Note

Alkene and alkyne insertion into the Ir–H bond: Synthesis of new mono- and dinuclear alkyl and alkenyl iridium–pybox complexes

Paloma Paredes, Josefina Díez, M. Pilar Gamasa *

Instituto Universitario de Química Organometálica "Enrique Moles" (Unidad Asociada al CSIC), Departamento de Química Orgánica e Inorgánica, Facultad de Química, Universidad de Oviedo, 33071 Oviedo, Spain

ABSTRACT

The treatment of the complex $[Ir(\eta^2\text{-}C_2H_4)_2(L)][PF_6]$ (L = κ^3-N,N,N-(S,S)-^{i}Pr-pybox) with acetic acid (1:1 molar ratio) at $-10\,^\circ$C affords the complex $[Ir(C_2H_5)(\kappa^2\text{-}O,O\text{-}O_2CCH_3)(L)][PF_6]$ (**1**). The dinuclear iridium(III) complex $[Ir_2(\mu\text{-}Cl)_2(C_2H_5)_2(L)_2][PF_6]_2$ (**2**) is stereoselectively obtained by spontaneous intramolecular insertion of ethylene into the iridium-hydride bond of the mononuclear complex $[IrClH(\eta^2\text{-}C_2H_4)(L)][PF_6]$. The single bridging chloride dinuclear derivative $[Ir_2(\mu\text{-}Cl)(C_2H_5)_2Cl_2(L)_2][PF_6]$ (**3**) is prepared by reaction of **2** with one equivalent of NaCl. The intramolecular insertion reaction of methyl and ethyl propiolate into the Ir–H bond of the complex $[IrClH(MeCN)(L)][PF_6]$ gives stereoselectively the dinuclear complexes $[Ir_2(\mu\text{-}Cl)_2(HC=CHCO_2R)_2(L)_2][PF_6]_2$ (R = Me (**4**), Et (**5**)). The reaction of the complexes **4**, **5** with one equivalent of NaCl or with an excess of sodium acetate yields the dinuclear $[Ir_2(\mu\text{-}Cl)(HC=CHCO_2R)_2Cl_2(L)_2][PF_6]$ (R = Me (**6**), Et (**7**)) or the mononuclear $[IrCl(HC=CHCO_2Et)(\kappa^1\text{-}O\text{-}O_2CMe)(L)]$ (**8**) complexes, respectively. The structure of the dinuclear complex **3** · CH_2Cl_2 has been determined by an X-ray monocrystal study.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

The insertion reaction of alkenes and alkynes into a metal-hydride bond is a common method for the generation of metal-alkyl and -alkenyl complexes [1]. Importantly, it is considered as a fundamental step in a variety of stoichiometric and catalytic processes [2].

Recently we have reported the synthesis of the enantiopure iridium–pybox complex (**A**), as well as its transformation into hydride-iridium(III) complexes (**B** and **C**). Thus, the stereoselective oxidative addition of HCl to the complex (**A**) results in the formation of the complex (**B**), which in turn leads to the complex (**C**) by ethylene-acetonitrile exchange [3,4].

Continuing our studies on iridium–pybox complexes, we report on new findings that reveal that the ethylene ligand of (**B**) – readily released from the iridium coordination sphere by acetonitrile to give (**C**) [4] – is not an "innocent" ligand under mild reactions conditions and in the presence of less coordinating ligands, but it is capable of undergoing insertion into the Ir–H bond. Therefore, the ethylene ligand in the coordination sphere might play a decisive role in reactions wherein the cation complex $[IrClH-(\eta^2\text{-}C_2H_4)(L)]^+$ is involved as precatalyst. We believe that assuming this fact could be helpful for us and others for designing new reactions based on the use of complex (**B**) as the precatalyst.

The Ir–H insertion has also been observed when the acetonitrile ligand of the complex (**C**) is replaced with activated alkynes. Herein
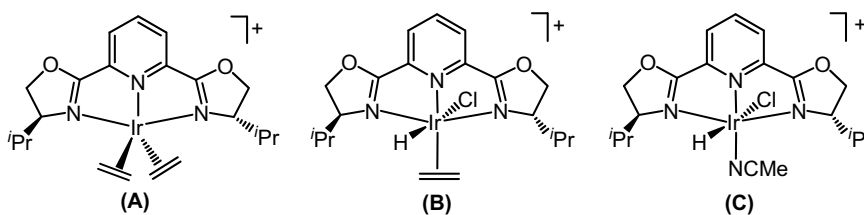
we report the synthesis of mono and dinuclear alkyl and alkenyl complexes through the insertion reaction of the ethylene and propiolate esters into the Ir–H bond, respectively.

2. Results and discussion

2.1. Synthesis of the complex [Ir(C$_2$H$_5$)(κ^2-O,O-O$_2$CCH$_3$)(L)][PF$_6$] (1)

The treatment of the complex [Ir(η^2-C$_2$H$_4$)$_2$(L)][PF$_6$] (L = κ^3-N,N,N-(S,S)-^{i}Pr-pybox) with acetic acid (1:1 molar ratio) at −10 °C gives rise immediately to a colour-mixture change from red to deep yellow. After the work-up of the reaction, the complex [Ir(C$_2$H$_5$)(κ^2-O,O-O$_2$CCH$_3$)(L)][PF$_6$] (1) is isolated in very good yield (92%) (Scheme 1). Complex 1 has been characterized by elemental analyses, molar conductivity and NMR spectroscopy (see Section 4 for details). In particular: (a) the appearance of one singlet in the ^{1}H NMR spectrum (2.11 ppm) and two singlets in the ^{13}C{^{1}H} NMR spectrum [184.2 and 23.3 ppm] confirms the presence of the acetate group; (b) the proton and carbon resonances of the ethyl group in the NMR spectra: one pseudotriplet at 0.23 ppm (CH$_3$) and two multiplets at 1.70 and 0.98 ppm (CH$_2$), the latter being assigned by COSY experiments because of partially overlapped by the methyl signals of the ^{i}Pr-pybox ligand. The carbon atoms appear as singlets at 14.4 (CH$_3$) and −6.7 (IrCH$_2$) ppm.

The reaction presumably involves the formation of a non-detected monoolefin hydride-iridium(III) intermediate species in which the acetate group participates as a monodentate ligand. The insertion of the cis-ethylene unit into the Ir–H bond would give rise to an ethyl κ^1-O-acetate 16-electron cationic complex. The presence of the very poor donor PF$_6$ group should favour the chelate coordination of the resulting κ^1-O-acetate group to give the observed 18-electron κ^2-O,O-acetate complex 1.

2.2. Synthesis of the complexes [Ir$_2$(μ-Cl)$_2$(C$_2$H$_5$)$_2$(L)$_2$][PF$_6$]$_2$ (2) and [Ir$_2$(μ-Cl)(C$_2$H$_5$)$_2$Cl$_2$(L)$_2$][PF$_6$] (3)

Alkyl-iridium(III) complexes can also be prepared by intramolecular insertion of ethylene into the Ir–H bond of the complex [IrClH(η^2-C$_2$H$_4$)(L)][PF$_6$]. We have recently reported that the addi-

tion of acetonitrile to an acetone solution of the complex [IrClH(η^2-C$_2$H$_4$)(L)][PF$_6$] results in the ethylene-acetonitrile ligand exchange affording the complex [IrClH(MeCN)(L)][PF$_6$] [4]. However, we now report that the complex [IrClH(η^2-C$_2$H$_4$)(L)][PF$_6$] is not stable in concentrated solutions of acetone at room temperature. Thus, in the absence of acetonitrile, it spontaneously evolves to stereoselectively produce the dinuclear complex [Ir$_2$-(μ-Cl)$_2$(C$_2$H$_5$)$_2$(L)$_2$][PF$_6$]$_2$ (2) which is isolated as a green solid (68% yield) (Scheme 2). Their analytical, conductivity and spectroscopic data (^{1}H and ^{13}C{^{1}H} NMR, and IR) are in accordance with the proposed formulation (see Section 4 for details). The ^{1}H NMR spectrum of complex 2 shows two multiplets (2.36 and 1.34 ppm; CH$_2$) and a multiplet (0.07 ppm; CH$_3$) assigned to the ethyl group. In addition, the ^{13}C{^{1}H} NMR resonances of this group are observed at 18.9 (CH$_3$) and −13.7 (IrCH$_2$) ppm.

