$[IrCp^*(NCMe)_2(PPh_2Me)][PF_6]_2$ as Catalyst for the Meyer–Schuster Rearrangement of Aryl Propargylic Alcohols under Mild Conditions.

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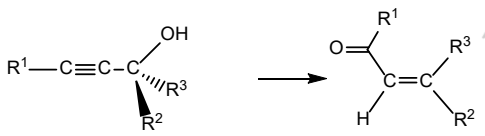
Abstract: The novel iridium complex $[IrCp^*(NCMe)_2(PPh_2Me)][PF_6]_2$ (**I**) efficiently catalyzes the Meyer–Schuster rearrangement of selected aryl propargylic alcohols into α,β-unsaturated aldehydes under mild conditions and without the need of a cocatalyst. A mechanism involving a (hydroxy)alkenylcarbene intermediate is proposed.

Introduction

Propargylic alcohols are organic substrates with a wide range of applications from synthesis to catalytic reactions[1] which make them very attractive as organic synthons.[2]
The isomerization of propargylic alcohols to α,β-unsaturated carbonyl compounds is a typical example of atom economic processes where no secondary products are generated: it formally involves the 1,3–shift of the hydroxy moiety, followed by tautomerization (Meyer–Schuster rearrangement, Scheme 1).



Scheme 1. Meyer–Schuster Rearrangement of Propargylic Alcohols.

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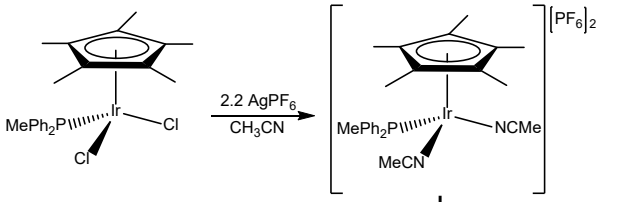
α,β-Unsaturated carbonyl compounds represent an interesting class of organic molecules because undergo typical reactions of alkenes and carbonyl compounds, are valuable building blocks in organic synthesis and are important intermediates in the production of natural products of biological or pharmaceutical application.[3] The traditional synthesis of α,β-unsaturated carbonyl compounds, for example aldol-like condensations, are generally multistep sequences not endowed with atom economy. Thus, the quest for catalytic atom efficient protocols running at lower temperature and under generally milder conditions are of interest for both academia and industry. A possible answer to these requirements is the Meyer–Schuster rearrangement of propargylic alcohols, which has been reported to be efficiently catalyzed by different systems such as rhenium(I) and silver(I) complexes containing iminophosphorane-phosphane ligands, copper (I)–diaryliodonium salts, rhodium(I) complexes with bidentate phosphane ligands (*rac*-BINAP, dppe, or dcpe) and allyl-ruthenium(II) and rhenium(V)-oxo complexes.[4] A drawback of this catalytic method is however the need of relatively high temperatures (323–433 K) and/or the use of acid medium.[4]
We have recently reported on the reactions of $[IrCp^*Cl(NCMe)(L)][PF_6]$ (L = PMe_3, PPh_2Me) with propargylic alcohols.[5,6] The (methoxy)alkenylcarbene complexes obtained undergo a cyclometallation reaction yielding iridacycles with different ring members.[6] Following on our interest in the organometallic reactivity of these species, and in order to understand the mechanism of these reactions we synthesized the complex $[IrCp^*(NCMe)_2(PPh_2Me)][PF_6]_2$ (**I**) and studied its reactivity with different propargylic alcohols. Unexpectedly **I** resulted to be a good catalyst for propargylic alcohols isomerization by Meyer–Schuster rearrangement. A wider scope of the catalyst was studied using a small library of propargylic alcohols. Interestingly, it was possible to run the catalytic reactions under very mild temperature conditions with good to excellent conversions. A mechanistic interpretation is also proposed based on NMR studies on stoichiometric reactions.

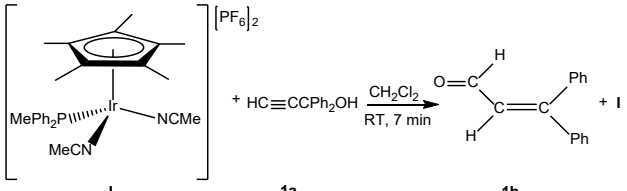
Results and Discussion

$[IrCp^*(NCMe)_2(PPh_2Me)][PF_6]_2$ (I) as Propargylic Alcohols Isomerization Catalyst.
Complex **I** was easily synthesized as shown in the eq 1. Experimental conditions and characterization data for **I** are reported in the Experimental Section.



(1)

At first, we studied the stoichiometric reaction of **I** with the 1,1-diphenyl-2-propyn-1-ol (**1a**) in dichloromethane at room temperature. To our surprise, instead of the expected formation of a well-defined organometallic derivative, quantitative yield of 3,3-diphenylpropenal (**1b**) was obtained together with **I** (eq. 2).



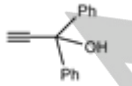
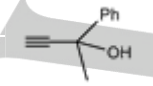
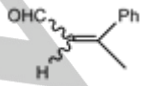
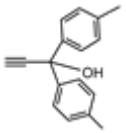
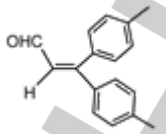
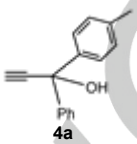
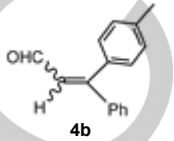
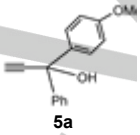
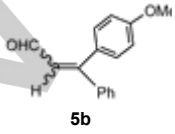
(2)

In order to check whether this reaction could occur under catalytic conditions, **1a** and **I** (5 mol %) were dissolved in 0.6 mL of CD_2Cl_2 and transferred into an NMR tube. After two hours at room temperature, total conversion to **1b** was observed (Table 1, entry 1). Lowering the catalyst loading to 1 mol % and running the reaction for 24 h gave a maximum conversion of ca. 70%.

