ELSEVIER

Journal of Organometallic Chemistry 564 (1998) 241–247

Journal of Organometallic Chemistry

C–H activation of methyl vinyl ketone in Ir(acac){η^2-CH_2=CHC(O)CH_3}(PCy_3)

Ricardo Castarlenas, Miguel A. Esteruelas *, Marta Martín, Luis A. Oro

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain

Received 30 March 1998

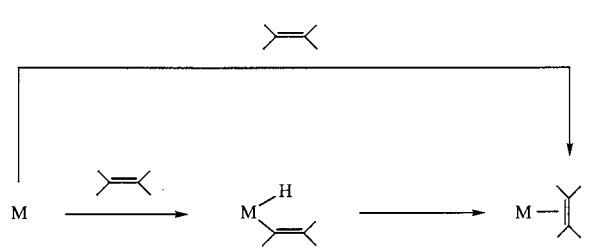
Abstract

The cyclooctene complex Ir(acac)(cyclooctene)(PCy_3) (**1**) reacts with methyl vinyl ketone to give Ir(acac){η^2-CH_2=CHC(O)CH_3}(PCy_3) (**2**) and cyclooctene. In benzene at 70°C, complex **2** affords by means of an intramolecular C–H activation process the thermodynamically favored alkenyl derivative Ir(acac)H{(*Z*)-CH=CHC(O)CH_3}(Pcy_3) (**3**), which was isolated as a mixture of the isomers **3a** (PCy_3 *trans* to carbonyl group of alkenyl ligand) and **3b** (PCy_3 *trans* to acac). Isomers **3a** and **3b** do not react with tricyclohexylphosphine. However, the complex Ir(acac)H{(E)-CH=CHC(O)CH_3}(PCy_3)$_2$ (**4**) can be obtained by treatment of **2** with the phosphine in benzene at 70°C. Complex **2** also reacts with HBF_4 at -78°C, to give the five-coordinate hydrido derivative [Ir(acac)H{η^2-CH_2=CHC(O)CH_3}(PCy_3)]BF_4 (**5**). In solution, complex **5** is only stable at temperatures lower than −40°C. At room temperature and in the presence of acetonitrile, it evolves into the alkyl compound [Ir(acac){$CH_2CH_2C(O)CH_3$}($NCCH_3$)(PCy_3)]BF_4 (**6**), as a result from the selective *anti*-Markovnikov insertion of the carbon–carbon bond of the activated olefin into the Ir–H bond of the **5**.

Keywords: C–H activation; Methyl vinyl ketone complexes; Iridium complexes; Hydrido complexes

1. Introduction

M(η^2-olefin) complexes, which are key intermediates in catalytic processes involving olefins, can be formed by direct π-complexation and by vinylic oxidative addition followed by intramolecular reductive elimination (Scheme 1). Thus, it has been observed that the reaction of ethylene with the coordinatively unsaturated fragment Ir(η^5-C_5Me_5)(PMe_3) leads not only to coordination but also to oxidative addition to give a hydrido–vinyl metal complex, which isomerizes into the thermodynamically favored π-olefin metal compound [1].



Scheme 1.

The majority of hydrido–alkenyl metal complexes are thermodynamically unstable with respect to the corresponding M(η^2-olefin) species [2–8]. However, in the iridium chemistry, there are a few notable exceptions in which the relative stabilities are reversed. In 1988, Werner et al. [9] found that a number of activated olefins reacted with [Ir(μ-Cl)(P^iPr_3)$_2$]$_2$ to form octahedral alkenyl-hydrido derivatives, via less stable Ir(η^2-olefin) intermediates. Subsequently, it was observed that in cyclohexane at 100°C the four-coordinate complex Ir(η^2-Tp^{Me, CF_3})(CO)(η^2-C_2H_4) completely isomerized into the hydrido-vinyl Ir(η^3-Tp^{Me, CF_3})H(CH=CH_2)(CO) [10], and that the reaction of

* Corresponding author. Fax: +34 97 61761187.

0022-328X/98/$19.00
PII S0022-328X(98)00690-1

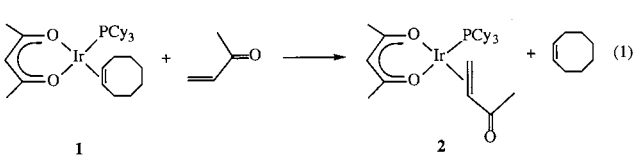
$[Ir(\mu\text{-}Cl)(cyclooctene)_2]_2$ with $Na[HB(pz)_3]$ gave $IrH[HB(pz)_3](\sigma\text{-}C_8H_{13})(C_8H_{14})$ [11]. Recently, Carmona et al. [12–14] have reported that $IrTp^{Me_2}(C_2H_4)_2$ thermally rearranges into $IrTp^{Me_2}H(CH{=}CH_2)(\eta^2\text{-}CH_2{=}CH_2)$, which undergoes intramolecular coupling of the vinyl and ethylene ligands with formation of the allylic complex $IrTp^{Me_2}H(\eta^3\text{-}CH_2CHCHMe)$, and is capable of regioselectively activating the two C–H bond of the O-bearing methylene groups of cyclic ethers with formation of Fischer-type carbene derivatives, which also contain an Ir–H and Ir–butyl functionality.

In the search for transition–metal complexes which are catalytically active in the hydrogenation, hydrosilylation and hydrostannylation of unsaturated organic substrates, we have recently reported on the reactivity of the acetylacetonato iridium compound Ir(acac)(cyclooctene)(PCy_3) [15]. As a continuation of this work, we became interested to know whether complex Ir(acac)(cyclooctene)(PCy_3) can also be used as starting material for the preparation of hydrido–alkenyl compounds by oxidative addition of methyl vinyl ketone. In this paper, we report on the synthesis of new alkenyl and alkyl complexes, starting from Ir(acac)(cyclooctene)(PCy_3) and methyl vinyl ketone.

