New iridium(I) complexes with labile ligands: reactivity and structural characterization by atmospheric pressure mass and tandem mass spectrometry

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Abstract

Reaction of diphosphine complexes $[IrCl\{(C_6F_5)_2P(CH_2)_2P(C_6F_5)_2\}]_2$ (**I**) and $[IrCl(dppe)]_2$ (**II**) with coordinating solvents (acetonitrile, acetone, DMSO) leads to several square-planar complexes of the type [IrCl(diphosphine)(solvent)] which are stable only in solution $([IrCl\{(C_6F_5)_2P(CH_2)_2P(C_6F_5)_2\}(NCCH_3)]$ (**III**) and $[IrCl\{(C_6F_5)_2P(CH_2)_2P(C_6F_5)_2\}(acetone)]$, **IV**) and/or can be detected only under APCI-MS/MS conditions ([IrCl(dppe)(solvent)]). When **III** is allowed to react with CO for at least 30 min, the unusual five coordinated *trans*-dicarbonyl complex $[IrCl\{(C_6F_5)_2P(CH_2)_2P(C_6F_5)_2\}(CO)_2]$ (**Vb**) is formed, as characterized by ^{1}H and ^{31}P NMR, FT-IR, TGA and APCI-MS/MS.

A new and stable square-planar complex $[Ir(OCH_3)(cod)(PClPh_2)]$ (**IX**) was also synthesized. Its APCI-MS/MS spectrum is simple and unique as it shows exclusively the loss of a neutral C_3H_2 species. Along with the APCI-MS and APCI-MS/MS analyses, whenever it was possible all complexes were also characterized by ^{1}H and ^{31}P NMR spectroscopy.
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1. Introduction

Four coordinate, 16-electron, square-planar Ir(I) complexes are important intermediates in organometallic chemistry. Depending on the nature of ligands, these complexes easily undergo oxidative addition, ligand substitution and even migratory insertion reactions [1–3]. Although convenient synthesis of Vaska-type complexes from $[IrCl(cod)]_2$ and monophosphines has been reported by Crabtree et al. [2], square-planar Ir(I) complexes with diphosphines are relatively rare [4], whereas alkoxide square-planar Ir(I) complexes are hard to isolate owing to easy decomposition by β-hydride elimination [5] or hydrolysis [6]. These relatively rare

Ir(I) complexes are, however, important synthetic targets as they can participate in several catalytic reactions such as hydrosilylation [7] and hydrogen-transfer [8]. Herein, we report the synthesis of new four-coordinate square-planar iridium(I) complexes by reacting $R_2P(CH_2)_2PR_2$ ($R = C_6H_5$ or C_6F_5) with $[IrCl(coe)_2]_2$, as well as $[Ir(OCH_3)(cod)(PClPh_2)]$ by reacting $PClPh_2$ with $[Ir(OCH_3)(cod)]_2$. These new Ir(I) complexes bear labile ligands and are therefore candidates for novel carbene precursors upon reaction with diazocompounds. Structural characterization of the Ir(I) complexes has been performed by ^{1}H, ^{13}C and ^{31}P NMR, and IR, but most particularly by atmospheric pressure chemical ionization mass and tandem mass spectrometry (APCI-MS and APCI-MS/MS), whereas some intermediates could only be identified by APCI-MS and APCI-MS/MS. APCI together with two other novel, soft and wide-ranging atmospheric pressure ionization (API) techniques: electrospray (ESI) [9], and APPI

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[10,11], as well as "in-vacuum" and atmospheric pressure matrix-assisted laser desorption ionization (MALDI) have recently revolutionized the way molecules are ionized and transferred to mass spectrometers for mass and property measurements, and structural characterization. API techniques have greatly expanded the applicability of mass spectrometry to a variety of new classes of molecules with thermal instability, high polarity and mass. Although APCI mass (and tandem mass) spectrometry has been mainly (and most successfully) applied to the analysis of bio-molecules [12–19], these techniques have also been proven as highly suitable for the structural characterization of inorganic and organometallic compounds [20–29]. Herein, we describe the synthesis of novel iridium(I) complexes and their detailed structural characterization, most particularly by APCI-MS and APCI-MS/MS.