The scope of the reaction was extended to a series of different substituted propagylic alcohols (**2a**–**5a**). The results, summarized in Table 1, showed that the corresponding aldehydes (**2b**–**5b**) were obtained in good yields under very mild conditions (RT, 5 mol % of **I**). Higher conversions could be obtained in most of the cases by increasing the amount of catalyst to 10 mol %.

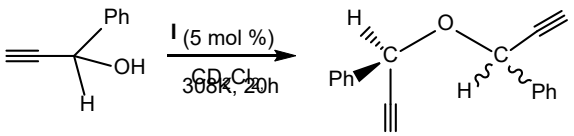
It is important to highlight that: *i)* all the reactions shown in Table 1 took place at room temperature and in absence of any cocatalyst unlike other examples reported,[4] *ii)* analytically pure aldehydes could be isolated from the reaction mixture by simple extraction with diethyl ether from the oily residue obtained after removal of the reaction solvent under vacuum and purification through silica column.

Table 1. Meyer–Schuster Rearrangement of a Small Library of Propargylic Alcohols Catalyzed by $[IrCp^*(NCMe)_2(PPh_2Me)][PF_6]_2$ (**I**) [a].

Entry	Substrate	Product	t(h)	Yield[c]	E:Z
1	 **1a**	 **1b**	2	99%(94%)	
2	 **2a**	 **2b**	24	80%(73%)	1:3
3[b]	**2a**	**2b**	24	96%(90%)	1:3
4	 **3a**	 **3b**	24	80%(70%)	
5[b]	**3a**	**3b**	4	97%(92%)	
6	 **4a**	 **4b**	24	88%(84%)	1:1.2
7[b]	**4a**	**4b**	4	95%(86%)	1:1
8	 **5a**	 **5b**	24	92%(80%)	1.2:1
9[b]	**5a**	**5b**	24	92%(80%)	1.2:1

All isomerization reactions were monitored by ^1H NMR. [a] The reactions were performed in NMR tube, at RT in CD_2Cl_2 and with a ratio [substrate]/[**I**] = 20. [b] [substrate]/[**I**] = 10. [c] Yields determinated by ^1H NMR spectroscopy; the yields of the isolated products (after purification) are given in brackets.

A different behavior was observed for propargylic alcohols 1-phenyl-2-propyn-1-ol (**6a**), 1-(4-nitrophenyl)-1-phenyl-2-propyn-1-ol (**7a**) and 3-butyn-1-ol (**8a**). Instead of the corresponding α,β-unsaturated aldehyde, the treatment of **6a** with **I** (5 mol %) in CD_2Cl_2 at moderate temperature (308 K) gave the diastereomeric mixture of the dipropargyl ether **6b** (eq. 3) in low conversion (~25%, estimated by NMR).



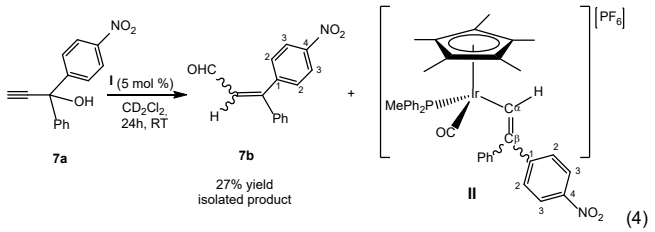
6a **6b**

25% conversion
(estimated by NMR)

(3)

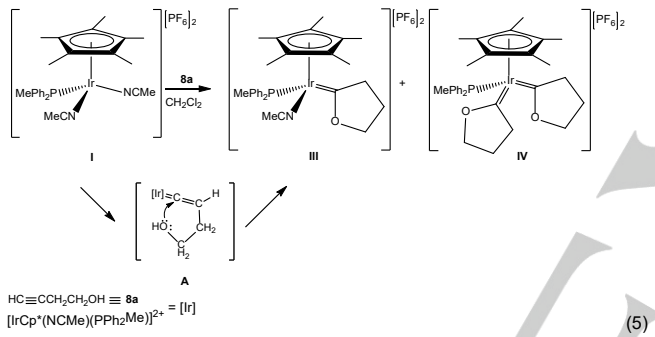
Interestingly, in the case of the reaction of **7a** with **I** (eq. 4), the isomerization reaction occurred giving the corresponding mixture of aldehyde **7b** as E:Z isomers (~1.2:1 mole ratio estimated by NMR) in low conversion (27% of the isolated isomers) together with the carbonyl complex $[IrCp^*\{CH=C(p\text{–}NO_2\text{–}C_6H_4)(Ph)\}(CO)(PPh_2Me)][PF_6]$ (**II**) (~1:1 mole ratio of the *cis*, *trans* isomers on the Cα–Cβ, estimated by NMR). The formation of compound **II** can be explained through decarbonylation of the "acyl intermediate" **D** (Scheme 2). **7b** and **II** were separated from

the reaction mixture, isolated and fully characterized (Experimental Section).