2. Results and discussion

2.1. Synthesis and characterization of alkenyl complexes

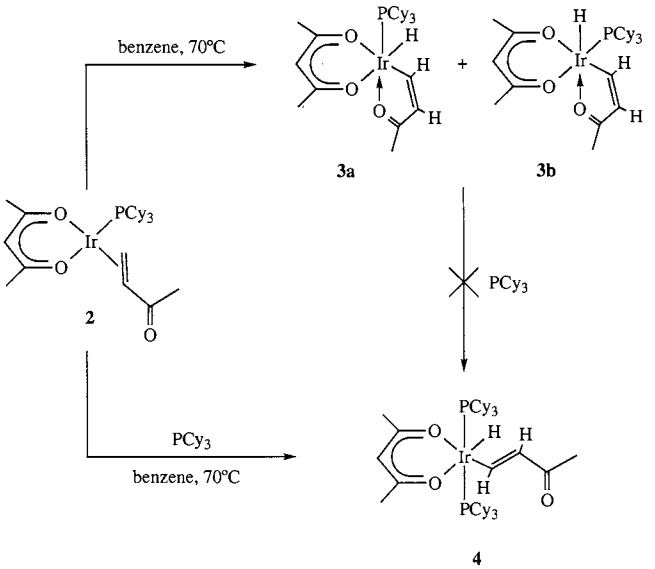
The cyclooctene ligand of Ir(acac)(cyclooctene)(PCy_3) (**1**) is easily displaced by methyl vinyl ketone. The addition of one equiv. of this activated olefin to pentane suspensions of **1** affords Ir(acac)$\{\eta^2\text{-}CH_2{=}CHC(O)CH_3\}(PCy_3)$ (**2**) after 5 min. The reaction proceeds at room temperature and the new compound is isolated as an orange solid in 81% yield (Eq. 1).



1 2

The IR spectrum of **2** in KBr shows at 1578 and 1521 cm^{-1} two strong ν(CO) absorptions for the carbonyl groups of the acetylacetonato ligand, indicating that this ligand is coordinated in a κ^2-oxygen bonding mode [16]. The presence of the α,β-unsaturated ketone in **2** is also supported by the IR spectrum which shows another ν(CO) band at 1657 cm^{-1}. This value is lower than the frequency for free methyl vinyl ketone observed at 1681 cm^{-1}. In agreement with the square-planar coordination of the iridium atom, at room temperature, the ^{1}H-NMR spectrum of **2** displays two singlets at 1.74 and 1.63 ppm for the protons of the methyl groups of the β-diketonato ligand. The olefinic protons of the activated olefin give rise to a doublet of doublets of doublets (=CH) at 3.95 ppm with H–H coupling constants of 11.1 and 7.2 Hz and a H–P coupling constant of 3.7 Hz, a doublet of doublets [=CH *cis* to –C(CO)CH_3] at 3.28 ppm with H–H coupling constants of 11.1 and 1.6 Hz, and a doublet of doublets of doublets [=CH *trans* to –C(O)CH_3] at 2.42 ppm with H–H coupling constants of 7.2 and 1.6 Hz and a H–P coupling constant also of 1.6 Hz. The low value (11.1 Hz) of the $J_{trans\,H-H}$ should be noted, which is reduced by 6.3 Hz with regard to the coupling constant between the hydrogen protons mutually *trans* disposed in the free methyl vinyl ketone (17.4 Hz). This suggests that the coordination of the carbon–carbon double bond of the α,β-unsaturated ketone to the iridium center of **2** produces a weaker intraligand carbon–carbon double bond than that expected, as a result of an unusually strong π-donor power of the metallic center, which is comparable to that of the metal-based half-sandwich complexes of type $(C_5R_5)ML_2$ [17,18]. This is also revealed by the $^{13}C\{^1H\}$-NMR spectrum, which shows the resonances of the olefinic carbon atoms at 39.2 and 22.3 ppm, shifted toward high field by about 100 ppm in comparison with the resonances of the free ligand (137.4 and 128.7 ppm). The $^{13}C\{^1H\}$-NMR spectrum of **2** also supports the square planar coordination of the iridium atom. Thus, it shows a singlet at 29.8 ppm and a doublet at 28.5 ($J_{P-C} = 5.4$ Hz) ppm, assigned to the inequivalent methyl groups of the acetylacetonato ligand. The chemical shift, and the multiplicity of these resonances as well as the value of the P–C coupling constant agree well with those previously found in the related complexes Rh(acac)$(\eta^2\text{-}RC{\equiv}CR)(PCy_3)$ (R = Ph, CO_2CH_3) [19]. Furthermore, the spectroscopic data indicated that only one of the two possible stereoisomers is formed.

The nucleophilic character of the metallic center of **2** is also revealed by means of the oxidative addition of the olefin C–H bond, disposed *cis* to the –C(O)CH_3 group of the coordinated methyl vinyl ketone molecule. Thus, after 9 days at 70°C, benzene solutions of **2** afford mixtures of the isomers **3a** and **3b** of the hydrido–alkenyl complex Ir(acac)H$\{(Z)\text{-}CH{=}CHC(O)CH_3\}(PCy_3)$ (Scheme 2) and **2** in a molar ratio of about 50:25:25. The isomerization was followed by ^{1}H- and $^{31}P\{^1H\}$-NMR spectroscopy and the formation of products resulting from the C–H activation of benzene was not observed. Because, in general, the C–H activation of benzene is kinetically more favored than that of a vinylic group [20], this observation suggests that the isomerization of **2** into **3** is an intramolecular process. This is confirmed by the fact that neither reaction rate nor the above mentioned



Scheme 2.

molar ratio are affected by the presence of an equivalent of methyl vinyl ketone in the solutions of **2.**

Isomers **3a** and **3b** were separated from the mixture by column chromatography (Al_2O_3 neutral, activity grade V) and characterized by MS, IR and ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$-NMR spectroscopy.