In accordance with its proposed dinuclear structure, a solution of the complex 2 in MeOH was treated with one equivalent of NaCl to afford the single bridged chloride dinuclear complex 3 in good yield (86%) (Scheme 2). The ^{1}H, ^{13}C{^{1}H} NMR spectra, elemental analysis, conductance measurements in solution, and ESI mass spectrometry are consistent with the proposed dinuclear formulation (see Section 4 for details).

The first step of the reaction is presumably the insertion of ethylene in the Ir–H bond to give a cationic 16-electron alkyl-iridium(III) complex. All attempts to isolate this intermediate species have failed due to its rapid transformation into the dinuclear complex 2. Unlike the case of complex 1, wherein a mononuclear 18-electron stable complex is formed by κ^2-O,O-acetate coordination, the stabilization of the presumed 16-electron precursor of complex 2 takes place by dimerization via intermolecular chloride-metal coordination. Apparently, the formation of the dichloride bridging system [Ir$_2$(μ-Cl)$_2$] is preferred over the 16-electron mononuclear chloride complex [IrCl(C$_2$H$_5$)(L)][PF$_6$].

The NMR spectroscopic data do not allow to ascertain the stereochemistry of complex 2 among the two possible isomers (Chart 1, A and B). The stereoisomer A is tentatively proposed on the basis of less sterically demanding arrangement of the isopropyl groups of both pybox ligands over the stereoisomer B. Unfortunately, an X-ray analysis could not been performed since all attempts to
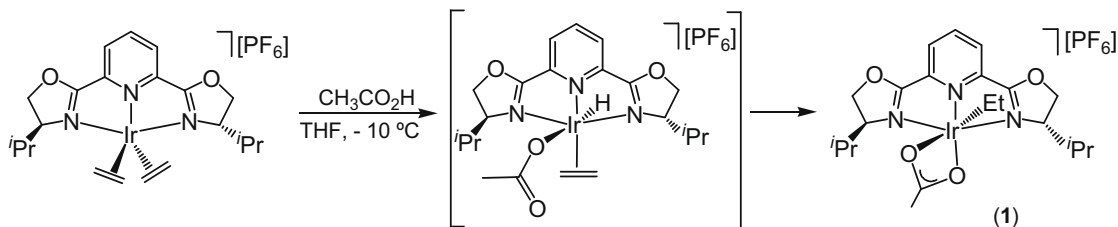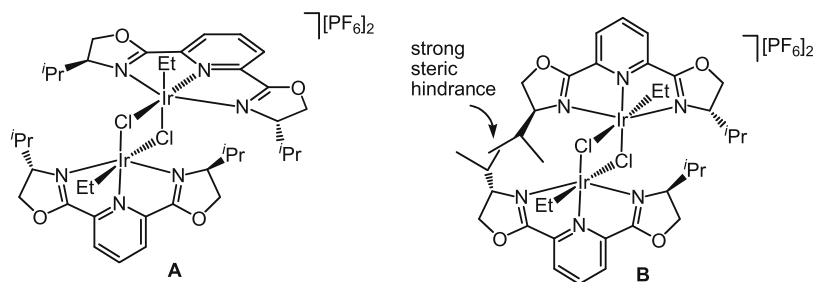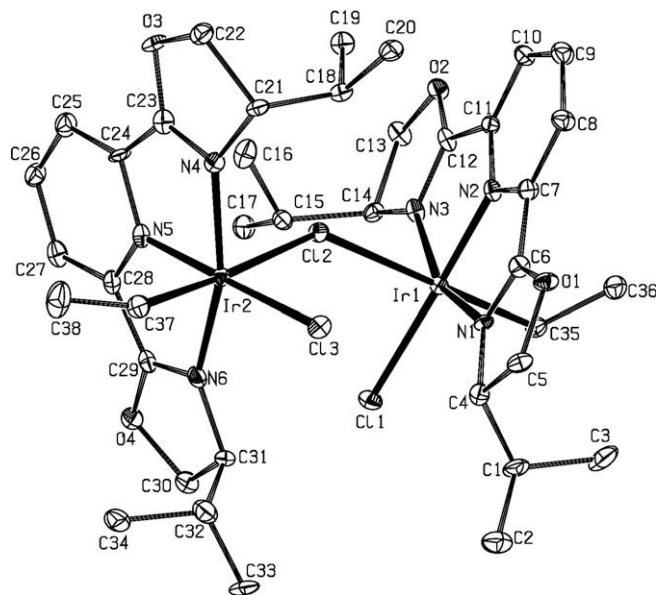

Scheme 1.
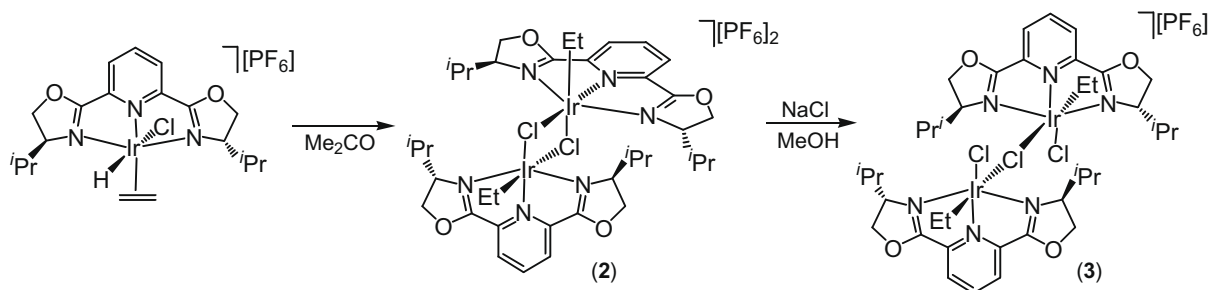
Scheme 2.

Chart 1.

Fig. 1. ORTEP type view of the molecular structure of the cation of complex [Ir₂-(μ-Cl)(C₂H₅)₂Cl₂{κ³-N,N,N-(S,S)-^{i}Pr-pybox}₂][PF₆] · CH₂Cl₂ (3 · CH₂Cl₂) showing atom-labeling scheme. Thermal ellipsoids are drawn at 10% probability level. Hydrogen atoms have been omitted for clarity. Selected bond lengths (Å) and angles (°): Ir(1)–Cl(1), 2.341(3); Ir(2)–Cl(3), 2.358(3); Ir(1)–Cl(2), 2.543(2); Ir(2)–Cl(2), 2.521(2); C(35)–Ir(1), 2.060(11); C(37)–Ir(2), 2.096(11); C(35)–C(36), 1.499(17); C(37)–C(38), 1.38(2); Ir(2)–Cl(2)–Ir(1), 139.17(11); C(35)–Ir(1)–Cl(1), 88.0(3); C(35)–Ir(1)–Cl(2), 178.8(3); C(36)–C(35)–Ir(1), 118.3(8); Cl(1)–Ir(1)–Cl(2), 92.34(10); C(38)–C(37)–Ir(2), 118.0(12); C(37)–Ir(2)–Cl(2), 176.1(4); C(37)–Ir(2)–Cl(3), 86.5(4).

crystallize complex **2** from different solvents have been unsuccessful. However, the structure of complex **3** has been confirmed by a single-crystal X-ray analysis. An ORTEP view of the molecular structure is shown in Fig. 1 and selected bonding data are collected in the caption.