2. Experimental

All reactions were carried out under an atmosphere of argon using Schlenk techniques. Solvents were dried by known procedures and distilled before use. The start materials [IrCl(coe)$_2$]$_2$, [IrCl(cod)]$_2$ and [Ir(OCH$_3$)(cod)] were prepared as described in the literature [30]. NMR spectra were recorded at room temperature on Gemini 300 MHz or Inova 500 MHz instruments. The ^{1}H and ^{13}C spectra were referenced to the solvent resonance and are reported relative to TMS. ^{31}P chemical shifts were referenced to external 85% H$_3$PO$_4$. FT-IR spectra were measured on a Nicolet–Nexus spectrometer. Elemental analyses (C, H) were carried out on a Perkin Elmer Series 11 2400 Analyzer. Mass and tandem mass spectrometric data were acquired using a Q-Tof (micromass®, UK) high-resolution hybrid Qq(orthogonal)Tof mass spectrometer operating at near 7000 resolution using atmospheric pressure chemical ionization. Thermo Gravimetric Analysis was performed using a TGA 2050, TA 5100 instrument, under an atmosphere of argon.

2.1. Synthesis of [IrCl{(C$_6$F$_5$)$_2$P(CH$_2$)$_2$P(C$_6$F$_5$)$_2$}]$_2$ (I)

A solution of [IrCl(coe)$_2$]$_2$ (30 mg, 3.3 × 10^{-2} mmol) in toluene (4 mL) was treated with (C$_6$F$_5$)$_2$PCH$_2$CH$_2$P(C$_6$F$_5$)$_2$ (68 mg, 88 μmol) under continuous stirring for 50 min at room temperature. Upon addition of the phosphine, the color changed from orange to yellow. After removal of the solvent under reduced pressure, the residue was washed with hexane and dried under vacuum: yield 58.5 mg (90%). mp: 143 °C; ^{1}H NMR (CDCl$_3$, 300 MHz): δ 1.88 (m, CH$_2$); ^{31}P{^{1}H} NMR (CDCl$_3$, 121.46 MHz): δ 6.70 (s). Mass analysis: *m/z* 1972.05.

2.2. Synthesis of [IrCl(dppe)]$_2$ (II)

A solution of [IrCl(coe)$_2$]$_2$ (60 mg, 6.6 × 10^{-2} mmol) in toluene (4 mL) was treated with dppe (106 mg, 2.7 × 10^{-1} mmol) under continuous stirring at room temperature, leading to the formation of an orange precipitate. The solution was stirred for 30 min. The precipitate was filtered, washed with toluene and dried under reduced pressure. Yield: 75 mg (90%); mp. 181 °C; ^{1}H NMR (CDCl$_3$, 300.06 MHz) δ 2.32 (br m, 1H, CH$_2$ of dppe), 2.54 (br m, 1H, CH$_2$ of dppe), δ 7.55 (m, 20H, Ph); ^{31}P{^{1}H} NMR (CDCl$_3$, 121.46 MHz): δ 51.00 (s). Mass analysis: *m/z* 1252.35.

2.3. Synthesis of [IrCl{(C$_6$F$_5$)$_2$P(CH$_2$)$_2$P(C$_6$F$_5$)$_2$}(NCCH$_3$)] (III)

A solution of I (60 mg, 3.0 × 10^{-2} mmol) in NCCH$_3$ (4 mL) was stirred for 50 min at 40 °C. The ^{31}P{^{1}H} NMR of the solution was obtained using a capillary tube of D$_2$O. ^{31}P{^{1}H} NMR (D$_2$O, 121.46 MHz): δ 1.8 (br s) and δ 14.0 (br s). Mass analysis: *m/z* 1026.55.

2.4. Attempted synthesis of [IrCl{(C$_6$F$_5$)$_2$P(CH$_2$)$_2$P(C$_6$F$_5$)$_2$}(acetone)] (IV)

A solution of I (30 mg, 1.5 × 10^{-2} mmol) in NCCH$_3$ (4 mL) was stirred for 50 min at 40 °C. The solution was concentrated and the addition of 2 mL of acetone resulted in a color change from orange to yellow after 2 days in a freezer. The solvent was removed under vacuum and the yellow powder washed with hexane. The ^{31}P{^{1}H} NMR shows several peaks, suggesting the formation of many unidentified products.

2.5. Synthesis of [IrCl(CO){(C$_6$F$_5$)$_2$PCH$_2$CH$_2$P(C$_6$F$_5$)$_2$}] (Va) and [IrCl(CO)$_2${(C$_6$F$_5$)$_2$PCH$_2$CH$_2$P(C$_6$F$_5$)$_2$}] (Vb)