In agreement with the structure shown in Scheme 2, in high field region of the ^1H-NMR spectrum, the isomer **3a** displays at -24.47 ppm a doublet with a H–P coupling constant of 24.0 Hz, which strongly supports the *cis* disposition of the hydrido and phosphine ligands. In low field region, the most noticeable resonances appear at 11.34 and 6.98 ppm as doublets of doublets with a H–H coupling constant of 7.5 Hz and H–P coupling constants of 1.8 and 1.4 Hz, respectively, and were assigned to the vinylic hydrogen atoms of the alkenyl ligand. With regard to the value of the H–H coupling constant there is no doubt about the mutually *cis* disposition of these atoms. The coordination of the carbonyl group of the alkenyl ligand and its disposition *trans* in relation to the phosphine ligand is strongly supported by the $^{13}C\{^1H\}$-NMR spectrum, which shows at 208.4 ppm a doublet with a P–C coupling constant of 3.2 Hz. The resonances of the α- and β-carbon atoms of the alkenyl ligand are observed at 201.9 and 135.2 ppm, respectively. In agreement with the mutually *cis* disposition of the α-carbon and the tricyclohexylphosphine ligand, the first of them appears as a doublet with a P–C coupling constant of 6.8 Hz, and the second one as a singlet. The $^{31}P\{^1H\}$-NMR spectrum shows a singlet at 15.8 ppm, which under off-resonance conditions due to the P–H coupling is split into a doublet.

The ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$-NMR spectra of **3b** also agree well with the structure proposed for this compound in Scheme 2. In the ^1H-NMR spectrum, the resonance due to the hydrido ligand is observed at -24.03 ppm as a doublet with a H–P coupling constant of 23.7 Hz, while those corresponding to the =CH protons of the alkenyl ligand appear at 11.56 and 7.31 ppm as doublets with a H–H coupling constants of 7.5 Hz. In the $^{13}C\{^1H\}$-NMR spectrum, the resonance of the carbon atom of the carbonyl group of the alkenyl ligand, in contrast to that of **3a**, appears as a singlet at 207.0 ppm. The resonances corresponding to the α- and β-carbon atoms of the alkenyl ligand are observed at 199.6 and 137.9 ppm as doublets with P–C coupling constants of 15.0 and 3.2 Hz, respectively. In addition it should be mentioned a doublet ($J_{P-C} = 6.1$) at 27.5 ppm, due to a methyl group of the β-diketonato ligand, which supports the *trans* disposition of the tricyclohexylphosphine and a carbonyl group of the acetylacetonate. The $^{31}P\{^1H\}$-NMR spectrum contains a singlet at 13.0 ppm, which under off-resonance conditions due to the P–H coupling is split into a doublet.

The structures of **3a** and **3b** were confirmed by NOE experiments. Irradiating the hydrido resonance of **3a** gave an increase in the intensities of the both signals of the vinylic protons of the alkenyl ligand, whereas irradiating the hydrido resonance of **3b** gave an increase in the intensities of the α-vinylic proton of the alkenyl group and the –CH– proton of the acetylacetonato ligand, and the signal of the β-vinyl proton of the alkenyl group showed a negative NOE.

Isomers **3a** and **3b** do not regenerate the π-olefin complex **2** even after 2 months, suggesting that the hydrido-alkenyl-iridium moiety is thermodynamically more stable than the Ir{η^2-CH_2=CHC(O)CH_3} unit. The stabilization of the hydrido-alkenyl-iridium moiety caused by the chelate formation also manifests itself in isomers **3a** and **3b** being inert towards tricyclohexylphosphine. So, the addition of this phosphine to toluene solutions of **3a** and **3b** does not open the chelate ring by breaking of the Ir–O bond, even under reflux conditions. However, a new compound containing a monodentate alkenyl ligand is obtained from the reaction of **2** with tricyclohexylphosphine. Thus, the treatment of **2** in benzene with one equiv. of tricyclohexylphosphine at 70°C affords after 7 days the hydrido–alkenyl complex Ir(acac)H{(E)–CH=CHC(O)-CH_3}(PCy_3)$_2$ (**4**), which was isolated as a white solid in 78% yield (Scheme 2).

The behavior of **2** is similar to that of the related ethylene derivative Ir(acac)(η^2-CH_2=CH_2)(P^iPr_3) which evolves in benzene at 60°C, in the presence of triisopropylphosphine, into the hydrido–vinyl compound Ir(acac)H(CH=CH_2)(P^iPr_3)$_2$ [21].

Previously, we have observed that in the presence of tricyclohexylphosphine, the complex Ir(acac)(cyclooctene)(PCy_3) reacts with molecular hydrogen, phenylacetylene, silanes and $HSnPh_3$ to afford six-coordinate

iridium(III) derivatives Ir(acac)HX(PCy_3)$_2$ (X = H, C_2Ph, SiR_3, $SnPh_3$). Because, the related five-coordinate complexes Ir(acac)HX(PCy_3) do not react with tricyclohexylphosphine to give Ir(acac)HX(PCy_3)$_2$, we have suggested that the formation of the six-coordinate iridium(III) compounds proceeds via four-coordinate iridium(I) intermediates containing the acetylacetonate coordinated in a η^1-C^3-fashion [15]. The formation of **4** according to Scheme 2 and the inertia of **3a** and **3b** towards tricyclohexylphosphine are new evidences in favor of this proposal.