The dinuclear cationic structure exhibits two iridium atoms bonded through a bridge chlorine atom. We observe the expected distorted octahedral coordination of each iridium atom that is bonded to two chlorine atoms (terminal and bridge, respectively) with a *cis* arrangement, as well as to the ethyl and ^{i}Pr-pybox ligands (Fig. 1). The ethyl and bridging chlorine groups are located in a nearly *trans* orientation. The Ir(1)–Cl(2) and Ir(2)–Cl(2) distances [2.543(2) and 2.521(2) Å, respectively] are considerably longer than the Ir(1)–Cl(1) and Ir(2)–Cl(3) distances [2.341(3) and 2.358(3) Å]. The latter are in the range of those found in the complex [IrCl₂(κ³-N,N,N-(S,S)-^{i}Pr-pybox)(μ-Cl)Tl][PF₆] [Ir–Cl 2.351–2.385 Å] [4]. The Ir–N distances [1.927(8)–2.058(9) Å] as well as the N–Ir–N bond angles [79.1(3)–79.4(4) and 158.5(3)–158.6(4)°] fall in the range observed for mononuclear iridium–pybox complexes [3,5]. The Ir–C distances [2.060(11) Å for Ir(1)–C(35); 2.096(11) Å for Ir(2)–C(37)] are in the range observed for other Ir(III)–Et bonds (ranges 2.086–2.192 Å) [6]. The C–C distances of the ethyl groups are 1.499(17) Å (C(35)–C(36)) and 1.38(2) Å (C(37)–C(38)). The latter distance is slightly shorter than that expected for a C(sp³)–C(sp³) bond in accordance with the disorder observed for the chain carbons of the ethyl group (C(37) and C(38)). The dihedral angle between the planes N(1)–N(2)–N(3) and N(4)–N(5)–N(6) of pybox ligands is 67.29(33)° and the Ir(1)–(μ-Cl)–Ir(2) angle is 139.17(11)°. The torsion angle between the pyridine nitrogen N(2), both iridium atoms and the pyridine nitrogen N(5) is 101.1(38)° (N(2)–Ir(1)–Ir(2)–N(5) angle). Probably, this particular arrangement arises from a minimization of the steric hindrance between both pybox ligands in the crystal structure.

Importantly, the complex **3** · CH₂Cl₂ represents the first reported dinuclear iridium complex containing pybox ligands. Analogous dinuclear structures have been recently described for rhodium–pybox complexes [7].

2.3. Synthesis of the complexes [Ir₂(μ-Cl)₂(HC=CHCO₂R)₂(L)₂][PF₆]₂ (R = Me (**4**), Et (**5**))

The reaction of the complex [IrClH(MeCN)(L)][PF₆] with methyl or ethyl propionate (1:2 molar ratio) in THF at 50 °C leads stereoselectively to the dinuclear complexes [Ir₂(μ-Cl)₂(HC=CHCO₂R)₂-(L)₂][PF₆]₂ (R = Me (**4**), R = Et (**5**)) (Scheme 3). These complexes

R = Me (**4**), R = Et (**5**)
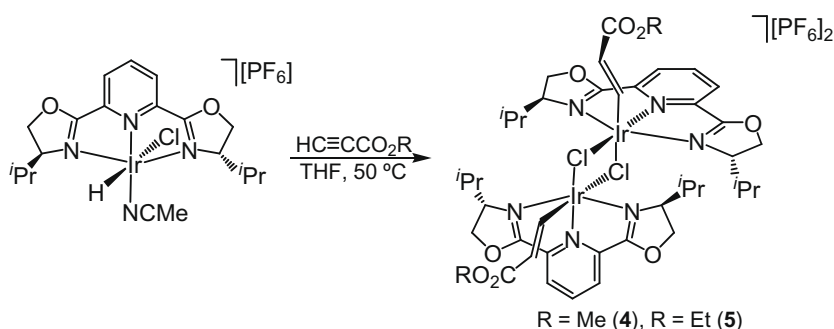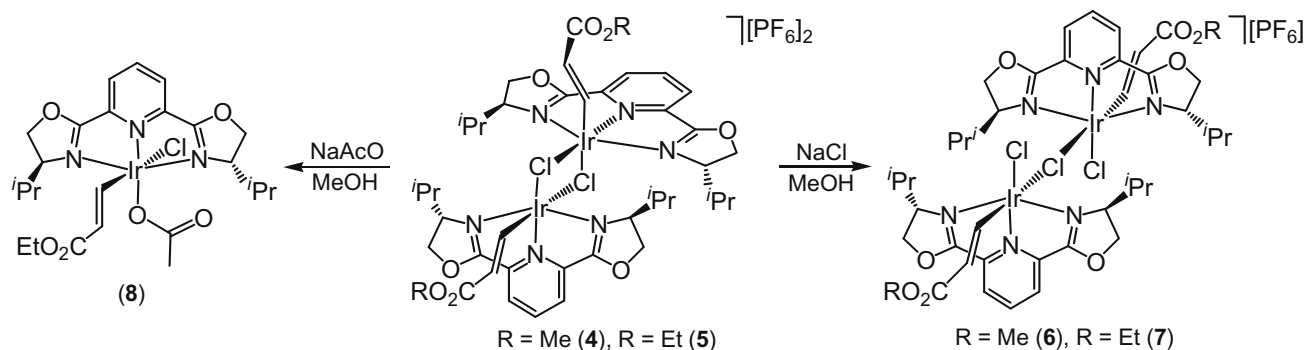
Scheme 3.

Scheme 4.

have been isolated as orange solids in 89–88% yield. Their analytical, spectroscopic (^{1}H and ^{13}C{^{1}H} NMR, and IR) and conductance data are in accordance with the proposed formulations (see Section 4 for details). Significant spectroscopic data are given: (a) the IR spectra show ν(C=O) absorptions in the range of 1710–1684 cm^{-1} as expected for uncoordinated CO$_2$R groups; (b) the ^{1}H NMR resonance shows the olefinic hydrogens as two doublets [9.09 and 4.40 ppm (**4**) and 8.94 and 4.38 ppm (**5**)] with a large coupling constant [J_{HH} = 15.7 Hz (**4**) and J_{HH} = 15.8 Hz) (**5**)] as expected for a *trans* arrangement; (c) the ^{13}C{^{1}H} NMR spectra show singlet signals for the alkenyl carbons at 140.1 (IrCH) and 122.4 (*C*HCO$_2$R) ppm (**4**) and 139.8 (IrCH) and 122.8 (*C*HCO$_2$R) ppm (**5**). In addition, the carboxylate carbon resonates at 162.4 (**4**) and 161.9 (**5**) ppm.

Analogously to the results reported above, the formation of the dichloride bridging system [Ir$_2$(μ-Cl)$_2$] seems to be preferred over the 16-electron mononuclear complex [IrCl(HC=CHCO$_2$R)(L)][PF$_6$], which presumably results from MeCN-alkyne exchange in the complex [IrClH(MeCN)(L)][PF$_6$] followed by insertion of the alkyne into the Ir–H bond [8]. At the present, we assume that complexes **4** and **5** present the same stereochemical arrangement as complex **2**, the alkenyl and the chlorine bridging ligands being placed *trans* to each other.

2.4. Synthesis of the complexes [Ir$_2$(μ-Cl)(HC=CHCO$_2$R)$_2$Cl$_2$(L)$_2$][PF$_6$] (R = Me (6), Et (7)) and [IrCl(HC=CHCO$_2$Et)(κ^1-O-O$_2$CMe)(L)] (8)

When complexes **4** and **5** are treated with NaCl (1:1 molar ratio) in MeOH the single bridged chloride dinuclear complexes **6** and **7**, respectively, are formed in good yield (80–77%) (Scheme 4). The ^{1}H and ^{13}C{^{1}H} NMR spectra, elemental analysis, and conductance measurements in solution are consistent with the proposed dinuclear formulation (see Section 4 for details).

On the other hand, attempts to transform complexes **6**, **7** into the corresponding mononuclear dichloro alkenyl iridium(III) complexes by cleavage of the remaining chloride bridge with an excess of NaCl have failed. However, the reaction of the complex **5** with an excess of sodium acetate in methanol leads to the complex [IrCl(HC=CHCO$_2$Et)(κ^1-O-O$_2$CMe)(L)] (**8**) in 82% yield (Scheme 4). The complex **8** has been isolated as a yellow solid and characterized by elemental analyses and NMR spectroscopy (see Section 4 for details).