(4)

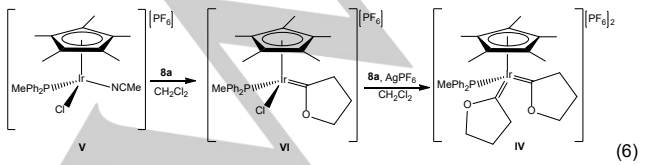
Finally, when **8a** was treated with **I** under the standard conditions described above (Table 1). The reaction was repeated in stoichiometric conditions, and in this case it was possible to obtain the oxacyclocarbene complexes $[IrCp^*\{=\overline{CO(CH_2)_2CH_2}\}(NCMe)(PPh_2Me)][PF_6]_2$ (**III**) and $[IrCp^*\{=CO(CH_2)_2CH_2\}_2(PPh_2Me)][PF_6)_2$ (**IV**) in a ~3:1 mole ratio (estimated by NMR), respectively (eq. 5).



(5)

The formation of the cyclic carbene ligand in **III** and **IV** from 3-butyn-1-ol (**8a**) can be explained from the formation of a hydroxyvinylidene intermediate **A** which undergoes an intramolecular nucleophilic attack of the alcohol functionality at metal-coordinated vinylidene carbon atom. The formation of hydroxyvinylidene intermediates from propargylic alcohols is well known in literature. [7]

A slightly different behavior was observed by repeating the latter reaction with the monoacetonitrile complex analogue of **I**, $[IrCp^*Cl(NCMe)(PPh_2Me)][PF_6]$ (**V**). In this case, formation of the oxacyclocarbene complex $[IrCp^*Cl\{=\overline{CO(CH_2)_2CH_2}\}(PPh_2Me)][PF_6]$ (**VI**) was obtained, and upon treatment with $AgPF_6$ and **8a** the aforementioned complex **IV** was obtained (eq. 6). Compounds **III, IV, VI** were fully characterized (Experimental Section).

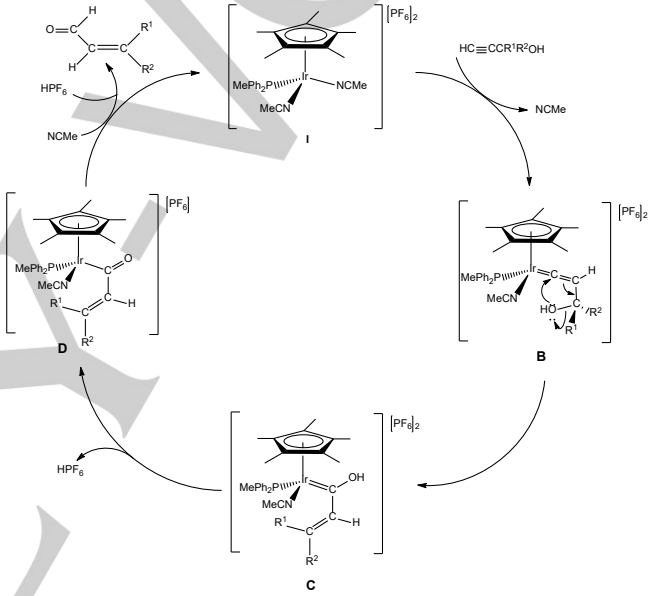


(6)

In order to establish further the scope of this method to alkyl propargylic alcohols, 2-methyl-3-butyn-2-ol, 3-methyl-1-pentyn-3-ol, 3-ethyl-1-pentyn-3-ol, 1-ethynyl-1-cyclopentanol and 1-ethynyl-1-cyclohexanol were tested as substrates under the conditions described above (Table 1). In all cases only decomposition products were observed, so the Meyer–Schuster rearrangement can not occur under these conditions.

Proposed Mechanism for the Meyer–Schuster Rearrangement Catalyzed by I.

Based on the experimental results and the formation of complexes **II** and **III**, the following mechanism can be proposed (Scheme 2).



Scheme 2. Proposed Mechanism for the Meyer–Schuster Rearrangement Catalyzed by **I**.

The first step involves decoordination of one acetonitrile ligand followed by coordination of the substrate to give a vinylidene intermediate **B**. Then, intramolecular nucleophilic attack of the OH group on the α-carbon of the vinylidene ligand give the (hydroxy)alkenylcarbene complex **C**. Upon tautomerization, **C** transforms into the acyl complex **D** which eliminates the corresponding aldehyde through a demetallation process regenerating the catalyst **I**.

This mechanism proposal differs to what suggested by Gimeno *et al.*[4g] based on the formation of an allenylidene intermediate by dehydration of the (hydroxy)vinylidene complex, with the subsequent readdition of water on α-carbon of the allenylidene ligand to give a (hydroxy)alkenylcarbene.

To further validate our working hypothesis, our catalytic reactions were carried out in the presence of molecular sieves as drying agent, in order to ensure that the water is not involved in our reactions. The Meyer–Schuster rearrangement products are also formed with the same yields as in the original experiments (Table

1). This result indicates the absence of an allenylidene intermediate in our reactions because the presence of the drying agent precludes the formation of the (hydroxyl)alkenylcarbene by addition of water (to the allenylidene moiety).