A solution of III (30 mg, 2.9 × 10^{-2} mmol) in NCCH$_3$ (4 mL) was treated with CO for 6 min at atmospheric pressure. The solvent was removed under vacuum. Yield: 14.7 mg (97%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ 2.85 (m, 4H, CH$_2$P); ^{31}P{^{1}H} NMR (CDCl$_3$, 121.46 MHz): δ 0.62 (s); 30.00 (s). IR (nujol, cm^{-1}): 2028.2 (ν_{CO}). Mass analysis (Va$^+$): *m/z* 1014.20. When the solution of III was allowed to react with CO for at least 30 min, after removal of the solvent under vacuum, Vb was isolated as a yellow powder. Yield: 15 mg (97%). mp. 118°C; ^{1}H NMR (CDCl$_3$, 300 MHz): δ 2.10 (m 1H, CH$_2$P), 2.74 (m, 1H, CH$_2$P), 2.94 (m, 1H, CH$_2$P) and 3.34 (m, 1H, CH$_2$P); ^{31}P{^{1}H} NMR (CDCl$_3$, 121.46 MHz): δ −17.0 (s). IR (nujol, cm^{-1}): ν 1999.2 (ν_{CO}). Mass analysis (Vb$^+$): *m/z* 1043.14. All attempts to recrystallize Vb from benzene, toluene, hexane or acetonitrile solutions have failed owing to its decomposition

when allowed to stand in such solutions for long periods of time.

2.6. Attempted synthesis of [IrCl(dppe)(NCCH₃)]

A solution of [IrCl(dppe)]$_2$ (60 mg, 4.8×10^{-1} mmol) in NCCH$_3$ (3 mL) was stirred for 5 h at 55 °C. The ^{31}P{^{1}H} NMR of the solution was obtained using a capillary tube of D$_2$O. ^{31}P{^{1}H} NMR (D$_2$O, 121.46 MHz): δ 13.27(s) and δ 17.82 (s). Mass analysis: m/z 667.62.

2.7. Attempted synthesis of **VI**

A solution of [IrCl(dppe)]$_2$ (60 mg, 4.8×10^{-1} mmol) in NCCH$_3$ (3 mL) was stirred for 5 h at 55 °C. The solution was concentrated and the addition of 2 mL of acetone resulted in a color change from orange to yellow after 2 days in a freezer. The solvent was removed under vacuum and the yellow powder washed with hexane. Yield: 64.5 mg (98%). mp. 170 °C (dec.); ^{1}H NMR (CDCl$_3$, 300 MHz): δ 1.58 (br m, 1H, CH$_2$ of dppe), 1.95 (br m, 1H, CH$_2$ of dppe), 2.31 (br m, 1H, CH$_2$ of dppe), 2.36 (br m, 1H, CH$_2$ of dppe), δ 7.55 (m, 20H, Ph); ^{31}P{^{1}H} NMR (CDCl$_3$, 121.46 MHz): δ 13.73 (t, $J = 4.5$ Hz) and δ 18.25 (s). Mass analysis: m/z 684.74.

2.8. Synthesis of [Ir(cod)(Cl)P(Cy)₃] (**VIII**)

To a solution of [Ir(Cl)(cod)]$_2$ (60 mg, 9.0×10^{-2} mol) in methanol (4 mL), a solution of PCy$_3$ (25 mg, 9.0×10^{-2} mmol) in hexane was added dropwise under continuous stirring. A color change from pale yellow to gold yellow was observed. The solvent was removed under vacuum and the solid washed with hexane. Yield: 49.85 mg (90%). mp. 185.1 °C; ^{1}H NMR (CDCl$_3$, 300 MHz): δ 4.72 (br s, 2H, CH of cod), δ 3.10 (br s, 2H, CH of cod), δ 2.00–2.15 (m, 8H, CH2 of cod), 1.55–1.82 (m 33H of Cy); ^{13}C{^{1}H} NMR (CDCl$_3$, 75.45 MHz): δ 88.48 (CH, cod), δ 88.41 (CH, cod), δ 50.39 (2, CH, cod), δ 32.67 (CH$_2$ of cod), δ 32.63 (CH$_2$ of cod), δ 31.40 (CH$_2$ of cod), δ 31.10 (CH$_2$ of cod), δ 29–25(CH$_2$ of cy); ^{31}P{^{1}H} NMR (CDCl$_3$, 121.46 MHz): δ 15.07 (s). Mass analysis (**VIII** + H$^+$): m/z 615.85.

2.9. Synthesis of [Ir(OCH₃)(cod)(PClPh₂)] (**IX**)

To a solution of [Ir(OCH$_3$)(cod)]$_2$ (60 mg, 9×10^{-2} μmol) in hexane (4 mL), a solution of PPh$_2$Cl (50 mg, $2, 3 \times 10^{-1}$ μmol) in hexane (1 mL) was added dropwise. A color change from yellow to orange and a white precipitate were observed. The solution was filtered and cooled to -20 °C until an orange complex precipitated. The orange solid was washed thrice with hexane (2 mL) and dried under vacuum. Yield: 10 mg (20%). mp. 97 °C; ^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.79–7.27 (m, Ph of PPh$_2$Cl); δ 5.30 (s, 2H, CH of cod), δ 3.16 (s, 3H, OCH$_3$), δ 2.26–1.76 (m, 2H (CH) and 8H (CH$_2$) of cod); ^{31}P{^{1}H} NMR (CDCl$_3$, 121.46 MHz): δ 103.09 (s). *Anal*. Calc. for C$_{23}$H$_{22}$ClOPIr: C 45.67; H 4.50. Found: C, 46.08; H 4.33%. Mass analysis (**IX** + H$^+$): m/z 552.09.