The most relevant data for complex **8** are as follows: (a) the ^{1}H NMR resonances for the alkenyl group appear as two doublets (9.66 and 4.31 ppm), while the large proton coupling constant observed (J_{HH} = 16.6 Hz) is in accordance with a *trans* H/H arrangement; (b) the ^{13}C{^{1}H} NMR spectrum shows the alkenyl carbons at 149.1 (IrCH) and 121.8 (*C*HCO$_2$Et) ppm and the carboxylate carbon at 162.7 ppm; (c) the proton and carbon resonances of the acetate function are observed as singlets at 1.50 (O$_2$CC*H$_3$*), 176.8

(O$_2$CCH$_3$), and 24.0 (O$_2$CCH$_3$) ppm. Although various stereoisomers might be obtained, a single reaction product is formed according to the NMR and IR spectroscopic data of the reaction crude. Unfortunately, an X-ray analysis of the complex **8** could not be performed since all attempts to crystallize it were unsuccessful. On the other hand, ROESY experiments performed on the complex **8** does not allow to unambiguously ascertain the stereochemistry as no through-space interaction between the acetate and/or the alkenyl groups with the ^{i}Pr group of the oxazoline could be detected. Therefore, just one out of the possible isomers is displayed in Scheme 4.

3. Summary

In summary, we have accomplished the synthesis of enantio-pure mononuclear and dinuclear alkyl- and alkenyl-pybox–Ir(III) complexes by insertion of ethylene and activated terminal alkynes, respectively, into the Ir–H bond of hydride-iridium(III) complexes. Particularly, the complex [IrClH(η^2-C$_2$H$_4$)(L)][PF$_6$] spontaneously evolves to give the dinuclear complex [Ir$_2$(μ-Cl)$_2$(C$_2$H$_5$)$_2$(L)$_2$][PF$_6$]$_2$ with complete stereoselectivity. Interestingly, the first examples of dinuclear iridium–pybox complexes are reported. Specifically, the synthesis of complexes [Ir$_2$(μ-Cl)$_2$(R)$_2$(L)$_2$][PF$_6$]$_2$ and [Ir$_2$-(μ-Cl)(R)$_2$Cl$_2$(L)$_2$][PF$_6$] (R = C$_2$H$_5$, HC=CHCO$_2$Me, HC=CHCO$_2$Et) as well as the X-ray crystal structure of the complex [Ir$_2$-(μ-Cl)(C$_2$H$_5$)$_2$Cl$_2$(L)$_2$][PF$_6$] are described in this paper.

4. Experimental

The reactions were performed under an atmosphere of dry nitrogen using vacuum-line and standard Schlenk techniques. Solvents were dried by standard methods and distilled under nitrogen before use. The complexes [Ir(η^2-C$_2$H$_4$)$_2$(L)][PF$_6$] (L = κ^3-N,N,N-(S,S)-^{i}Pr-pybox), [IrClH(η^2-C$_2$H$_4$)(L)][PF$_6$] and [IrClH(MeCN)(L)][PF$_6$] were prepared by previously reported methods [3,4]. Other reagents were obtained from commercial suppliers and used without further purification. Infrared spectra were recorded on a Perkin–Elmer 1720-XFT spectrometer. The conductivities were measured at room temperature, in ca. 5×10^{-4} mol L^{-1} acetone solutions, with a Jenway PCM3 conductimeter. The C, H and N analyses were carried out with a Perkin–Elmer 240-B microanalyzer. Mass spectra (FAB) were determined with a VG-AUTOSPEC mass spectrometer, operating in the positive mode; 3-nitrobenzyl alcohol (NBA) was used as the matrix. Mass spectra (MALDI-TOF) were determined with a MICROFLEX Bruker spectrometer, operating in the positive mode; dihydroxyanthranol was used as the matrix. Electrospray mass spectra (ESI-MS) were recorded on a Bruker MicroTof-Q instrument, operating in the positive mode and using methanol solutions. NMR spectra were recorded on Bruker

instruments: AC300 (DPX-300 or AV-300) at 300 MHz (^{1}H) or 75.5 MHz (^{13}C), AMX-400 at 400 MHz (^{1}H) or 100.6 MHz MHz (^{13}C) and AV-600 at 600 MHz (^{1}H) or 150.9 MHz (^{13}C), using SiMe$_4$ as standard. DEPT experiments were carried out for all of the compounds reported. 2D-NMR (COSY, HSQC, ROESY) were performed in selected complexes. Coupling constants J are given in Hertz. Abbreviations used: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet; q, quartet; br, broad; pt, pseudotriplet.

4.1. Synthesis of complex [Ir(C_2H_5)(κ^2-O,O-O_2CCH_3)(L)][PF$_6$] (1)

To a solution of [Ir(η^2-C_2H_4)$_2$(L)][PF$_6$] (L = κ^3-N,N,N-(S,S)-^{i}Pr-py-box) (0.069 g, 0.1 mmol) in THF (5 mL) at −10 °C, 1M solution of acetic acid in diethyl ether (0.100 mL, 0.1 mmol) was added. The colour of the mixture changes immediately from red to deep yellow. After 5 min, hexane (30 mL) was added and the resulting green pale solid was filtered, washed with hexane (3 × 5 mL) and then vacuum-dried. Yield: 92% (0.067 g). IR (KBr, cm^{-1}): v 845 vs (PF$_6^-$). ^{1}H NMR (400 MHz, acetone-d_6, 293 K): δ 8.12 (m, 3H, C$_5$H$_3$N), 5.33 (m, 2H, OCH$_2$), 5.23 (m, 2H, OCH$_2$), 4.63 (m, 1H, CH^{i}Pr), 4.53 (m, 1H, CH^{i}Pr), 2.44 (m, 1H, CHMe$_2$), 2.38 (m, 1H, CHMe$_2$), 2.11 (s, 3H, O$_2$CCH$_3$), 1.70 (m, 1H, IrCH$_2$CH$_3$), 1.09 (d, J_{HH} = 7.1 Hz, 3H, CHMe$_2$), 1.05 (d, J_{HH} = 7.1 Hz, 3H, CHMe$_2$), 0.98 (m, 1H, IrCH$_2$CH$_3$), 0.90 (d, J_{HH} = 6.8 Hz, 3H, CHMe$_2$), 0.89 (d, J_{HH} = 6.8 Hz, 3H, CHMe$_2$), 0.23 (pt, J_{HH} = 7.4 Hz, 3H, IrCH$_2$CH$_3$). ^{13}C{^{1}H} NMR (75.5 MHz, acetone-d_6, 293 K): δ 184.2 (s, O$_2$CCH$_3$), 174.4 (s, OCN), 173.7 (s, OCN), 148.6 (s, C^{2,6} C$_5$H$_3$N), 148.0 (s, C^{2,6} C$_5$H$_3$N), 137.7 (s, C^{4}H C$_5$H$_3$N), 127.3 (s, C^{3,5}H C$_5$H$_3$N), 127.2 (s, C^{3,5}H C$_5$H$_3$N), 73.9 (s, OCH$_2$), 73.6 (s, OCH$_2$), 70.4 (s, CH^{i}Pr), 70.1 (s, CH^{i}Pr), 29.5 (s, CHMe$_2$), 23.3 (s, O$_2$CCH$_3$), 19.3 (s, CHMe$_2$), 18.7 (s, CHMe$_2$), 15.0 (s, CHMe$_2$), 14.5 (s, CHMe$_2$), 14.4 (s, IrCH$_2$CH$_3$), −6.7 (s, IrCH$_2$CH$_3$). Molar conductivity (acetone, Ω^{-1} cm^2 mol^{-1}): 124. Anal. Calc. for C$_{21}$H$_{31}$F$_6$IrN$_3$O$_4$P (726.67): C, 34.71; H, 4.30; N, 5.78. Found: C, 34.29; H, 4.28; N, 5.84%.