In addition, it should be mentioned the high stability of the hydrido-alkenyl-iridium moiety of **4** toward the reductive elimination of methyl vinyl ketone. In this case, it can be related to the *cis* constraint imposed by the chelating acetylacetonato ligand and the fact that in a concerted reductive elimination the ligands *trans* to the leaving groups move into mutually *trans* positions in the resulting four-coordinate complex [22–24].

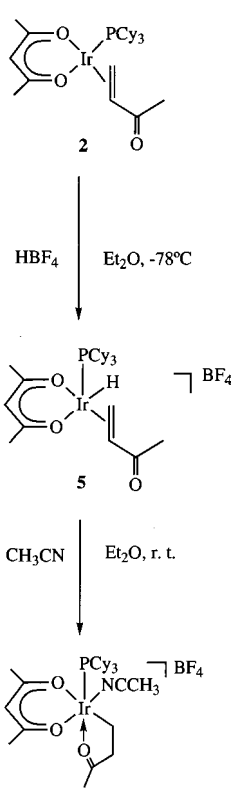
Complex **4** was characterized by elemental analysis, MS, IR and ^{1}H-, ^{13}C{^{1}H}- and ^{31}P{^{1}H}-NMR spectroscopy. In the IR spectrum of **4** in KBr, the most prominent feature is a ν(Ir–H) band at 2243 cm^{-1}. In the ^{1}H-NMR spectrum the resonance due to the hydrido ligand is observed at −24.46 ppm, as a triplet with a H–P coupling constant of 16.2 Hz. The resonances corresponding to the vinylic hydrogen atoms of the alkenyl group appear at 10.91 (Ir–C*H*=) and 6.48 (=C*H*–) ppm as doublets with a H–H coupling constant of 16.5 Hz. This value strongly supports the *trans* stereochemistry at the carbon–carbon double bond [25]. In the ^{13}C{^{1}H}-NMR spectrum the resonances due to the Ir–*C*H= and =*C*H– alkenyl carbon atoms are observed at 160.5 and 141.1 ppm, respectively. The ^{31}P{^{1}H}-NMR spectrum shows a singlet at 14.0 ppm, which under off-resonance conditions due to the P–H coupling is split into a doublet.

2.2. Synthesis and characterization of alkyl complexes

The nucleophilic character of the metallic center of **2** is not only revealed by the reactions shown in Scheme 2 but also by the reaction of this complex with HBF_4 (Scheme 3). Treatment of diethyl ether suspensions of **2** with 1 equiv. of $HBF_4.OEt_2$ at −78°C affords the hydrido-π-olefin complex [Ir(acac)H{η^2-CH_2=CHC(O)-CH_3}(PCy_3)]BF_4 (**5**), which was isolated as a white solid in 71% yield.

The IR spectrum of **5** in KBr strongly supports the presence of the hydrido ligand, showing the Ir–H stretching frequency at 2232 cm^{-1}. This spectrum also contains two ν(CO) bands at 1583 and 1523 cm^{-1} in agreement with the κ^2-oxygen coordination bonding mode of the acetylacetonato group. Furthermore, the spectrum shows the ν(CO) band corresponding to the carbonyl group of the coordinated methyl vinyl ketone at 1686 cm^{-1}, and an absorption due to the $[BF_4]^-$ anion with T_d symmetry centered at 1061 cm^{-1}, indicating that, although the metallic center of **5** is coordinatively unsaturated, the anion is not coordinated to the iridium atom.

The presence of the hydrido ligand in **5** is also supported by the ^{1}H- and ^{31}P{^{1}H}-NMR spectra in dichloromethane-d_2 at 213 K. Thus, the ^{1}H-NMR spectrum shows a hydrido resonance at −17.19 ppm, which appears as a doublet with a H–P coupling constant of 18.0 Hz, and the ^{31}P{^{1}H}-NMR spectrum contains a singlet at 7.4 ppm, which under off-resonance conditions due to the P–H coupling is split into a doublet. In the ^{1}H-NMR spectrum, the olefinic protons of the methyl vinyl ketone give rise to a doublet of doublets (=CH) at 4.54 ppm with H–H coupling constants of 12.1 and 6.0 Hz, another doublet of doublets [=CH *cis* to –C(O)CH_3] at 4.10 ppm with H–H and H–P coupling constants of 12.1 and 2.7 Hz, respectively, and a doublet [=CH *trans* to –C(O)CH_3] at 3.63 ppm with a H–H coupling constant of 6.0 Hz. In addition, it should be noted that the value of the $J_{trans\ H-H}$ of **5** is 1.0 Hz higher than that of **2**, in agreement with the expected decrease of the nucleophilic character of the metallic center of **2** as a result from the protonation. This is also revealed by the ^{13}C{^{1}H}-NMR spectrum of **5** in dichloromethane-d_2 at



Scheme 3.

213 K, which shows the resonances of the olefinic carbon atoms as singlets at 52.9 and 24.8 ppm. The first of them shifted 13.7 ppm to lower field in comparison with related resonance of **2**. Furthermore, it must be mentioned that, in agreement with the structure proposed for **5** in Scheme 3, the resonances corresponding to the carbonyl group of the methyl vinyl ketone and the methyl groups of the acetylacetonato ligand appear as singlets at 214.0, 29.6 and 27.9 ppm, respectively.

In the solid state, complex **5** is stable for a week if kept under argon at −20°C. Under argon and at temperatures lower than −40°C, the dichloromethane solutions of **5** are also stable. However at higher temperatures, these solutions rapidly evolve to a mixture of eight products, according to the $^{31}P\{^1H\}$-NMR spectra, which could not be identified.

Attempts to stabilize **5** by addition of acetonitrile lead to a white solid in 92% yield. According to the elemental analysis, the composition corresponds to a 1:1 adduct of **5** and acetonitrile. The ^1H-NMR spectrum of this new compound does not contain a signal in the hydrido region, which suggests that an insertion reaction of the activated olefin into the Ir–H bond of **5** has taken place.