An indirect proof of the conversion of **B** to **C** is the formation of the oxacyclocarbene **III**, which was obtained through an intramolecular attack of the hydroxy group on the α-carbon (eq. 5), while the formation of the acyl complex **D** is compatible with the reactivity observed to give product **II**. The formation of an Ir–carbonyl complex via an acyl complex, which was previously observed by us,[5] may be probably linked to catalyst deactivation as it prevents the regeneration of **I** lowering the reaction yield as in the case of the catalytic runs using **7a**. This reactivity can be due to the electron-withdrawing effect of the -NO_2 substituent on phenyl group because when a π donor (-OMe) or a weak electron-donor (-Me) are the substituents on phenyl group, the Ir–carbonyl complex was not formed.

Conclusions

In this work, we have synthesized the new iridium complex $[IrCp^*(NCMe)_2(PPh_2Me)][PF_6]_2$ (**I**) which was used as homogeneous catalyst for the Meyer–Schuster rearrangement of propargylic alcohols without the need of a cocatalyst working at room temperature with good yields in of the corresponding aldehydes. Whereas the catalytic protocol is efficient for aryl substrates, in the case of $HC{\equiv}CCR^1R^2OH$, where both R are not phenyl groups, no activity was observed.

A mechanistic proposal involving the formation of a (hydroxy)alkenylcarbene intermediate arising from the intramolecular attack of the OH group to α–carbon of the vinylidene formed in the first step of the catalytic cycle, is proposed. The (hydroxy)alkenylcarbene evolves to an acyl complex to finally releases the α,β-unsaturated aldehyde.

Experimental Section

All experiments were carried out under an atmosphere of argon by Schlenk techniques. Solvents were dried by the usual procedures[8] and distilled under argon prior to use. The starting materials $[IrCp^*Cl_2(PPh_2Me)]$[9] and $[IrCp^*Cl(NCMe)(PPh_2Me)]PF_6$ (**V**)[5] were prepared as described in the literature. All reagents were obtained from commercial sources except for propargylic alcohols **3a**, **4a**, **5a** and **7a** which were synthesized following the method described by Mantovani et al.[10] Aldehydes **1b**[4g], **2b**[11], **5b**[12] and dipropargyl ether **6b**[13] were identified by comparison with the spectroscopic data reported in the literature. Unless stated, NMR spectra were recorded at room temperature on a Bruker ARX–400 instrument, with resonating frequencies of 400 MHz (^{1}H), 161 MHz (^{31}P{^{1}H}), and 100 MHz (^{13}C{^{1}H}) using the solvent as the internal lock. ^{1}H and ^{13}C{^{1}H} signals are referred to internal TMS and those of ^{31}P{^{1}H} to 85% H_3PO_4; downfield shifts (expressed in ppm) are considered positive. ^{1}H and ^{13}C{^{1}H} NMR (or JMOD) signal assignments were confirmed by {^{1}H, ^{1}H} COSY, {^{1}H, ^{1}H} NOESY, {^{1}H,^{13}C} HSQC, {^{1}H,^{13}C} HMBC and DEPT experiments. Coupling constants are given in hertz. Infrared spectra were run on a Jasco FT/IR–6100 spectrometer using KBr pellets. C, H, and N analyses were carried out with a Carlo Erba 1108 analyzer. Mass spectra were acquired using an Apex–Qe spectrometer by high resolution electrospray technique for organometallic complexes and high and low resolution electron impact technique for organic compounds.

Preparation of $[IrCp^*(NCMe)_2(PPh_2Me)][PF_6]_2$ (I)

An orange solution of $[IrCp^*Cl_2(PPh_2Me)]$ (500 mg, 0.83 mmol) in acetonitrile (35 mL) was treated with silver (I) hexafluorophosphate (465 mg, 1.84 mmol). The reaction mixture was stirred for 5 min at room temperature, and then was decanted and filtered to give a yellow solution. Solvent was removed under vacuum and the solid obtained was redissolved in dichloromethane. The solution was filtered through Celite® and the solvent was removed under vacuum to yield a yellow solid that was washed with diethyl ether (3 x 5 mL) and vacuum-dried. Yield: 450 mg (60%).

IR (cm^{-1}): *v* (CN) 2329 and 2301 (w); (PF_6) 837 (s). ^{1}H NMR (CD_2Cl_2): δ 7.65–7.60 (m, 6H, P*Ph*$_2$CH$_3$); 7.55–7.47 (m, 4H, P*Ph*$_2$CH$_3$); 2.59 (d, $^5J_{HP}$ = 1.1 Hz, 6H, NCC*H*$_3$); 2.47 (d, $^2J_{HP}$ = 10.6 Hz, 3H, PPh$_2$C*H*$_3$); 1.66 (d, $^4J_{HP}$ = 2.5 Hz, 15H, C$_5$(C*H*$_3$)$_5$) ppm. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ –8.85 (s, *P*Ph$_2$CH$_3$); –144.13 (sept, $^1J_{PF}$ = 710.7 Hz, *P*F$_6$) ppm. ^{13}C{^{1}H} NMR (CD_2Cl_2): δ 133.1 (s, 1C P*Ph*$_2$Me); 132.3 (d, $^3J_{CP}$ = 9.9 Hz, 2C PPh$_2$Me); 129.9 (d, $^2J_{CP}$ = 11.1 Hz, 2C P*Ph*$_2$Me); 127.5 (d, $^1J_{CP}$ = 58.2 Hz, 2C *C*$_{ipso}$); 98.1 (s, *C*$_5$(CH$_3$)$_5$); 124.5 (s, NC*C*H$_3$); 12.5 (d, $^1J_{CP}$ = 40.3 Hz, PPh$_2$*C*H$_3$); 8.8 (s, C$_5$(*C*H$_3$)$_5$); 4.0 (s, NC*C*H$_3$) ppm.