4.2. Synthesis of complex [Ir$_2$(μ-Cl)$_2$(C_2H_5)$_2$(L)$_2$][PF$_6$]$_2$ (2)

A solution of [IrClH(η^2-C_2H_4)(L)][PF$_6$] (0.070 g, 0.1 mmol) in acetone (0.6 mL) was stirred at room temperature for 12 h. The colour of the mixture changes from yellow to green. A (1:1) diethyl ether/hexane mixture (20 mL) was added and the resulting green solid was filtered, washed with hexane (3 × 5 mL) and then vacuum-dried. Yield: 68% (0.048 g). IR (KBr, cm^{-1}): v 843 vs (PF$_6^-$). ^{1}H NMR (400 MHz, acetone-d_6, 293 K): δ 8.33 (m, 2H, H^4 C$_5$H$_3$N), 8.22 (m, 4H, H^{3,5} C$_5$H$_3$N), 5.02 (m, 4H, OCH$_2$), 4.90 (m, 4H, OCH$_2$), 4.54 (m, 2H, CH^{i}Pr), 3.85 (m, 2H, CH^{i}Pr), 2.72 (m, 2H, CHMe$_2$), 2.36 (m, 2H, IrCH$_2$CH$_3$), 1.74 (m, 2H, CHMe$_2$), 1.34 (m, 2H, IrCH$_2$CH$_3$), 1.02 (m, 6H, CHMe$_2$), 0.93 (m, 6H, CHMe$_2$), 0.70 (m, 6H, CHMe$_2$), 0.50 (m, 6H, CHMe$_2$), 0.07 (m, 6H, IrCH$_2$CH$_3$). ^{13}C{^{1}H} NMR (75.5 MHz, acetone-d_6, 293 K): δ 175.2 (s, OCN), 174.4 (s, OCN), 149.2 (s, C^{2,6} C$_5$H$_3$N), 149.1 (s, C^{2,6} C$_5$H$_3$N), 139.4 (s, C^{4}H C$_5$H$_3$N), 127.2 (s, C^{3,5}H C$_5$H$_3$N), 73.7 (s, OCH$_2$), 73.6 (s, OCH$_2$), 69.4 (s, CH^{i}Pr), 67.8 (s, CH^{i}Pr), 29.1 (s, CHMe$_2$), 28.9 (s, CHMe$_2$), 19.4 (s, CHMe$_2$), 18.9 (s, CHMe$_2$, IrCH$_2$CH$_3$), 14.6 (s, CHMe$_2$), 13.9 (s, CHMe$_2$), −13.7 (s, IrCH$_2$CH$_3$). Molar conductivity (acetone, Ω^{-1} cm^2 mol^{-1}): 200. MS (FAB+): m/z 558 [IrCl(C_2H_5)(^{i}Pr-pybox)]$^+$. Anal. Calc. for C$_{38}$H$_{56}$Cl$_2$F$_{12}$Ir$_2$N$_6$O$_4$P$_2$ (1406.16): C, 32.46; H, 4.01; N, 5.98. Found: C, 32.55; H, 4.16; N, 5.97%.

4.3. Synthesis of complex [Ir$_2$(μ-Cl)(C_2H_5)$_2$Cl$_2$(L)$_2$][PF$_6$] (3)

To a solution of [Ir$_2$(μ-Cl)$_2$(C_2H_5)$_2$(L)$_2$][PF$_6$]$_2$ (2) (0.281 g, 0.2 mmol) in methanol (1 mL), NaCl (0.058 g, 0.2 mmol) was added. The resulting solution was stirred at room temperature for 5 min and the volatiles were removed in vacuo. The residue was extracted with dichloromethane and filtered through kies-

elguhr. The solvent was then concentrated to ca. 2 mL. A (1:1) diethyl ether/hexane mixture (40 mL) was added and the resulting green solid was filtered, washed with hexane (3 × 5 mL) and then vacuum-dried. Yield: 86% (0.223 g). IR (KBr, cm^{-1}): v 843 vs (PF$_6^-$). ^{1}H NMR (400 MHz, acetone-d_6, 223 K): δ 8.18 (m, 4H, H^{3,5} C$_5$H$_3$N), 8.06 (m, 2H, H^4 C$_5$H$_3$N), 5.52 (m, 2H, OCH$_2$), 5.27 (m, 2H, OCH$_2$), 5.13 (m, 4H, OCH$_2$), 5.04 (m, 2H, CH^{i}Pr), 4.28 (m, 2H, CH^{i}Pr), 2.67 (m, 2H, CHMe$_2$), 2.32 (m, 2H, CHMe$_2$), 1.97 (m, 2H, IrCH$_2$CH$_3$), 1.21 (m, 2H, IrCH$_2$CH$_3$), 1.08 (m, 6H, CHMe$_2$), 0.84 (m, 12H, CHMe$_2$), 0.17 (m, 6H, CHMe$_2$), −0.08 (pt, J_{HH} = 7.4 Hz, 6H, IrCH$_2$CH$_3$). ^{13}C{^{1}H} NMR (100.6 MHz, acetone-d_6, 223 K): δ 172.9 (s, OCN), 172.5 (s, OCN), 148.0 (s, C^{2,6} C$_5$H$_3$N), 147.2 (s, C^{2,6} C$_5$H$_3$N), 135.4 (s, C^{4}H C$_5$H$_3$N), 127.0 (s, C^{3,5}H C$_5$H$_3$N), 126.7 (s, C^{3,5}H C$_5$H$_3$N), 73.2 (s, OCH$_2$), 73.1 (s, OCH$_2$), 71.0 (s, CH^{i}Pr), 68.5 (s, CH^{i}Pr), 28.6 (s, CHMe$_2$), 28.4 (s, CHMe$_2$), 19.4 (s, CHMe$_2$), 18.7 (s, CHMe$_2$), 15.0 (s, CHMe$_2$), 14.6 (s, CHMe$_2$, IrCH$_2$CH$_3$), −7.7 (s, IrCH$_2$CH$_3$). Molar conductivity (acetone, Ω^{-1} cm^2 mol^{-1}): 148. MS (MALDI+): m/z = 558 [IrCl(C_2H_5)(^{i}Pr-pybox)]$^+$. MS (ESI+): m/z = 558 ([IrCl-(C_2H_5)(^{i}Pr-pybox)]$^+$, 100%), 1151 ([Ir$_2$Cl$_3$(C_2H_5)$_2$(^{i}Pr-pybox)$_2$]$^+$, 68%), 494 ([Ir(^{i}Pr-pybox)]$^{3+}$, 55%). Anal. Calc. for C$_{38}$H$_{56}$Cl$_3$F$_6$Ir$_2$-N$_6$O$_4$P (1296.65): C, 35.20; H, 4.35; N, 6.48. Found: C, 35.17; H, 4.36; N, 6.12%.

4.4. Synthesis of complexes [Ir$_2$(μ-Cl)$_2$(HC=CHCO$_2$R)$_2$(L)$_2$][PF$_6$]$_2$ (R = Me (4), Et (5))

To a solution of [IrClH(MeCN)(L)][PF$_6$] (0.069 g, 0.1 mmol) in THF (12 mL), methyl or ethyl propiolate (0.2 mmol) was added. The reaction mixture was stirred at 50 °C for 4 h. After cooling to room temperature, the solvent was concentrated to ca. 3 mL. Then, a (1:1) diethyl ether/hexane mixture (60 mL) was added and the resulting orange solid was filtered, washed with diethyl ether (3 × 5 mL) and then vacuum-dried.