3. Results

[IrCl(coe)$_2$]$_2$ reacts with diphosphines via replacement of coe (cyclooctene) without breaking the bridge. Thus, reaction of [IrCl(coe)$_2$]$_2$ with (C$_6$F$_5$)$_2$P(CH$_2$)$_2$P(C$_6$F$_5$)$_2$ or 1,2-bis(diphenylphosphino)ethane (dppe) in toluene affords [IrCl{(C$_6$F$_5$)$_2$P(CH$_2$)$_2$P(C$_6$F$_5$)$_2$}]$_2$ (**I**) (Scheme 1) and [IrCl(dppe)]$_2$ (**II**) (Scheme 2), respectively, in high yields (near 90% in both cases).

The ^{31}P{^{1}H} NMR spectrum of **I** shows a single signal in δ 6.70; for **II**, the signal appears in δ 51.00. The APCI-MS spectra of **I** (Fig. 1(a)) and **II** taken from acetone solutions show mainly the ionized complexes which form clusters of isotopomeric ions with the most intense ones of m/z 1972.05 (**I**$^+$) and m/z 1252.35 (**II**$^+$), respectively, and with isotopic patterns that clearly reveal the presence of the multiple isotopic elements iridium and chlorine. The observed isotopic patterns match perfectly the theoretical isotopic patterns calculated for their elemental compositions. The APCI-MS/MS tandem mass spectra of **I** and **II** taken from acetone solutions also support their bridged spiro square-planar 5-4-5-membered tricyclic structure, since **I**$^+$ (Fig. 1(b)) and **II**$^+$ are found to dissociate under low energy collisions with argon nearly exclusively by the pathway depicted in Scheme 3, with the symmetrical breaking of the most labile four-membered square-planar Ir–Cl ring. When dissolved in more coordinating solvents, these complexes react as discussed below.

Scheme 1.

Scheme 2.

R = C_6F_5, *m/z* 1972
R = C_6H_5, *m/z* 1252

R = C_6F_5, *m/z* 986
R = C_6H_5, *m/z* 626
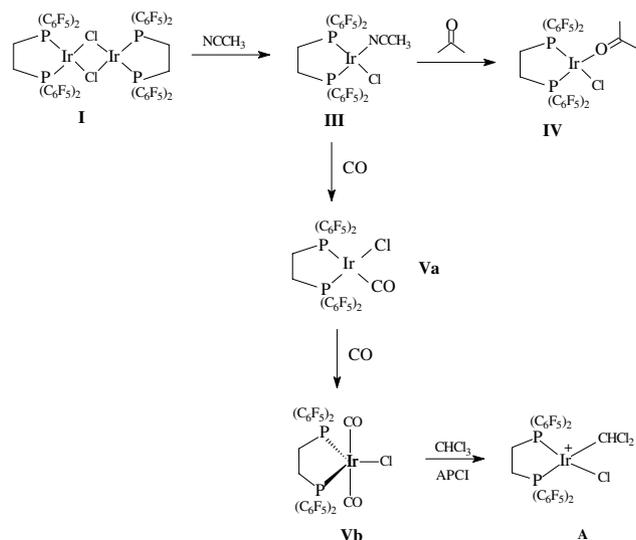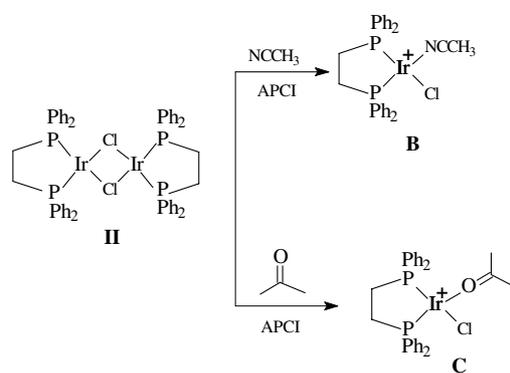
Scheme 3.