General Procedure for the Catalytic Isomerization of Propargylic Alcohols into α,β-Unsaturated Aldehydes.

In an NMR tube the catalyst (5 mg, 0.006 mmol) was dissolved under an argon atmosphere in CD_2Cl_2 (0.6 mL). After that, the corresponding propargylic alcohol (0.12 mmol) was added and the reaction mixture was left at room temperature for the chosen time (see Table 1). Solvent was removed under vacuum and the corresponding aldehyde was extracted from the obtained oil with diethylether and purified through a silica column using hexane/AcOEt (4:1) as eluent.

3,3-di-*p*-tolylacrylaldehyde (3b)

IR (cm^{-1}): *v* (CO) 1661 (s). MS (m/z, referred to the most abundant isotopes): m/z: 237.1239 [M+1]$^+$; 236.1202 [M]; 221.10 [M–CH$_3$]$^+$. ^{1}H NMR (CD_3Cl): δ 9.50 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C*H*O); 7.28–7.21 (m, 4H, *Ph*); 7.21–7.14 (m, 4H, *Ph*); 6.45 (d, $^3J_{HH}$ = 7.9 Hz, 1H, =C*H*); 2.42 (s, 3H, C*H*$_3$); 2.37 (s, 3H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (CD_3Cl): δ 193.9 (s, *C*HO); 162.7 (s, =*C*); 141.1 (s, *C*–CH$_3$); 139.8 (s, *C*–CH$_3$); 137.3 (s, *C*$_{ipso}$); 134.1 (s, *C*$_{ipso}$); 131.0 (s, 2C, *Ph*); 129.5 (s, 2C *Ph*); 129.1 (s, 2C, *Ph*); 128.9 (s, 2C, *Ph*); 126.6 (s, =*C*H); 21.5 (s, 2C *C*H$_3$) ppm.

(*Z,E*)-3-phenyl-3-(*p*-tolyl)acrylaldehyde (4b)

IR (cm^{-1}): *v* (CO) 1666 (s). MS (m/z, referred to the most abundant isotopes): m/z: 223.1076 [M+1]$^+$; 222.1042 [M]; 207.06 [M–CH$_3$]$^+$; 178.06 [M–CH$_3$–CHO]$^+$.

Z-isomer: ^{1}H NMR (CD_3Cl): δ 9.55 (d, $^3J_{HH}$ = 7.9 Hz, 1H, C*H*O); 7.39–7.34 (m, 4H, *Ph*); 7.34–7.29 (m, 1H, *Ph*); 7.23–7.16 (m, 4H, *Ph*–CH$_3$); 6.57 (d, $^3J_{HH}$ = 7.9 Hz, 1H, =C*H*); 2.39 (s, 3H, C*H*$_3$) ppm. ^{13}C{^{1}H} NMR (CD_3Cl): δ 193.8 (s, *C*HO); 162.4 (s, =*C*); 139.9 (s, *C*–CH$_3$); 137.0 (s, *C*$_{ipso}$–Ph–CH$_3$); 133.9 (s, *C*$_{ipso}$–Ph); 131.0–128.4 (all s, *Ph* + *Ph*–CH$_3$); 127.3 (s, =CH); 21.5 (s, *C*H$_3$) ppm.

E-isomer: ^{1}H NMR (CD_3Cl): δ 9.51 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C*H*O); 7.51–7.39 (m, 4H, *Ph*); 7.34–7.29 (m, 1H, *Ph*); 7.29–7.23 (m, 4H, *Ph*–CH$_3$); 6.60 (d,

$^3J_{HH}$ = 8.0 Hz, 1H, =C*H*); 2.44 (s, 3H, CH_3); ppm. $^{13}C\{^1H\}$ NMR (CD_3Cl): *δ* 193.8 (s, *C*HO); 162.6 (s, =*C*); 141.2 (s, *C*–CH_3); 137.0 (s, C_{ipso}–Ph–CH_3); 137.0 (s, C_{ipso}–Ph); 131.0–128.4 (all s, *Ph* + *Ph*–CH_3); 126.7 (s, =*C*H); 21.5 (s, *C*H_3) ppm.

(*Z,E*)-3-phenyl-3-(*p*-nitrophenyl)acrylaldehyde (7b)

After 2 days at room temperature, the solvent was removed under vacuum and the organic fraction was extracted from the obtained oil with diethylether, a mixture of **7a** and **7b** (~70:30 mole ratio estimated by NMR, respectively). Thus, they were separated and purified through a silica column using, in this case, hexane/AcOEt (9:1) as eluent. The mixture of E and Z isomers of **7b** was obtained in a ~1.2:1 mole ratio (estimated by NMR), respectively. Yield (isolated isomers mixture): 16.3 mg (27%).

IR (cm^{-1}): *v* (CO) 1663 (s); (NO_2) 1518 (s) and 1347 (s).

Z-isomer: ^1H NMR (CD_3Cl): *δ* 9.49 (d, $^3J_{HH}$ = 8.0 Hz, 1H, C*H*O); 8.26–8.20 (m, 2H, C^3*H*); 7.56–7.48 (m, 2H, C^2*H*); 7.48–7.44 (m, 1H, *Ph*); 7.34–7.27 (m, 4H, *Ph*); 6.69 (d, $^3J_{HH}$ = 8.0 Hz, 1H, =C*H*) ppm. $^{13}C\{^1H\}$ NMR (CD_3Cl): *δ* 192.1 (s, *C*HO); 159.4 (s, =*C*); 148.5 (s, *C*^{4}); 143.4 (s, *C*^{1}); 138.5 (s, C_{ipso}–Ph); 131.6–128.2 (all s, *Ph* + *C*^{2}); 129.1 (s, =*C*H); 124.0 (s, *C*^{3}) ppm.