4: Yield: 89% (0.068 g). IR (KBr, cm^{-1}): v 1710m (CO$_2$Me), 1692m (CO$_2$Me), 846 vs (PF$_6^-$). ^{1}H NMR (300 MHz, acetone-d_6, 293 K): δ 9.09 (d, J_{HH} = 15.7 Hz, 2H, IrCH), 8.43 (t, J_{HH} = 7.6 Hz, 2H, H^4 C$_5$H$_3$N), 8.31 (d, J_{HH} = 7.6 Hz, 2H, H^{3,5} C$_5$H$_3$N), 8.23 (d, J_{HH} = 7.6 Hz, 2H, H^{3,5} C$_5$H$_3$N), 5.59 (m, 2H, OCH$_2$), 5.22 (m, 2H, OCH$_2$), 5.11 (m, 2H, OCH$_2$), 5.03 (m, 2H, OCH$_2$), 4.54 (m, 2H, CH^{i}Pr), 4.40 (d, J_{HH} = 15.7 Hz, 2H, CHCO$_2$Me), 4.12 (m, 2H, CH^{i}Pr), 3.46 (s, 6H, CHCO$_2$Me), 2.58 (m, 2H, CHMe$_2$), 2.44 (m, 2H, CHMe$_2$), 1.00–0.70 (m, 18H, CHMe$_2$), 0.30 (d, J_{HH} = 6.8 Hz, 6H, CHMe$_2$). ^{13}C{^{1}H} NMR (100.6 MHz, acetone-d_6, 293 K): δ 172.9 (s, OCN), 172.7 (s, OCN), 162.4 (s, CO$_2$Me), 147.9 (s, C^{2,6} C$_5$H$_3$N), 147.1 (s, C^{2,6} C$_5$H$_3$N), 140.5 (s, C^{4}H C$_5$H$_3$N), 140.1 (s, IrCH), 127.6 (s, C^{3,5}H C$_5$H$_3$N), 122.4 (s, CHCO$_2$Me), 73.8 (s, OCH$_2$), 73.3 (s, OCH$_2$), 70.7 (s, CH^{i}Pr), 69.2 (s, CH^{i}Pr), 49.8 (s, CO$_2$Me), 28.2 (s, CHMe$_2$), 28.0 (s, CHMe$_2$), 18.8 (s, CHMe$_2$), 18.3 (s, CHMe$_2$), 14.3 (s, CHMe$_2$), 14.2 (s, CHMe$_2$). Molar conductivity (acetone, Ω^{-1} cm^2 mol^{-1}): 211. Anal. Calc. for C$_{42}$H$_{56}$Cl$_2$F$_{12}$Ir$_2$N$_6$O$_8$P$_2$ (1518.20): C, 33.23; H, 3.72; N, 5.54. Found: C, 33.36; H, 3.45; N, 5.50%.

5: Yield: 88% (0.068 g). IR (KBr, cm^{-1}): v 1700m (CO$_2$Et), 1684m (CO$_2$Et), 846 vs (PF$_6^-$). ^{1}H NMR (400 MHz, CD$_2$Cl$_2$, 293 K): δ 8.94 (d, J_{HH} = 15.8 Hz, 2H, IrCH), 8.10 (t, J_{HH} = 8.0 Hz, 2H, H^4 C$_5$H$_3$N), 7.88 (d, J_{HH} = 8.0 Hz, 4H, H^{3,5} C$_5$H$_3$N), 5.59 (m, 2H, OCH$_2$), 4.96 (m, 4H, OCH$_2$), 4.77 (pt, J_{HH} = 9.0 Hz, 2H, OCH$_2$), 4.38 (d, J_{HH} = 15.8 Hz, 2H, CHCO$_2$Et), 4.04 (m, 8H, CH^{i}Pr, CO$_2$CH$_2$CH$_3$), 2.57 (m, 4H, CHMe$_2$), 1.17 (m, 6H, CO$_2$CH$_2$CH$_3$), 1.05 (d, J_{HH} = 7.1 Hz, 6H, CHMe$_2$), 0.84 (d, J_{HH} = 7.1 Hz, 6H, CHMe$_2$), 0.73 (d, J_{HH} = 6.7 Hz, 6H, CHMe$_2$), 0.26 (d, J_{HH} = 6.7 Hz, 6H, CHMe$_2$). ^{13}C{^{1}H} NMR (100.6 MHz, acetone-d_6, 293 K): δ 172.9 (s, OCN), 172.7 (s, OCN), 161.9 (s, CO$_2$Et), 147.9 (s, C^{2,6} C$_5$H$_3$N), 147.1 (s, C^{2,6} C$_5$H$_3$N), 140.5 (s, C^{4}H C$_5$H$_3$N), 139.8 (s, IrCH), 127.7 (s, C^{3,5}H C$_5$H$_3$N), 127.6 (s, C^{3,5}H C$_5$H$_3$N), 122.8 (s, CHCO$_2$Et), 73.8 (s, OCH$_2$), 73.7 (s, OCH$_2$), 70.8 (s, CH^{i}Pr), 69.2 (s, CH^{i}Pr), 58.8 (s, CO$_2$CH$_2$CH$_3$), 28.2 (s, CHMe$_2$), 28.0 (s, CHMe$_2$), 18.9 (s, CHMe$_2$), 18.3 (s, CHMe$_2$), 14.3 (s, CHMe$_2$), 14.2

(s, CHMe_2), 13.8 (s, CO$_2$CH$_2$CH$_3$). Molar conductivity (acetone, Ω^{-1} cm^2 mol^{-1}): 190. MS (ESI+): m/z = 628 [IrCl(CH=CO$_2$Et)(^{i}Pr-pybox)]$^+$. Anal. Calc. for C$_{44}$H$_{60}$Cl$_2$F$_{12}$Ir$_2$N$_6$O$_8$P$_2$ (1546.25): C, 34.18; H, 3.91; N, 5.44. Found: C, 34.08; H, 3.62; N, 5.61%.

4.5. Synthesis of complexes [Ir$_2$(μ-Cl)(HC=CHCO$_2$R)$_2$Cl$_2$(L)$_2$][PF$_6$] (R = Me (6), Et (7))

To a solution of [Ir$_2$(μ-Cl)$_2$(HC=CHCO$_2$R)$_2$(L)$_2$][PF$_6$]$_2$ (R = Me (4), Et (5)) (0.1 mmol) in methanol (2 mL), NaCl (0.029 g, 0.1 mmol) was added. After stirring at room temperature for 50 min, the volatiles were removed in vacuo. Then dichloromethane was added and the resulting solution was filtered through kieselguhr and concentrated to ca. 2 mL. The addition of a diethyl ether/hexane (1:1) mixture (40 mL) afforded 6 or 7 as yellow solids, which were washed with hexane (3 × 5 mL) and vacuum-dried.

6: Yield: 80% (0.113 g). IR (KBr, cm^{-1}): ν 1710m (CO$_2$Me), 1690m (CO$_2$Me), 844 vs (PF$_6^-$). ^{1}H NMR (300 MHz, acetone-d_6, 293 K): δ 9.58 (d, J_{HH} = 16.4 Hz, 2H, IrCH), 8.24 (t, J_{HH} = 7.9 Hz, 2H, H^4 C$_5$H$_3$N), 8.14 (m, 4H, H^{3,5} C$_5$H$_3$N), 5.08 (m, 8H, OCH$_2$), 4.43 (d, J_{HH} = 16.4 Hz, 2H, CHCO$_2$Me), 4.40 (m, 2H, CH^{i}Pr), 4.22 (m, 2H, CH^{i}Pr), 3.45 (s, 6H, CO$_2$Me), 3.01 (m, 2H, CHMe$_2$), 2.77 (m, 2H, CHMe$_2$), 1.03 (d, J_{HH} = 6.8 Hz, 6H, CHMe$_2$), 0.99 (d, J_{HH} = 7.1 Hz, 6H, CHMe$_2$), 0.98 (d, J_{HH} = 7.1 Hz, 6H, CHMe$_2$), 0.73 (d, J_{HH} = 6.8 Hz, 6H, CHMe$_2$). ^{13}C{^{1}H} NMR (100.6 MHz, acetone-d_6, 293 K): δ 171.9 (s, OCN), 171.8 (s, OCN), 163.4 (s, CO$_2$Me), 149.3 (s, IrCH), 147.4 (s, C^{2,6} C$_5$H$_3$N), 147.1 (s, C^{2,6} C$_5$H$_3$N), 138.4 (s, C^{4}H C$_5$H$_3$N), 126.8 (s, C^{3,5}H C$_5$H$_3$N), 121.3 (s, CHCO$_2$Me), 73.3 (s, OCH$_2$), 73.2 (s, OCH$_2$), 69.7 (s, CH^{i}Pr), 69.1 (s, CH^{i}Pr), 49.6 (CO$_2$Me), 28.2 (s, CHMe$_2$), 27.7 (s, CHMe$_2$), 18.6 (s, CHMe$_2$), 18.5 (s, CHMe$_2$), 14.7 (s, CHMe$_2$), 13.9 (s, CHMe$_2$). Molar conductivity (acetone, Ω^{-1} cm^2 mol^{-1}): 155. Anal. Calc. for C$_{42}$H$_{56}$Cl$_3$F$_6$Ir$_2$N$_6$O$_8$P (1408.69): C, 35.81; H, 4.01; N, 5.97. Found: C, 35.40; H, 4.00; N, 5.95%.