With regard to the IR and ^1H- and $^{13}C\{^1H\}$-NMR spectra, there is no doubt that an *anti*-Markovnikov type of insertion has taken place and the alkyl complex [Ir(acac){$CH_2CH_2C(O)CH_3$}($NCCH_3$)(PCy_3)] BF_4 (**6** in Scheme 3) has been formed.

The IR spectrum in KBr shows together with the ν(CO) bands of the acetylacetonato ligand at 1587 and 1514 cm^{-1}, a C=O stretching frequency at 1630 cm^{-1} corresponding to a coordinated ketonic C=O group (for comparison, see Refs. [26–28]). In the ^1H-NMR spectrum, besides the signals of the phosphine, acetylacetonato and acetonitrile protons three absorptions are observed at 2.95, 2.65 and 2.43 ppm, which are assigned to the $IrCH_2$, $–CH_2–$ and $–CH_3$ protons of the metallacycle. The resonances of $IrCH_2$ and $–CH_2–$ carbon atoms of metallacycle appear in the $^{13}C\{^1H\}$-NMR spectrum at −8.9 and 52.5 ppm, respectively, the first one is observed as a doublet with a P–C coupling constant of 5.6 Hz, while the second one is observed as a singlet. Furthermore, the spectrum contains at 236.2 ppm a doublet with a P–C coupling constant of 3.2 Hz, for the ketonic carbon atom of alkyl ligand, which supports its coordination and its *trans* disposition in relation to the phosphine ligand. The $^{31}P\{^1H\}$-NMR spectrum shows a singlet at −4.3 ppm.

3. Concluding remarks

This study has revealed that the reaction of the cyclooctene complex Ir(acac)(cyclooctene)(PCy_3) with methyl vinyl ketone yields the derivative Ir(acac){η^2-CH_2=CHC(O)CH_3}(PCy_3), where the iridium atom shows a strong π-donor power. The nucleophilic character of the metallic center of this complex is evident in the intramolecular oxidative addition of a C–H olefinic bond of the coordinated α,β-unsaturated ketone to give the thermodynamically favored alkenyl complex Ir(acac)H{(*Z*)–CH=CHC(O)CH_3}(PCy_3), and in the reaction with HBF_4 to afford the five-coordinate hydrido compound [Ir(acac)H{η^2-CH_2=CHC(O)CH_3}(PCy_3)]-BF_4.

The high stability of the hydrido-alkenyl-iridium moiety of Ir(acac)H{(*Z*)–CH=CHC(O)CH_3}(PCy_3), caused by the chelated formation, is also manifested by its inertia towards PCy_3. Although this complex does not react with the phosphine, an Ir(acac)H{(E)–CH=CHC(O)CH_3}(PCy_3)$_2$ derivative is obtained by treatment of Ir(acac){η^2-CH_2=CHC(O)-CH_3}(PCy_3) with PCy_3. This complex is also very stable, and its stability can be related to the *cis* constraint imposed by chelating acetylacetonato ligand, and the fact that in a concerted reductive elimination the ligands *trans* to the leaving groups move into mutually *trans* positions in the resulting four-coordinate complex.

The five coordinate hydrido complex [Ir(acac)-H{η^2-CH_2=CHC(O)CH_3}(PCy_3)]BF_4 is only stable at very low temperature. Attempts to stabilize it by addition of acetonitrile lead to the alkyl derivative [Ir(acac){$CH_2CH_2C(O)CH_3$}($NCCH_3$)(PCy_3)]BF_4, as a result from the selective *anti*-Markovnikov insertion of the carbon–carbon double bond of the activated olefin into the Ir–H bond.

In conclusion, we report the synthesis of a new olefin complex with a very remarkable nucleophilic character, which allows the preparation of new alkenyl and alkyl compounds by means of oxidative addition reactions.

4. Experimental section

All reactions were carried out under argon atmosphere using Schlenk tube techniques. Solvents were dried by known procedures and distilled under argon prior to use. The starting complex Ir(acac)(coe)(PCy_3) (**1**) was prepared by the published method [29]. IR spectra were recorded on a Perkin Elmer 883 spectrometer, and the NMR spectra on Varian UNITY 300, Varian GEMINI 2000 (300 MHz) and Bruker ARX 300 instruments. The ^{13}C-NMR signals were assigned by DEPT experiments. C, H and N analyses were carried out with a Perkin Elmer 2400 CHNS/O microanalyzer. MS data were recorded on a VG Auto Spec instrument. The ions were produced, FAB^+ mode, with the standard Cs^+ gun at ca. 30 kV, and 3-nitrobenzyl alcohol (NBA) was used as the matrix.