E-isomer: ^1H NMR (CD_3Cl): *δ* 9.59 (d, $^3J_{HH}$ = 7.7 Hz, 1H, C*H*O); 8.37–8.31 (m, 2H, C^3*H*); 7.56–7.48 (m, 2H, C^2*H* + *Ph*); 7.44–7.37 (m, 2H, *Ph*); 6.62 (d, $^3J_{HH}$ = 7.7 Hz, 1H, =C*H*) ppm. $^{13}C\{^1H\}$ NMR (CD_3Cl): *δ* 192.9 (s, *C*HO); 159.4 (s, =*C*); 148.8 (s, *C*^{4}); 146.1 (s, *C*^{1}); 135.6 (s, C_{ipso}–Ph); 131.6–128.2 (all s, *Ph* + *C*^{2}); 130.3 (s, =*C*H); 123.8 (s, *C*^{3}) ppm.

[IrCp*{CH=C(*p*–NO_2–C_6H_4)(Ph)}(CO)(PPh_2Me)]PF_6 (II)

From the previous experiment, the remaining solid after the extraction of **7a** and **7b** was washed with pentane (2 mL) and dried in vacuum yielding a mixture of the two isomers *cis*- and *trans*- (~1:1 mole ratio of the *cis*, *trans* isomers on the C*α*–C*β*, estimated by NMR, respectively). Yield (isolated isomers mixture): 5.3 mg (95%).

IR (cm^{-1}): *v* (CO) 2029 (s); (PF_6) 841 (s). MS (m/z, referred to the most abundant isotopes): m/z: 780 $[M]^+$. Anal. Calcd for $C_{38}H_{39}O_3NF_6IrP_2$ (926 g/mol): C 49.30, H 4.25, N 1.51; found: C 49.51, H 4.33, N 1.60.

Cis: ^1H NMR (CD_2Cl_2): *δ* 8.07 (d, 2H, $^3J_{HH}$ = 8.7 Hz, C^3*H*); 7.61–7.74 (m, 2H, P*Ph*$_2$CH$_3$); 7.39–7.56 (m, 5H, P*Ph*$_2$CH$_3$); 7.20–7.34 (m, 6H, *Ph* + P*Ph*$_2$CH$_3$); 7.18 (d, 1H, $^3J_{HP}$ = 8.6 Hz, C$_α$*H*); 7.07 (d, 2H, $^3J_{HH}$ = 8.4 Hz, *Ph*); 6.57 (d, 2H, $^3J_{HH}$ = 8.5 Hz, C^2*H*); 2.37 (d, 3H, $^2J_{HP}$ = 10.5 Hz, PPh$_2$C*H*$_3$); 1.86 (d, 15H, $^4J_{HP}$ = 2.8 Hz, C$_5$(C*H*$_3$)$_5$) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): *δ* –14.92 (s, *P*PH$_2$CH$_3$); –144.49 (sept, $^1J_{PF}$ = 710.7 Hz, *P*F$_6$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): *δ* 166.5 (d, $^2J_{CP}$ = 13.7 Hz, *C*O); 152.7 (s, C$_β$); 150.6 (s, *C*^{1}); 147.5 (s, *C*^{4}); 143.3 (s, C_{ipso}); 126.6–133.6 (*Ph* + P*Ph*$_2$Me); 131.0 (s, 2C *C*^{2}); 124.0 (s, 2C *C*^{3}); 116.2 (d, $^2J_{CP}$ = 13.7 Hz, C$_α$); 104.2 (s, *C*$_5$(CH$_3$)$_5$); 12.4 (d, $^1J_{CP}$ = 43.8 Hz, PPh$_2$C*H*$_3$); 9.0 (s, C$_5$(C*H*$_3$)$_5$) ppm.

Trans: ^1H NMR (CD_2Cl_2): *δ* 8.10 (d, 2H, $^3J_{HH}$ = 8.7 Hz, C^3*H*); 7.63–7.74 (m, 4H, P*Ph*$_2$CH$_3$); 7.45 (d, 1H, $^3J_{HP}$ = 7.8 Hz, C$_α$*H*); 7.39–7.55 (m, 6H, P*Ph*$_2$CH$_3$); 7.22-7.34 (m, 5H, *Ph* + C^2*H*); 6.46 (d, 2H, $^3J_{HH}$ = 6.5 Hz, *Ph*); 2.40 (d, 3H, $^2J_{HP}$ = 10.5 Hz, PPh$_2$C*H*$_3$); 1.85 (d, 15H, $^4J_{HP}$ = 2.3 Hz, C$_5$(C*H*$_3$)$_5$) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): *δ* –14.51 (s, *P*PH$_2$CH$_3$); –144.49 (sept, $^1J_{PF}$ = 710.7 Hz, *P*F$_6$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): *δ* 165.2 (d, $^2J_{CP}$ = 12.9 Hz, *C*O); 150.4 (s, C$_β$); 149.6 (s, *C*^{1}); 146.6 (s, *C*^{4}); 144.8 (s, C_{ipso}); 126.6–133.6 (*Ph* + P*Ph*$_2$Me + *C*^{2}); 124.0 (s, 2C *C*^{3}); 122.4 (d, $^2J_{CP}$ = 13.6 Hz, C$_α$); 104.0 (s, *C*$_5$(CH$_3$)$_5$); 13.3 (d, $^1J_{CP}$ = 43.4 Hz, PPh$_2$CH$_3$); 9.0 (s, C$_5$(C*H*$_3$)$_5$) ppm.