3.1. Reactivity of *I*

When (**I**) [IrCl{$(C_6F_5)_2$P$(CH_2)_2$P$(C_6F_5)_2$}]$_2$, is dissolved in acetonitrile, acetonitrile breaks the Ir–Cl bonds of the four-membered ring and the corresponding square-planar complex [IrCl{$(C_6F_5)_2$P$(CH_2)_2$P$(C_6F_5)_2$}(NCCH$_3$)] (**III**) is formed (Scheme 1). Formation of **III** is suggested by ^{31}P{^{1}H} NMR spectrum (CDCl$_3$), which shows broad signals centered at δ 1.8 and 14.0, hampering the determination of the coupling constants between the P atoms.

When recorded using deuterated acetonitrile (NCCD$_3$), the ^{1}H NMR of **III** shows two multiplets at δ
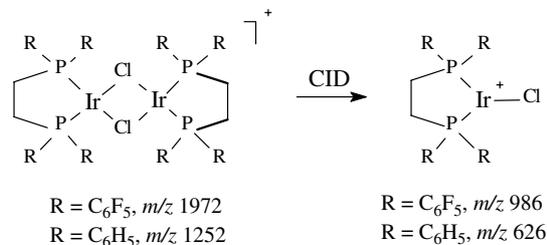
2.41 and 2.44, corresponding to the CH$_2$ groups of the phosphine. The APCI-MS spectrum of **III** in acetonitrile shows a major cluster of ions centered at *m/z* 1026.55 (**III$^+$**) with an isotopic pattern that fully supports its composition assignment. The APCI-MS/MS spectrum of **III$^+$** also supports its structural assignment, since **III$^+$** is found to dissociate mainly by acetonitrile (41 u) loss. This dissociation indicates therefore that Ir–acetonitrile is the weakest bond for complex **III**, which is stable only in acetonitrile; fast decomposition of **III** occurs when acetonitrile is removed under vacuum.

When acetone is added to a concentrated solution of **III** in acetonitrile, and the corresponding system is allowed to stand at −20 °C for 48 h, the color of the solution changes from orange to yellow, suggesting that a new complex is formed, **IV** (Scheme 1). Now, when the APCI-MS spectrum is taken from this acetone solution, a major cluster of ions centered at *m/z* 1044.60 (**IV$^+$**) is
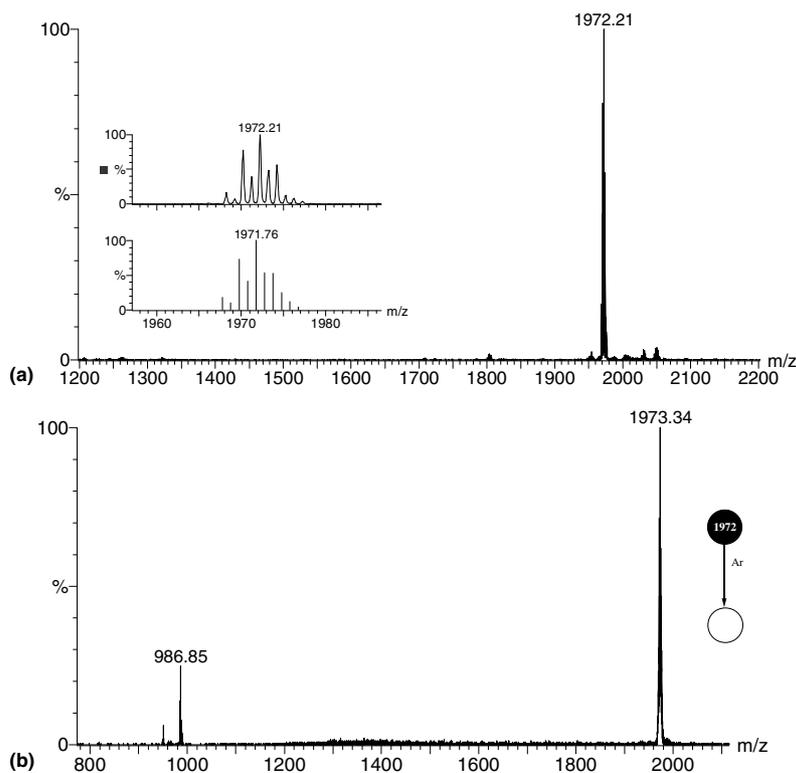
Fig. 1. (a) APCI-MS spectrum of the Ir(I) complex **I** and (b) APCI-MS/MS spectrum of **I$^+$**. The insets in (a) show the observed and theoretical isotopic patterns for **I$^+$**.