7: Yield: 77% (0.111 g). IR (KBr, cm^{-1}): ν 1700m (CO$_2$Et), 1685m (CO$_2$Et), 846 vs (PF$_6^-$). ^{1}H NMR (300 MHz, acetone-d_6, 293 K): δ 9.55 (d, J_{HH} = 16.0 Hz, 2H, IrCH), 8.33 (t, J_{HH} = 8.0 Hz, 2H, H^4 C$_5$H$_3$N), 8.14 (d, J_{HH} = 8.0 Hz, 2H, H^{3,5} C$_5$H$_3$N), 8.11 (d, J_{HH} = 8.0 Hz, 2H, H^{3,5} C$_5$H$_3$N), 5.17 (m, 8H, OCH$_2$), 4.42 (d, J_{HH} = 16.0 Hz, 2H, CHCO$_2$Et), 4.40 (m, 2H, CH^{i}Pr), 4.22 (m, 2H, CH^{i}Pr), 3.92 (m, 4H, CO$_2$CH$_2$CH$_3$), 3.03 (m, 2H, CHMe$_2$), 2.79 (m, 2H, CHMe$_2$), 1.10 (m, 6H, CO$_2$CH$_2$CH$_3$), 1.04 (d, J_{HH} = 6.9 Hz, 6H, CHMe$_2$), 1.00 (d, J_{HH} = 6.9 Hz, 6H, CHMe$_2$), 0.98 (d, J_{HH} = 6.9 Hz, 6H, CHMe$_2$), 0.75 (d, J_{HH} = 6.9 Hz, 6H, CHMe$_2$). ^{13}C{^{1}H} NMR (150.9 MHz, acetone-d_6, 293 K): δ 171.9 (s, OCN), 171.8 (s, OCN), 163.0 (s, CO$_2$Et), 149.1 (s, IrCH), 147.5 (s, C^{2,6} C$_5$H$_3$N), 147.2 (s, C^{2,6} C$_5$H$_3$N), 138.3 (s, C^{4}H C$_5$H$_3$N), 126.7 (s, C^{3,5}H C$_5$H$_3$N), 121.6 (s, CHCO$_2$Et), 73.2 (s, OCH$_2$), 73.1 (s, OCH$_2$), 69.7 (s, CH^{i}Pr), 69.1 (s, CH^{i}Pr), 58.4 (s, CO$_2$CH$_2$CH$_3$), 28.2 (s, CHMe$_2$), 27.7 (s, CHMe$_2$), 18.6 (s, CHMe$_2$), 18.5 (s, CHMe$_2$), 14.7 (s, CHMe$_2$), 13.9 (s, CHMe$_2$), 13.8 (s, CO$_2$CH$_2$CH$_3$). Molar conductivity (acetone, Ω^{-1} cm^2 mol^{-1}): 124. Anal. Calc. for C$_{44}$H$_{60}$Cl$_3$F$_6$Ir$_2$N$_6$O$_8$P (1436.74): C, 36.78; H, 4.21; N, 5.85. Found: C, 36.58; H, 3.91; N, 5.93%.

4.6. Synthesis of complex [IrCl(HC=CHCO$_2$Et)(κ^1-O-O$_2$CMe)(L)] (8)

To a saturated solution of sodium acetate in methanol (5 mL), [Ir$_2$(μ-Cl)$_2$(HC=CHCO$_2$Et)$_2$(L)$_2$][PF$_6$]$_2$ (5) (0.116 g, 0.1 mmol) was added. After stirring at room temperature for 12 h, the volatiles were removed in vacuo. Then dichloromethane was added and the resulting solution was filtered through kieselguhr and concentrated to ca. 2 mL. The addition of a diethyl ether/hexane (1:1) mixture (30 mL) afforded 8 as a yellow solid, which was washed with hexane (3 × 5 mL) and vacuum-dried. Yield: 82% (0.113 g). IR (KBr, cm^{-1}): ν 1700 br (CO$_2$Et). ^{1}H NMR (400 MHz, acetone-d_6, 293 K): δ 9.66 (d, J_{HH} = 16.6 Hz, 1H, IrCH), 8.14 (t, J_{HH} = 7.9 Hz, 1H, H^4 C$_5$H$_3$N), 8.04 (d, J_{HH} = 7.9 Hz, 1H, H^{3,5} C$_5$H$_3$N), 7.96 (d, J_{HH} = 7.9 Hz, 1H, H^{3,5}

C$_5$H$_3$N), 5.08 (m, 4H, OCH$_2$), 4.43 (m, 1H, CH^{i}Pr), 4.31 (d, J_{HH} = 16.6 Hz, 1H, CHCO$_2$Et), 4.23 (m, 1H, CH^{i}Pr), 3.90 (m, 2H, CO$_2$CH$_2$CH$_3$), 2.99 (m, 1H, CHMe$_2$), 2.76 (m, 1H, CHMe$_2$), 1.50 (s, 3H, O$_2$CMe), 1.09 (m, 3H, CO$_2$CH$_2$CH$_3$), 0.97 (d, J_{HH} = 6.8 Hz, 6H, CHMe$_2$), 0.91 (d, J_{HH} = 6.8 Hz, 3H, CHMe$_2$), 0.73 (d, J_{HH} = 6.8 Hz, 3H, CHMe$_2$). ^{13}C{^{1}H} NMR (100.6 MHz, acetone-d_6, 293 K): δ 176.8 (s, O$_2$CCH$_3$), 173.1 (s, OCN), 172.6 (s, OCN), 162.7 (s, CO$_2$Et), 149.1 (s, IrCH), 147.6 (s, C^{2,6} C$_5$H$_3$N), 146.7 (s, C^{2,6} C$_5$H$_3$N), 137.8 (s, C^{4}H C$_5$H$_3$N), 125.9 (s, C^{3,5}H C$_5$H$_3$N), 125.6 (s, C^{3,5}H C$_5$H$_3$N), 121.8 (s, CHCO$_2$Et), 73.1 (s, OCH$_2$), 72.9 (s, OCH$_2$), 69.5 (s, CH^{i}Pr), 69.4 (s, CH^{i}Pr), 58.3 (s, CO$_2$CH$_2$CH$_3$), 28.3 (s, CHMe$_2$), 27.8 (s, CHMe$_2$), 24.0 (s, O$_2$CCH$_3$), 18.6 (s, CHMe$_2$), 18.5 (s, CHMe$_2$), 14.0 (s, CHMe$_2$), 13.9 (s, CHMe$_2$), 13.8 (s, CO$_2$CH$_2$CH$_3$). Anal. Calc. for C$_{24}$H$_{33}$ClIrN$_3$O$_6$ (687.21): C, 41.95; H, 4.84; N, 6.11. Found: C, 41.85; H, 4.79; N, 6.20%.

4.7. X-ray crystal structure determination of complex 3 · CH$_2$Cl$_2$

Crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of hexane into a saturated solution of the complex 3 in dichloromethane. The complex crystallizes with one molecule of CH$_2$Cl$_2$. Data collection, crystal, and refinement parameters are collected in Table 1. Diffraction data were recorded at 150(2) K on an Oxford Diffraction Xcalibur Nova single-crystal diffractometer using Cu Kα radiation (λ = 1.5418 Å). The crystal-to-detector distance was fixed at 65 mm and the frames were collected using the oscillation method, with 1° oscillation and variable exposure time per frame (5–20 s). Data collection strategy was calculated with the program CRYSALIS PRO CCD [9]. Data reduction and cell refinement was performed using the program CRYSALIS PRO RED [9]. An empirical absorption correction was applied using the SCALE3 AB-SPACK algorithm as implemented in the program CRYSALIS PRO RED [9].

