence of the vinyl ligand showing a triplet at 113.6–111.5 ppm ($J_{CP} = 10.0$ Hz) attributed to the Cα carbon resonance. The HMQC and HMBC experiments confirm the attribution showing the correlation between the triplet at 113–111 ppm in the ^{13}C spectra with the proton signals at 10.90–8.59 ppm of the Hα vinyl resonance. The ^{13}C signal near 137 ppm, instead, is correlated to the signal at 5.97–5.60 ppm of the Hβ vinyl proton, in agreement with the proposed assignment for the signals.

The IR spectra of the vinyl complexes **7a** and **10a** show, in the far region, only one band at 324 cm^{-1} (**7a**) and 321 cm^{-1} (**10**) attributable to the stretching of the IrCl bond, in agreement with the mutually *trans* position of the two chloride ligands. On the basis of these data, a *trans–trans* geometry of the VII type, exactly like that observed in the solid state, can be proposed for the $IrCl_2\{CH{=}C(H)R1\}LP_2$ (**7–10**) (L = HRpz, HIm; P = PPh_3, P^iPr_3) vinyl derivatives (Chart 4).



(VII)

Chart 4.

4. Conclusions

The synthesis of a series of neutral and cationic hydride complexes of iridium(III) containing N-donor ligands such as pyrazole, imidazole and 2,2′-bipyridine has been achieved using $IrHCl_2(PPh_3)_3$ as a precursor. Protonation of the azole complexes $IrHCl_2L(PPh_3)$ (L = HRpz, HIm) with Brønsted acids does not give any η^2-H_2 species, but proceeds with the loss of the nitrogenous ligand and formation of the unstable pentacoordinate $IrHCl_2(PPh_3)_2$ derivative. Among the properties shown by the new hydride complexes, the facile insertion of terminal alkyne into the Ir–H bond to give a series of stable and isolable vinyl $IrCl_2\{CH{=}C(H)R1\}L(PPh_3)_2$ derivatives can be highlighted.

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