observed, which is assigned to [IrCl{(C$_6$F$_5$)$_2$P(CH$_2$)$_2$-P(C$_6$F$_5$)$_2$}(acetone)]. The APCI-MS/MS spectrum of **IV**$^+$ shows major dissociation by acetone loss (58 u). Complex **IV** is therefore stable in acetone solution, but all attempts to isolate **IV** have failed. Complex **III** also reacts quickly, in 6 min, with CO under atmospheric pressure to produce a yellow complex, **Va** (Scheme 1), in good yield (97%). The infrared spectrum of **Va** shows a single $_{CO}$ at 2028.2 cm^{-1}. The APCI-MS spectrum of **Va** taken from a benzene solution shows two clusters of ions centered at m/z 986.88 [**Va**–1CO]$^+$ and 1014.20 [**Va**]$^+$, whereas the APCI-MS/MS spectra of the **Va**$^+$ shows a fragment ion at m/z 986.88, corresponding to the loss of CO as observed under APCI conditions. Its ^{31}P{^{1}H} NMR shows two broad singlets at δ 0.62 and 30.00 and not the doublets expected for a square-planar Ir(I) complex (Scheme 1). The non-observation of doublets could be associated to the broadening of the signals owing to the presence of *meta*, *ortho* and *para*-fluorine atoms [35]. The corresponding ^{1}H NMR spectrum shows a large multiplet (CH$_2$ groups of dppe), characteristic of this kind of complex [31]. Interestingly, when the reaction of **III** with CO is carried out for a longer time (at least 30 min), a new yellow complex is observed, **Vb** (Scheme 1). Isolation of **Vb** is relevant since complexes of the type [Ir(X)(dppe)(CO)$_2$] are normally very unstable and have been characterized only in solution [31]. The reported infrared spectra of such complexes show two bands; their ^{1}H NMR spectra are characterized by four large multiplets (CH$_2$ groups of dppe), and the ^{31}P{^{1}H} spectra show only one signal.

While the IR spectrum of **Vb** shows only one band at 1999.2 cm^{-1}, its ^{1}H NMR shows four multiplets at δ 2.10, 2.74, 2.94 and 3.34 for the CH$_2$ groups of [(C$_6$F$_5$)$_2$P(CH$_2$)$_2$P(C$_6$F$_5$)$_2$]. A ^{1}H × ^{1}H correlation (COSY) shows interactions among the four atoms. The corresponding ^{31}P{^{1}H} NMR spectrum shows only one singlet at δ −17.00, implying that the phosphorous atoms are equivalent. Therefore, **Vb** should present a trigonal bipyramidal structure, with the two carbonyls in *trans* positions (Scheme 1). The APCI-MS spectrum of **Vb** taken from a benzene solution shows three major clusters of ions centered at m/z 987.14 [**Vb**–2CO]$^+$, 1015.20 [**Vb**–CO]$^+$, and 1043.14 [**Vb**]$^+$, whereas the APCI-MS/MS spectrum of **Vb**$^+$ shows two major fragment ions of m/z 987 and 1015 corresponding to the sequential losses of CO as observed under APCI conditions. When the APCI-MS spectrum of **Vb** is taken from a chloroform solution, the formation of the cationic square-planar complex [IrCl{(C$_6$F$_5$)$_2$P(CH$_2$)$_2$P-(C$_6$F$_5$)$_2$}(CHCl$_2$)]$^+$ (**A**) is observed as a cluster of isotopomeric ions centered at m/z 1068.45 (Scheme 1). A TGA study of **Vb** also supports its proposed structure, since a weight reduction of 78.22% (814.82 g/mol) corresponding to the loss of two CO molecules and the phosphine ligand was observed. This is the first example

of an Ir(I) complex with two carbonyls in *trans* positions characterized in the solid state.

3.2. Reactivity of [IrCl(dppe)]$_2$ (**II**)

When **II** is dissolved in CH$_3$CN, formation of a new species is suggested by the ^{31}P{^{1}H} NMR spectrum (CDCl$_3$), which shows signals at δ 13.00 and 18.00. The APCI-MS spectrum shows a cluster of ions centered at m/z 667.72 (**B**), Scheme 2. When the APCI-MS spectrum of **II** is taken from an acetone/acetonitrile solution, a cluster of ions centered at m/z 684.74 (**C**) is detected with masses and isotopic patterns that suggests the [IrCl(dppe)(acetone)] composition. However, the ^{1}H NMR (CDCl$_3$) spectrum of the yellow powder resulting from the addition of acetone to an acetonitrile solution of **II**, from now on called **VI**, does not show the coordination of acetone to the iridium atom: only signals at δ 2.05 (m), 2.28 (m) and 2.60 (m), related to the CH$_2$ groups from dppe, and at δ 6.28–7.68 (m), corresponding to the phenyl groups of dppe are observed. The later signals appear in a broad range, suggesting that the phenyl groups are located in distinct chemical environments. This kind of spectrum suggests either an orthometallation [32] or the addition of the phenyl group to the coordination sphere of the metal [33]. Since a hydride is not observed, an orthometallation is ruled out. According to the P × H (HETCOR) correlation spectrum of **VI**, only the signal at δ 2.28 (m) interacts with the two phosphorous atoms, showing that these signals correspond to the equatorial Hs from CH$_2$. The corresponding ^{31}P{^{1}H} NMR spectrum shows a singlet at δ 18.25 and a pseudo triplet at 13.73 (t, J = 4.5 Hz). When the ^{31}P{^{1}H} NMR spectrum of **VI** is obtained in DMSO, the two signals appear as pseudo triplets. These results strongly suggest a fluxional process at room temperature. If a dynamic rearrangement were taking place, such a process should be frozen at lower temperatures. However, at least down to −40 °C, the ^{31}P{^{1}H} spectrum does not change. (The temperature could not be lowered further owing to the low solubility of the complex.) In addition, during experiments to determine the melting point of **VI**, color changed from yellow to orange at 170 °C, but melting takes place at 181 °C, the same melting temperature determined for the parent complex **II**. All these results suggest that complex **VI** does not present a square-planar structure. A possibility to be considered is that a molecule of acetonitrile would coordinate to each metal center of **II** without breaking the bridge. One phenyl group of each dppe would coordinate to an iridium atom via a 3c,2e bonding (Scheme 4).