The software package WINGX [10] was used for space group determination, structure solution and refinement. The structure was solved by direct methods, using the program SIR-92 [11]. Anisotropic least squares refinement was carried out with SHELXL-97 [12]. All non-hydrogen atoms were anisotropically refined.

Table 1
Crystal data and structure refinement for 3 · CH$_2$Cl$_2$

Chemical formula	C$_{39}$H$_{58}$Cl$_5$F$_6$Ir$_2$N$_6$O$_4$P
Formula weight	1381.53
Temperature (K)	150(2)
Wavelength (Å)	1.5418
Crystal system	Monoclinic
Space group	P2
a (Å)	12.9194 (1)
b (Å)	11.9393 (1)
c (Å)	16.2210(2)
β (°)	97.566 (1)
V (Å^3)	2480.28(4)
Z	2
$\rho_{calcd.}$ (g cm^{-3})	1.850
μ (mm^{-1})	13.601
F(000)	1348
Crystal size (mm)	0.08 × 0.05 × 0.01
θ range (°)	2.75–74.01
Index ranges	$-15 \leq h \leq 16$
	$-14 \leq k \leq 14$
	$-20 \leq l \leq 19$
No. of reflections collected	27571
No. of independent reflections [$R_{(int)}$]	9250 [0.0327]
Completeness to θ_{max} (%)	97.3
No. parameters/restraints	578/1
Goodness-of-fit (GOF) on F^2	1.145
R ($I > 2\sigma(I)$)[a]	R_1 = 0.0360, wR_2 = 0.1036
R (all data)	R_1 = 0.0411, wR_2 = 0.1082
Absolute structure parameter	−0.019(14)
Largest difference peak and hole (e Å^{-3})	1.368 and −1.152

[a] R_1 = Σ(|F_o| − |F_c|)/Σ|F_o|; wR_2 = {$\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]$}$^{1/2}$.

Hydrogen atoms were geometrically placed riding on their parent atoms with isotropic displacement parameters set to 1.2 times the U_{eq} of the atoms to which they are attached (1.5 for methyl groups). In all cases, the maximum residual electron density is located near to heavier atoms. The function minimized was $[\sum w(F_o^2 - F_c^2)/\sum w(F_o^2)]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (0.0424P)^2 + 12.1966P]$, with $\sigma(F_o^2)$ from counting statistics and $P = (\text{Max}(F_o^2, 0) + 2F_c^2)/3$. Atomic scattering factors were taken from the International Tables for X-Ray Crystallography [13]. Geometrical calculations were made with PARST [14]. The crystallographic plots were made with PLATON [15].

Acknowledgements

Appendix A. Supplementary material

CCDC 691413 contains the supplementary crystallographic data for $3 \cdot CH_2Cl_2$. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.09.012.

References

[1] (a) For recent examples of alkyne or alkene insertion into the Ir–H bond see: R. Ghosh, X. Zhang, P. Achord, T.J. Emge, K. Krogh-Jespersen, A.S. Goldman, J. Am. Chem. Soc. 129 (2007) 853;
(b) T. Dirnberger, H. Werner, Inorg. Chim. Acta 360 (2007) 1339;
(c) M. Paneque, C.M. Posadas, M.L. Poveda, N. Rendón, K. Mereiter, Organometallics 26 (2007) 3120;
(d) X. Li, T. Vogel, C.D. Incarvito, R.H. Crabtree, Organometallics 24 (2005) 62;
(e) X. Li, L.N. Appelhans, J.W. Faller, R.H. Crabtree, Organometallics 23 (2004) 3378;
(f) J. Navarro, E. Sola, M. Martin, I.T. Dobrinovitch, F.J. Lahoz, L.A. Oro, Organometallics 23 (2004) 1908;
(g) M. Martin, E. Sola, O. Torres, P. Plou, L.A. Oro, Organometallics 22 (2003) 5406;
(h) C.S. Chin, H. Lee, H. Park, M. Kim, Organometallics 21 (2002) 3889.

[2] (a) C.S. Chin, H. Lee, S. Noh, H. Park, M. Kim, Organometallics 22 (2003) 2119 and references therein;
(b) See [1d] and references therein;
(c) I.D. Gridnev, T. Imamoto, Acc. Chem. Res. 37 (2004) 633;
(d) J.P. Collman, L.S. Hegedus, J.R. Norton, R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1987;
(e) P.A. Chaloner, M.A. Esteruelas, F. Joó, L.A. Oro, Homogeneous Hydrogenation, Kluwer, Dordrecht, The Netherlands, 1994;
(f) B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, VCH, Weinheim, Germany, 1996;
(g) R.H. Crabtree, The Organometallic Chemistry of the Transition Metals, 4th ed., Wiley & Sons, New Jersey, 2005.
[3] J. Díez, M.P. Gamasa, J. Gimeno, P. Paredes, Organometallics 24 (2005) 1799.
[4] P. Paredes, J. Díez, M.P. Gamasa, Organometallics 27 (2008) 2597.
[5] D. Cuervo, J. Díez, M.P. Gamasa, J. Gimeno, P. Paredes, Eur. J. Inorg. Chem. (2006) 599.
[6] (a) See for example: S. Thewissen, M.D.M. Reijnders, J.M.M. Smits, B. de Bruin, Organometallics 24 (2005) 5964;
(b) L. Gonsalvi, H. Adams, G.J. Sunley, E. Ditzel, A. Haynes, J. Am. Chem. Soc. 124 (2002) 13597;
(c) E. Sola, J. Navarro, J.A. López, F.J. Lahoz, L.A. Oro, H. Werner, Organometallics 18 (1999) 3534;
(d) P. Moore, H.A.A. Omar, N.W. Alcock, G.A. Pike, J. Chem. Soc., Chem. Commun. (1990) 280;
(e) C. Slugovc, K. Mereiter, S. Trofimenko, E. Carmona, J. Chem. Soc., Chem. Commun. (1990) 121;
(f) D.L. Thorn, R.L. Haelow, J. Am. Chem. Soc. 111 (1989) 2575;
(g) D.L. Thorn, T.H. Tulip, J. Am. Chem. Soc. 103 (1981) 5984.
[7] (a) D. Cuervo, J. Díez, M.P. Gamasa, J. Gimeno, Organometallics 23 (2005) 2224;
(b) D. Cuervo, M.P. Gamasa, J. Gimeno, J. Mol. Catal. A: Chem. 249 (2006) 60.
[8] In the case of rhodium, the 16-electron species [RhCl(HC=CHCO₂Me){κ^3-N,N,N-(S,S)-^{i}Pr-pybox}][PF₆], obtained from [Rh(μ-Cl)(η²-C₂H₄)₂]₂, ^{i}Pr-pybox, HBF₄ and alkyne, did not evolve into the corresponding dinuclear complex analogous to **4**, but the the mononuclear complex [RhCl(κ^2-C,O-CH=CHCO₂Me){κ^3-N,N,N-(S,S)-^{i}Pr-pybox}][BF₄] resulting from carboxylate-rhodium coordination was exclusively formed (see Ref. [7a]).
[9] CRYSALIS PRO, Oxford Diffraction Limited, 2007.
[10] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.
[11] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M.C. Burla, G. Polidori, M. Camalli, J. Appl. Crystallogr. 27 (1994) 435.
[12] G.M. Sheldrick, SHELXL-97, A Computer Program for Refinement of Crystal Structures, University of Gottingen, 1997.
[13] Tables for X-Ray Crystallography, Kynoch Press, Birminghan, UK, vol. IV (Present distributor: Kluwer Academic Publishers, Dordrecht), The Netherlands, 1974.
[14] M. Nardelli, Comput. Chem. 7 (1983) 95.
[15] A.L. Spek, PLATON: A Multipurpose Crystallographic Tool, University of Utrecht, The Netherlands, 2007.