4.1. Preparation of *Ir(acac){η²-CH₂=CHC(O)CH₃}(PCy₃)* (**2**)

A suspension of **1** (1009 mg, 1.48 mmol) in 25 ml of *n*-pentane was treated with methyl vinyl ketone (121 μl, 1.48 mmol). A spontaneous color change from yellow to orange occurred, and the mixture was stirred for 5 min at room temperature. Then the solution was concentrated in vacuo for about 5 ml yielding an orange precipitate. The solvent was decanted, and the solid was washed with *n*-pentane (3 × 1 ml) and dried in vacuo. Yield 775 mg (81%). Anal. Calcd. for $C_{27}H_{46}IrO_3P$: C, 50.53; H, 7.22. Found: C, 50.55; H, 7.53. IR (KBr, cm^{-1}): $\nu(CO)_{mvk}$ 1657; $\nu(CO)_{acac}$ 1578 and 1521. ^{1}H-NMR (300 MHz, C_6D_6): δ 5.19 (s, 1H, CH of acac); 3.95 (ddd, 1H, $J_{trans\ H-H} = 11.1$ Hz, $J_{cis\ H-H} = 7.2$ Hz, $J_{P-H} = 3.7$ Hz, =CH); 3.28 (dd, 1H, $J_{trans\ H-H} = 11.1$ Hz, $J_{gem\ H-H} = 1.6$ Hz, $=CH_2$); 2.42 (ddd, 1H, $J_{cis\ H-H} = 7.2$ Hz, $J_{gem\ H-H} = J_{P-H} = 1.6$ Hz, $=CH_2$); 2.34 (s, 3H, CH_3 of mvk); 1.74 and 1.63 (both s, 6H, CH_3 of acac); 2.2–1.1 (m, 33H, PCy_3). $^{13}C\{^1H\}$-NMR (75.4 MHz, C_6D_6): δ 206.7 (s, CO of mvk); 187.4 and 180.9 (both s, CO of acac); 101.4 (s, CH of acac); 39.2 (s, =CH); 31.6 (d, $J_{P-C} = 29.8$ Hz, CH of PCy_3); 30.4 and 30.2 (both s, CH_2 of PCy_3); 29.8 (s, CH_3 of acac); 28.5 (d, $J_{P-C} = 5.4$ Hz, CH_3 of acac); 28.1, 28.0 and 27.0 (all s, CH_2 of PCy_3); 26.2 (s, CH_3 of mvk); 22.3 (s, $=CH_2$). $^{31}P\{^1H\}$-NMR (121.4 MHz, C_6D_6): δ 0.1(s).

4.2. Preparation of *Ir(acac)H{(Z)–CH=CHC(O)CH₃}(PCy₃)* (**3a**,**b**)

A solution of **2** (300 mg, 0.47 mmol) in 15 ml of benzene was stirred for 9 days at 70°C and the color turned from orange to brown. The solution was concentrated to ca. 1 ml and chromatographed on alumina neutral (activity grade V). A diethyl ether/*n*-pentane (7/3) mixture eluted a yellow fraction from which the solvent was removed in vacuo affording a yellow oil that contained both isomers **a**,**b** (2/1). Data for **3a:** IR (CH_2Cl_2, cm^{-1}): ν(Ir–H) 2219; $\nu(CO)_{acac}$ 1585 and 1521; $\nu(CO)_{mvk}$ overlapped by $\nu(CO)_{acac}$. ^{1}H-NMR (300 MHz, C_6D_6): δ 11.34 (dd, 1H, $J_{cis\ H-H} = 7.5$ Hz, $J_{P-H} = 1.8$ Hz, IrCH=CH); 6.98 (dd, 1H, $J_{cis\ H-H} = 7.5$ Hz, $J_{P-H} = 1.4$ Hz, IrCH=CH); 5.31 (s, 1H, CH of acac); 2.06 (s, 3H, CH_3 of mvk); 1.89 and 1.79 (both s, 6H, CH_3 of acac); 2.2–1.0 (m, 33H, PCy_3); −24.47 (d, $J_{P-H} = 24.0$ Hz, IrH). $^{13}C\{^1H\}$-NMR (75.4 MHz, C_6D_6): δ 208.4 (d, $J_{P-C} = 3.2$ Hz, CO of mvk); 201.9 (d, $J_{P-C} = 6.8$ Hz, IrCH=CH); 185.5 and 185.2 (both s, CO of acac); 135.2 (s, IrCH=CH); 100.8 (d, $J_{P-C} = 1.9$ Hz, CH of acac); 33.7 (d, $J_{P-C} = 31.8$ Hz, CH of PCy_3); 28.9, 27.9, 27.8 and 26.8 (all s, CH_2 of PCy_3); 28.2 and 27.6 (both s, CH_3 of acac); 23.8 (s, CH_3 of mvk). $^{31}P\{^1H\}$-NMR (121.4 MHz, C_6D_6): δ 15.8 (s; d off-resonance). Data for **3b**: IR (CH_2Cl_2, cm^{-1}): ν(Ir–H) 2219; $\nu(CO)_{acac}$ 1585 and 1521; $\nu(CO)_{mvk}$ overlapped by $\nu(CO)_{acac}$. ^{1}H-NMR (300 MHz, C_6D_6): δ 11.56 (d, 1H, $J_{cis\ H-H} = 7.5$ Hz, IrCH=CH); 7.31 (d, 1H, $J_{cis\ H-H} = 7.5$ Hz, IrCH=CH); 5.22 (s, 1H, CH of acac); 2.10 (s, 3H, CH_3 of mvk); 1.83 and 1.75 (both s, 6H, CH_3 of acac); 2.2–1.0 (m, 33H, PCy_3); −24.03 (d, 1H, $J_{P-H} = 23.7$ Hz, IrH). $^{13}C\{^1H\}$-NMR (75.4 MHz, C_6D_6): δ 207.0 (s, CO of mvk); 199.6 (d, $J_{P-C} = 15.0$ Hz, IrCH=CH); 184.4 and 184.1 (both s, CO of acac); 137.9 (d, $J_{P-C} = 3.2$ Hz, IrCH=CH); 100.7 (d, $J_{P-C} = 1.4$ Hz, CH of acac); 33.7 (d, $J_{P-C} = 31.8$ Hz, CH of PCy_3); 27.5 (d, $J_{P-C} = 6.1$ Hz, CH_3 of acac); 25.4 (s, CH_3 of acac); 23.7 (s, CH_3 of mvk); 28.9, 27.9, 27.8 and 26.9 (all s, CH_2 of PCy_3). $^{31}P\{^1H\}$-NMR (121.4 MHz, C_6D_6): δ 13.0 (s; d off-resonance). MS (FAB+): $m/z = 641$ ($M^+ - 1$).