Synthesis of [IrCp*{=CO(CH$_2$)$_2$CH$_2$)}(NCMe)(PPh_2Me)][PF_6]$_2$ (III)

To a yellow solution of **I** (150 mg, 0.18 mmol) in dichloromethane (10 mL), 3-butyn-1-ol (31 µL, 0.39 mmol) was added and the mixture was stirred for 18h at room temperature. The brown solution obtained was vacuum concentrated and a brown solid precipitated. This product was washed with diethyl ether (3 × 3 mL) and dried in vacuum. A mixture of complexes **III** and **IV** was obtained in a ~3:1 mole ratio (estimated by NMR), respectively. Yield (isolated mixture): 105 mg (~67% for **III**).

III: IR (cm^{-1}): *v* (CN) 2292 and 2328 (w); *v* (PF_6) 837 (s). ^1H NMR (CD_2Cl_2): *δ* 7.67–7.56 (m, 6H, P*Ph*$_2$CH$_3$); 7.51–7.42 (m, 2H, P*Ph*$_2$CH$_3$); 7.35–7.27 (m, 2H, P*Ph*$_2$CH$_3$); 5.49–5.46 (m, 1H, O–C*H*$_2$); 5.18–5.08 (m, 1H, O–C*H*$_2$); 3.01–2.86 (m, 1H, =C–C*H*$_2$); 2.83 (s, 3H, NCC*H*$_3$); 2.46 (d, $^2J_{HP}$ = 10.7 Hz, 3H, PPh$_2$C*H*$_3$); 2.16–2.09 (m, 1H, CH$_2$C*H*$_2$CH$_2$); 1.89–1.76 (m, 1H, =C–C*H*$_2$); 1.72 (d, $^4J_{HP}$ = 2.1 Hz, 15H, C$_5$(C*H*$_3$)$_5$); 1.72–1.60 (m, 1H, CH$_2$C*H*$_2$CH$_2$) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): *δ* –14.05 (s, *P*PH$_2$CH$_3$); –144.11 (sept, $^1J_{PF}$ = 711.1 Hz, *P*F$_6$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): *δ* 271.6 (d, $^2J_{CP}$ = 10.4 Hz, Ir=*C*); 133.6–130.0 (P*Ph*$_2$Me); 128.9 (d, $^1J_{CP}$ = 60.9 Hz, C_{ipso}); 127.7 (d, $^1J_{CP}$ = 59.2 Hz, C_{ipso}); 124.9 (s, NC*C*H$_3$); 102.1 (d, $^2J_{CP}$ = 1.6 Hz, *C*$_5$(CH$_3$)$_5$); 92.6 (s, O–*C*H$_2$); 57.0 (s, =C–*C*H$_2$); 21.0 (s, CH$_2$*C*H$_2$CH$_2$); 12.2 (d, $^1J_{CP}$ = 42.6 Hz, PPh$_2$*C*H$_3$); 8.9 (s, C$_5$(*C*H$_3$)$_5$); 4.5 (s, NC*C*H$_3$) ppm.

Synthesis of [IrCp*{=CO(CH$_2$)$_2$CH$_2$)}$_2$(PPh_2Me)][PF_6]$_2$ (IV)

To a yellow solution of **VI** (150 mg, 0.19 mmol) in dichloromethane (10 mL), 3-butyn-1-ol (18 µL, 0.23 mmol) was added, stirred 5 min and finally, silver (I) hexafluorophosphate (59 mg, 0.23 mmol) was added. The mixture was stirred for 2h and then, the clear brown solution obtained was filtered through Celite® and the solvent was removed under vacuum to yield a brown solid that was washed with diethyl ether (3 × 4 mL) and dried in vacuum. Yield (isolated product): 182 mg (73%).

IR (cm^{-1}): *v* (PF_6) 838 (s). MS (m/z, referred to the most abundant isotopes): m/z: 667.23287 $[M]^+$. Anal. Calcd for $C_{31}H_{40}O_2F_{12}IrP_3$ (957.78 g/mol): C 38.88, H 4.21; found: C, 39.21; H, 4.29. ^1H NMR (CD_2Cl_2): *δ* 7.67–7.54 (m, 6H, P*Ph*$_2$CH$_3$); 7.17–7.07 (m, 4H, P*Ph*$_2$CH$_3$); 5.33–5.25 (m, 2H, O–C*H*$_2$); 5.07–4.96 (m, 2H, O–C*H*$_2$); 3.14 (t, $^2J_{HP}$ = 7.5 Hz, 4H, =C–C*H*$_2$); 2.34 (d, $^2J_{HP}$ = 10.5 Hz, 3H, PPh$_2$C*H*$_3$); 2.25–2.15 (m, 2H, CH$_2$C*H*$_2$CH$_2$); 2.07–1.98 (m, 2H, CH$_2$C*H*$_2$CH$_2$); 1.77 (d, $^4J_{HP}$ =2.0 Hz, 15H, C$_5$(C*H*$_3$)$_5$) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): *δ* –10.27 (s, *P*Ph$_2$CH$_3$); –144.14 (sept, $^1J_{PF}$ = 711.4 Hz, *P*F$_6$) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): *δ* 266.2 (d, $^2J_{CP}$ = 9.4 Hz, Ir=*C*); 133.4 (d, $^4J_{CP}$ = 2.6 Hz, P*Ph*$_2$Me); 132.1 (d, $^3J_{CP}$ = 10.4 Hz, P*Ph*$_2$Me); 130.0 (d, $^2J_{CP}$ = 11.5 Hz, P*Ph*$_2$Me); 128.0 (d, $^1J_{CP}$ = 61.8 Hz, C_{ipso}); 106.3 (s, *C*$_5$(CH$_3$)$_5$); 90.6 (s, 2*C*, O–*C*H$_2$); 58.3 (s, 2*C*, =C–*C*H$_2$); 21.9 (s, 2*C*, CH$_2$*C*H$_2$CH$_2$); 15.5 (d, $^1J_{CP}$ = 43.6 Hz, PPh$_2$*C*H$_3$); 9.3 (s, C$_5$(*C*H$_3$)$_5$) ppm.