When dissolved in acetone or in DMSO, the acetonitrile ligand would be replaced by the solvent. The square-planar complexes bearing acetonitrile, acetone or DMSO ligands would be formed only under the condi-
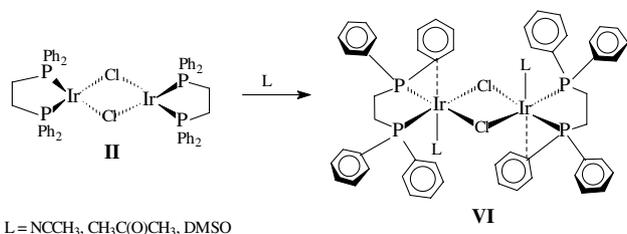
Scheme 4.

tions of mass analyses. Whatever its structure, under an argon atmosphere, **VI** is relatively stable in solution, undergoing a slow decomposition in 3–4 days. In the solid state, at −10 °C, under argon, it is stable for several weeks. In contrast with the behavior of **III**, when **VI** is allowed to react with CO in the same conditions employed to synthesize **V**, many species are formed.

All attempts to synthesize carbene complexes via reaction of **III**, **V** or **VI** with diazomethane or phenyl-diazomethane failed. Moreover, among all these complexes, only **III** presented some activity in the ring opening metathesis polymerization of norbornene in the presence of ethyldiazoacetate.

3.3. Synthesis of iridium(I) complexes bearing mono-phosphines

To study its activity in the ring opening metathesis polymerization, the iridium(I) complex [IrCl(cod)-(PCy$_3$)] (**VIII**) was also synthesized from the reaction of [IrCl(cod)]$_2$ with PCy$_3$ in hexane. DEPT analysis confirms the formation of **VIII**, whereas its ^{31}P$\{^1$H$\}$ NMR (CDCl$_3$) spectrum shows a singlet at δ 15.07, and its ^{13}C$\{^1$H$\}$ spectrum shows three singlets at δ 88.58, 88.41 and 50.40, and four singlets δ 32.67, 32.63, 31.40 and 31.10, corresponding to the four CH and to the four CH$_2$ from cod, respectively. The other signals in the range δ 25.40–29.00 can be assigned to the carbons of the cyclohexyl groups. The ^{1}H NMR shows broad singlets at δ 4.72 and 3.09, corresponding to the CH groups of cod, according to ^{1}H × ^{13}C (HETCOR) analysis, besides a multiplet at δ 2.0–2.15, assigned to CH$_2$ groups of cod, according to ^{1}H × ^{1}H (COSY), and a multiplet at δ 1.55–1.82 corresponding to CH$_2$ groups from Cy. The APCI-MS spectrum of **VIII** shows a cluster of ions centered at m/z 615.84 **VIII**$^+$ with an isotopic pattern that fully agrees with its expected composition and proposed structure. Although the synthesis of **VIII** has already been published [34], the synthetic route described here leads to higher yields (∼90%). In the presence of ethyldiazoacetate, **VIII** is active in the ring opening metathesis polymerization of norbornene and cyclooctene.