4.3. Preparation of *Ir(acac)H{(E)(CH=CHC(O)CH₃}(PCy₃)₂* (**4**)

A solution of **2** (300 mg, 0.47 mmol) in 15 ml of benzene was treated with PCy_3 (143 mg, 0.51 mmol) and stirred for 7 days at 70°C. During this time the color turned from orange to brown. The solution was concentrated to ca. 1 ml and chromatographed on alumina neutral (activity grade V). THF eluted a brown fraction from which the solvent was removed in vacuo affording a brown solid. The precipitate was washed twice with 2 ml of methanol yielding a white solid. Yield: 340 mg (78%). Anal. Calcd. for $C_{45}H_{79}IrO_3P_2$: C, 58.60; H, 8.63. Found: C, 58.51; H, 8.25. IR (KBr, cm^{-1}): ν(Ir–H) 2243; $\nu(CO)_{mvk}$ 1639; $\nu(CO)_{acac}$ 1590 and 1517. ^{1}H-NMR (300 MHz, C_6D_6): δ 10.91 (d, 1H, $J_{trans\ H-H} = 16.5$ Hz, IrCH=CH); 6.48 (d, 1H, $J_{trans\ H-H} = 16.5$ Hz, IrCH=CH); 5.23 (s, 1H, CH of acac); 2.33 (s, 3H, CH_3 of mvk); 1.84 and 1.68 (both s, 6H, CH_3 of acac); 2.1–1.1 (m, 66H, PCy_3); −24.46 (t, 1H, $J_{P-H} = 16.2$ Hz, IrH). $^{13}C\{^1H\}$-NMR (75.4 MHz, C_6D_6): δ 193.1 (s, CO of mvk); 186.5 and 184.0 (both s, CO of acac); 160.5 (t, $J_{P-C} = 7.4$ Hz, IrCH=CH); 141.1 (s, IrCH=CH); 103.2 (s, CH of acac); 32.8 (vt, $N = 24.4$ Hz, CH of PCy_3); 29.9 and 28.5 (both s, CH_3 of acac); 29.0 and 28.8 (both s, CH_2 of PCy_3); 28.2–28.0 (CH_2 of PCy_3); 25.4 (s, CH_3 of mvk). $^{31}P\{^1H\}$-NMR (121.4 MHz, C_6D_6): δ 14.0 (s; d off-resonance). MS (FAB$^+$): $m/z = 923$ ($M^+ + 1$).

4.4. Preparation of *[Ir(acac)H{η²-CH₂=CHC(O)CH₃}(PCy₃)]BF₄* (**5**)

A suspension of **2** (160 mg, 0.25 mmol) in diethyl ether (15 ml) was cooled to −78°C and treated with HBF_4 (34 μl, 0.25 mmol). The suspension was stirred for 30 min and the color changed from orange to brown. The solid was washed three times with 2 ml of cold diethyl ether and dried in vacuo to obtain **4** as a white solid. Yield 130 mg (71%). Anal. Calcd. for

$C_{27}H_{47}BF_4IrO_3P$: C, 44.44; H, 6.49. Found: C 44.33; H, 6.98. IR (KBr, cm^{-1}): ν(Ir–H) 2232; $\nu(CO)_{mvk}$ 1686; $\nu(CO)_{acac}$ 1583 and 1523; $\nu(BF_4)$ 1061. ^{1}H-NMR (300 MHz, CD_2Cl_2, 213 K): δ 5.63 (s, 1H, CH of acac); 4.54 (dd, 1H, $J_{trans\ H-H} = 12.1$ Hz, $J_{cis\ H-H} = 6.0$ Hz, =CH); 4.10 (dd, 1H, $J_{trans\ H-H} = 12.1$ Hz, $J_{P-H} = 2.7$ Hz, $=CH_2$); 3.63 (d, 1H, $J_{cis\ H-H} = 6.0$ Hz, $=CH_2$); 2.44 (s, 3H, CH_3 of mvk); 2.05 and 2.01 (both s, 6H, CH_3 of acac); 2.5–1.1 (m, 33H, PCy_3); −17.19 (d, 1H, J_{P-H} = 18.0 Hz, IrH). ^{13}C{^{1}H}-NMR (75.4 MHz, CD_2Cl_2, 213 K): δ 214.0 (s, CO of mvk); 187.7 and 185.3 (both s, CO of acac); 102.1 (s, CH of acac); 52.9 (s, =CH); 36.2 (s, CH_3 of mvk); 34.5 (d, J_{P-C} = 34.7 Hz, CH of PCy_3); 30.5–26.7(CH_2 of PCy_3); 29.6 and 27.9 (both s, CH_3 of acac); 24.8 (s, $=CH_2$). ^{31}P{^{1}H}-NMR (121.4 MHz, CD_2Cl_2, 213 K): δ 7.4 (s; d off-resonance).