Synthesis of [IrCp*Cl{=CO(CH$_2$)$_2$CH$_2$)}(PPh_2Me)]PF_6 (VI)

To a yellow solution of **V** (150 mg, 0.20 mmol) in methanol (15 mL), 3-butyn-1-ol (17.5 µL, 0.22 mmol) was added and the mixture was stirred for 20 min. The yellow solution obtained was vacuum concentrated *ca* 2ml and a yellow solid precipitated. This product was separated by decantation, washed with diethyl ether (3 × 3 mL) and dried in vacuum. Yield (isolated product): 91 mg (58%).

IR (cm^{-1}): *v* (PF_6) 838 (s). MS (m/z, referred to the most abundant isotopes): m/z: 633.16309 $[M]^+$. Anal. Calcd for $C_{27}H_{34}OClF_6IrP_2$ (778.18 g/mol): C 41.67, H 4.40; found: C 41.68, H 4.41. ^1H NMR (CD_2Cl_2): *δ* 7.62–7.41 (m, 10H, P*Ph*$_2$CH$_3$); 5.26–5.18 (m, 1H, O–C*H*$_2$); 5.03–4.95 (m, 1H, O–C*H*$_2$); 2.49–2.37 (m, 1H, =C–C*H*$_2$); 2.34 (d, $^2J_{HP}$ = 10.6 Hz, 3H, PPh$_2$C*H*$_3$); 2.25–2.13 (m, 1H, =C–C*H*$_2$); 1.97–1.85 (m, 1H, CH$_2$C*H*$_2$CH$_2$);

1.62 (d, $^4J_{HP}$ = 2.2 Hz, 15H, $C_5(CH_3)_5$); 1.50–1.38 (m, 1H, $CH_2CH_2CH_2$) ppm. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ –17.30 (s, PPh_2CH_3); –144.16 (sept, $^1J_{PF}$ = 710.6 Hz, PF_6) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 275.8 (d, $^2J_{CP}$ = 11.7 Hz, Ir=*C*); 132.7 (d, $^2J_{CP}$ = 9.9 Hz, P*Ph*$_2$Me); 132.3 (d, $^2J_{CP}$ = 9.6 Hz, P*Ph*$_2$Me); 132.25 (d, $^4J_{CP}$ = 3.7 Hz, P*Ph*$_2$Me); 132.2 (d, $^4J_{CP}$ = 2.8 Hz, P*Ph*$_2$Me); 130.9 (d, $^1J_{CP}$ = 59.6 Hz, C_{ipso}); 130.4 (d, $^1J_{CP}$ = 57.8 Hz, C_{ipso}); 129.2 (d, $^3J_{CP}$ = 4.0 Hz, P*Ph*$_2$Me); 129.1 (d, $^3J_{CP}$ = 4.1 Hz, P*Ph*$_2$Me); 99.7 (d, $^2J_{CP}$ = 2.0 Hz, $C_5(CH_3)_5$); 90.2 (s, O–*C*H$_2$); 56.7 (d, $^3J_{CP}$= 1.8 Hz, =C–*C*H$_2$); 21.0 (s, $CH_2CH_2CH_2$); 12.9 (d, $^1J_{CP}$ = 42.3 Hz, PPh_2CH_3); 8.8 (s, $C_5(CH_3)_5$) ppm.

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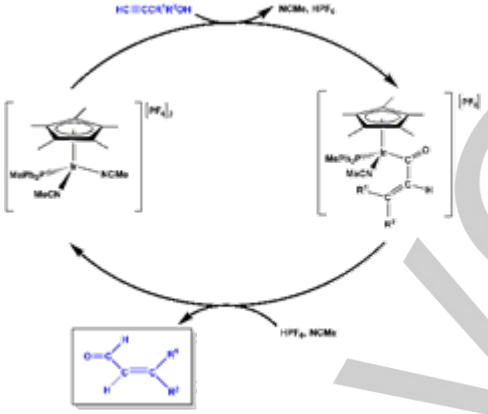
FULL PAPER

[IrCp*(NCMe)$_2$(PPh$_2$Me)][PF$_6$]$_2$ (**I**) efficiently catalyzes propargylic alcohols into α,β-unsaturated aldehydes under mild conditions and without the need of a cocatalyst.



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[IrCp*(NCMe)$_2$(PPh$_2$Me)][PF$_6$]$_2$ as Catalyst for the Meyer–Schuster Rearrangement of Aryl Propargylic Alcohols under Mild Conditions.