Whereas the reaction of [Ir(cod)(OCH$_3$)]$_2$ with dppe or [(C$_6$F$_5$)$_2$P(CH$_2$)$_2$P(C$_6$F$_5$)$_2$] leads to several products,

its reaction with PPh$_2$Cl in hexane yields only [Ir(OCH$_3$)(cod)(PClPh$_2$)] (**IX**). This complex was characterized by ^{31}P$\{^1$H$\}$ NMR (CDCl$_3$), showing a singlet at δ 103.9. Its ^{1}H NMR spectrum shows a signal at 5.30 (2H, CH) of cod, δ 3.15 (OCH$_3$) besides the resonances ascribed to cod at 1.80 (m), 2.00 (m) and 2.36 (m), and those ascribed to the phenyl groups at δ 7.4 (m). The APCI-MS spectrum of **IX** shows a cluster of ions at m/z 553.0 [**IX** + H]$^+$ with an isotopic pattern that fully agrees with its proposed composition. The so far exclusive formation of the protonated molecule for **IX** under APCI conditions, rather than the ionized molecules, is favored likely owing to the presence of the more basic methoxy group. The APCI-MS/MS spectrum of [**IX** + H]$^+$ (Fig. 2) is simple and unique as it shows dissociation mainly to m/z 515.

This dissociation is likely to involve the cod ligand, as confirmed by the Ir plus Cl-containing isotopic pattern of the ionic cluster centered at m/z 515, and occurs most likely therefore via the rare loss of a C$_3$H$_2$ neutral species (Scheme 5).

In contrast with the diphosphine complexes described herein, **IX** is active in the presence of ethyldiazoacetate for the ring opening metathesis polymerization of cyclic olefins. A detailed investigation of the catalytic properties of **IX** and other complexes prepared in this work is currently underway.
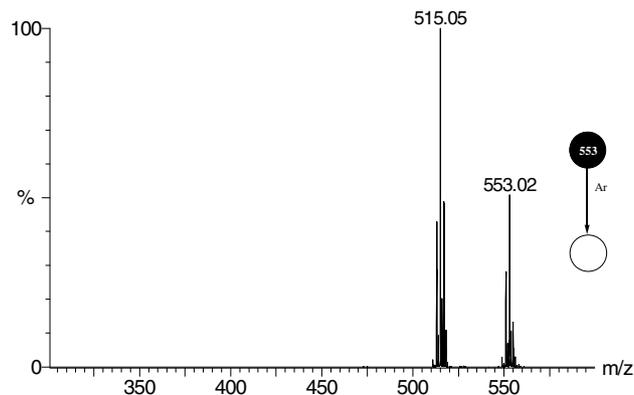
Fig. 2. APCI-MS/MS spectrum of the Ir(I) protonated complex [**IX** + H]$^+$.
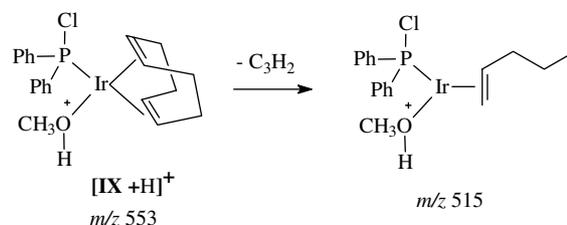
Scheme 5.

4. Conclusions

The diphosphine complexes [IrCl{$(C_6F_5)_2$P$(CH_2)_2$P-$(C_6F_5)_2$}]$_2$ (**I**) and [IrCl(dppe)]$_2$ (**II**) were successfully employed as precursors for new iridium(I) complexes with labile ligands. Although complex [IrCl{$(C_6F_5)_2$P-$(CH_2)_2$P$(C_6F_5)_2$}(NCCH$_3$)] (**III**) is stable only in solution, it could be fully characterized by NMR and APCI-MS/MS techniques. Complex **IV**, [IrCl{$(C_6F_5)_2$P-$(CH_2)_2$P$(C_6F_5)_2$}(acetone)], could only be detected by APCI-MS.

The APCI-MS analysis shows that the intact ionized species **I**$^+$ is stable in the gas phase and observed as so in the mass spectrum (Fig. 1). However, the gaseous intact **II**$^+$ is unstable and dissociates completely by breaking of the bridge thus forming, after solvent coordination, species **B** and **C** (Scheme 2), which are observed in the corresponding mass spectra. Interestingly, when **III** is allowed to react with CO for at least 30 min, the unusual five-coordinated *trans*-dicarbonyl complex [IrCl{$(C_6F_5)_2$P$(CH_2)_2$P$(C_6F_5)_2$}(CO)$_2$] (**Vb**) is formed, the first species of this type to be characterized in the solid state. All these complexes, along with [IrCl(cod)(PCy$_3$)] (**VIII**) and [Ir(OCH$_3$)(cod)(PClPh$_2$)] (**IX**) failed to produce carbene complexes upon reaction with diazocompounds. Nevertheless, preliminary experiments showed that **III**, **VIII** and **IX** have some activity in the ring opening metathesis polymerization of cyclic olefins in the presence of ethyldiazoacetate, warranting further investigations of such systems.

Acknowledgements

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