4.5. Preparation of *[Ir(acac){$CH_2CH_2C(O)CH_3$}($NCCH_3$)(PCy_3)]BF_4* (**6**)

A suspension of **5** (100 mg, 0.14 mmol) in 15 ml of diethyl ether was cooled to −78°C and treated with acetonitrile (9 μl, 0.15 mmol). After 5 min at low temperature the suspension was allowed to warm to room temperature and stirred 40 min. The color was clearer and the white precipitate was decanted, washed with diethyl ether (4 × 2 ml) and dried in vacuo. Yield 98 mg (91%). Anal. Calcd. for $C_{29}H_{50}NBF_4IrO_3P$: C, 45.19; H, 6.54. Found: C 45.15; H, 6.83. IR (KBr, cm^{-1}): ν(CN) 2239; $\nu(CO)_{mvk}$ 1630; $\nu(CO)_{acac}$ 1587 and 1514; $\nu(BF_4)$ 1060. ^{1}H-NMR (300 MHz, CD_2Cl_2): δ 5.48 (s, 1H, CH of acac); 2.95 (m, 2H, $IrC\underline{H}_2CH_2$); 2.73 (s, 3H, $NCC\underline{H}_3$); 2.65 (m, 2H, $IrCH_2C\underline{H}_2$) 2.43 (s, 3H, CH_3 of mvk); 2.07 and 1.81 (both s, 6H, CH_3 of acac); 2.0–1.1 (m, 33H, PCy_3). ^{13}C{^{1}H}-NMR (75.4 MHz, CD_2Cl_2): δ 236.2 (d, $J_{P-C} = 3.2$ Hz, CO of mvk); 189.7 and 184.7 (both s, CO of acac); 120.3 (s, $N\underline{C}CH_3$); 102.0 (d, $J_{P-C} = 3.2$ Hz, CH acac); 52.5 (s, $IrCH_2\underline{C}H_2$); 34.9 (d, $J_{P-C} = 31.3$ Hz, CH of PCy_3); 28.7, 28.1, 27.8 and 26.5 (all s, CH_2 of PCy_3); 28.6 and 28.0 (both s, CH_3 of acac); 26.9 (s, CH_3 of mvk); 4.3 (s, $NC\underline{C}H_3$); −8.9 (d, $J_{P-C} = 5.6$ Hz, $Ir\underline{C}H_2CH_2$). ^{31}P{^{1}H}-NMR (121.4 MHz, CD_2Cl_2): δ −4.3 (s).

Acknowledgements

We thank the DGICYT (Projects PB 94-1186 and PB 95-0806, Programa de Promoción General del Conocimiento) for financial support and R. Castarlenas thanks the Ministerio de Educación y Ciencia of Spain for a grant.

References

[1] P.O. Stoutland, R.G. Bergman, J. Am. Chem. Soc. 110 (1988) 5732.
[2] J. Silvestre, M.J. Calhorda, R. Hoffman, P.O. Stoutland, R.G. Bergman, Organometallics 5 (1986) 1841.
[3] M.V. Baker, L.D. Field, J. Am. Chem. Soc. 108 (1986) 7433.
[4] D.M. Haddleton, R.N. Perutz, J. Chem. Soc., Chem. Commun., (1986) 1734.
[5] S.T. Belt, S.B. Duckett, D.M. Haddleton, R.N. Perutz, Organometallics 8 (1989) 748.
[6] T.W. Bell, D.M. Haddleton, A. McCamley, M.G. Partridge, R.N. Perutz, H. Willner, J. Am. Chem. Soc. 112 (1990) 9212.
[7] M. Schulz, H. Werner, Organometallics 11 (1992) 2790.
[8] P.E. Siegbahn, M.R.A. Blomberg, M. Svenson, J. Am. Chem. Soc. 115 (1993) 1952.
[9] H. Werner, T. Dirnberger, M. Schulz, Angew. Chem. Int. Ed. Engl. 27 (1988) 948.
[10] C.K. Ghosh, J.K. Hoyano, R. Krentz, W.A.G. Graham, J. Am. Chem. Soc. 111 (1989) 5480.
[11] M.J. Fernandez, M.J. Rodriguez, L.A. Oro, F.J. Lahoz, J. Chem. Soc. Dalton Trans. (1989) 2073.
[12] Y. Alvarado, O. Boutry, E. Gutierrez, A. Monge, M.C. Nicasio, M.L. Poveda, P.J. Perez, C. Ruiz, C. Bianchini, E. Carmona, Chem. Eur. J. 6 (1997) 860.
[13] O. Boutry, E. Gutierrez, A. Monge, M.C. Nicasio, P. Perez, E. Carmona, J. Am. Chem. Soc. 114 (1992) 7288.
[14] E. Gutierrez, A. Monge, M.C. Nicasio, M.L. Poveda, E. Carmona, J. Am. Chem. Soc. 116 (1994) 791.
[15] M.A. Esteruelas, F.J. Lahoz, E. Oñate, L.A. Oro, L. Rodriguez, Organometallics 15 (1996) 823.
[16] L.A. Oro, D. Carmona, M.A. Esteruelas, C. Foces-Foces, F.H. Cano, J. Organomet. Chem. 307 (1986) 83.
[17] H. Werner, Angew. Chem. Int. Ed. Engl. 22 (1983) 927.
[18] M.A. Esteruelas, A.M. López, N. Ruiz, J.I. Tolosa, Organometallics 16 (1997) 4657.
[19] M.A. Esteruelas, F.J. Lahoz, E. Oñate, L.A. Oro, L. Rodriguez, P. Steinert, H. Werner, Organometallics 15 (1996) 3436.
[20] W.D. Jones, F.J. Feher, Acc. Chem. Res. 22 (1989) 91.
[21] B. Papenfuhs, N. Mahr, H. Werner, Organometallics 12 (1993) 4244.
[22] P.P. Deutsch, R. Eisenberg, J. Am. Chem. Soc. 112 (1990) 714.
[23] P.P. Deutsch, R. Eisenberg, Organometallics 9 (1990) 709.
[24] B.P. Cleary, R. Mehta, R. Eisenberg, Organometallics 14 (1995) 2297.
[25] H. Werner, M.A. Esteruelas, H. Otto, Organometallics 5 (1986) 2295.
[26] H. Werner, R. Weinand, H. Otto, J. Organomet. Chem. 307 (1986) 49.
[27] H. Werner, U. Meyer, K. Peters, H.G. von Schnering, Chem. Ber. 122 (1989) 2097.
[28] M.A. Esteruelas, F.J. Lahoz, J.A. Lopez, L.A. Oro, C. Schülnken, C. Valero, H. Werner, Organometallics 11 (1992) 2034.
[29] M.A. Esteruelas, F.J. Lahoz, E. Oñate, L.A. Oro, L. Rodriguez, Organometallics 14 (1995) 263.