Synthesis of iridaoxaphospholane complexes

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1. Introduction

The chemistry of metallacycles has increased enormously during the last decades due to the synergy among the organic and organometallic properties and reactivity they can display [1–5]. In this regard, iridium has emerged as one of the most promising transition metals with a wide variety of examples such as iridaaromatics [2,3,5,6], iridacyclopentadienes [7,8], iridacyclobutadienes [9] and mainly complexes bearing C=N or C=C chelating ligands [10–12], usually synthesized through C–H bond activations and presenting applications as anticancer agents, catalysts, photochemistry and in other areas [10].

Oxaphospholane compounds have risen as very important tools in enantioselective catalytic reactions due to their key role as chiral co-catalysts and the enormous demand of enantiopure products in different fields such as pharmaceutical and agrochemicals in recent years [13–16]. In this regard, different synthetic routes like dehydrohalogenation of phosphite ligands, reaction of a phosphine with a ketal or cyclocondensation reactions between phosphines and aldehydes have been developed [13,14,17,18].

Allylphosphinite ligands can coordinate with the transition metal through only the phosphorous atom κ1P or with the additional bonding to the C=C skeleton in a κ3(P, C, C) coordination mode. In similar systems, this coordination mode has enabled nucleophilic addition reactions to occur involving both the C=C fragment and the metal center making possible the cyclometalation of the phosphine ligand [19–22]. In spite of the versatility of allylphosphinite ligands, they have been scarcely studied, and only have been used by García-Fontán et al. for the synthesis of rhenium carbonyl complexes [ReX(CO)3(P-Ph2OCH2CH2CH2)] (X = Cl, Br) [23]. However, in that study, the allylphosphinite only acted as a κ2P ligand and reactivity studies were not performed.

Herein, it is presented the synthesis of the first metallooxaphospholane complexes based on the synthesis of the first iridium allylphosphinite complex through two coordination modes and its reactivity towards phosphines as nucleophiles.

2. Results and discussion

Treatment of the binuclear iridium complex [Ir(η5-C5Me5)Cl(μ-Cl)]2 with two equivalents of the alkylidinylphosphinite PH2OCH2CH2 = CH2 gave, after 3.5 h at room temperature the air-stable complex [Ir(η5-C5Me5)Cl2(κ1-P-Ph2OCH2CH2CH2)] (1) (Scheme 1). In the 31P{1H} NMR spectrum, complex 1 displays a unique peak as singlet at δ 73.1 ppm which is highly shifted compared to the free phosphinite (δ = +113 ppm) [24], confirming its coordination to the iridium center. The 1H NMR spectrum shows the most characteristic resonances of the complex belonging to the allyl moiety. Thus, there are two signals corresponding to the CH2 olefinic group at δ 5.39 and 5.20 ppm as doublet of pseudo quartets due to the coupling to all the protons of the allylic moiety with values similar to the ones observed for the free ligand [24]. Similarly, the CH group appears at δ 5.90 ppm as a doublet of doublet of triplet of doublets with the extra coupling to the phosphorus atom of 0.8
Hz. Finally, the OCH group appears at 4.29 ppm as a pseudo triplet of triplets with coupling to all the atoms involved. The $^{13}$C($^1$H) NMR spectrum displays three characteristic resonances at $\delta$ 131.2, 116.0 and 67.0 ppm for the CH, olefinic CH$_2$ and OCH$_2$ groups respectively. Note that for the two closest carbon atoms to the phosphorus atom, the signals appear as doublets due to the coupling between both nuclei. All these data are in accordance to the previously synthesized rhenium complexes with similar ligands. The change of the coordination mode is supported by the NMR spectroscopic data and reactivity of complex 2 towards phosphines as nucleophiles was developed. Thus, the NMR data also support the different orientation of the olefin with respect to the pentamethylpentadienyl ring. Consequently, the CH protons of the allylic chain appear as doublets of doublets at $\delta$ 4.71 and 5.76 ppm due to increase of the rigidity of the system and the terminal olefinic protons appear as doublets at $\delta$ 4.14 ppm. While the former has a coupling to phosphorus, both resonances present couplings to the CH moiety of 8.2 and 12.6 Hz due to their cis and trans arrangement, respectively. Finally, the two OCH$_2$ protons appear as doublet of doublets at $\delta$ 3.76 and 4.92 ppm, where the latter shows a high increment of the proton-phosphorus coupling to 39.8 Hz, as an effect of the coordination mode change.

The presence of two diastereotopic faces would imply the formation of two diastereoisomers, however, variable temperature NMR spectroscopy studies did not show the second isomer and ruled out a possible dynamic process between them. Thus, based on the NMR data, only one of the two diastereotopic faces of the $\kappa^3$P-Ph$_2$POCH$_2$CH$_2$CH$_2$ ligand coordinates with the metal center which implies a diastereoselective formation of complex 2, as it has been reported for analogous compound bearing alkenylphosphane ligands [20,22,25].

The structure of compound 2 was further confirmed by X-ray diffraction studies (Fig. 1). Suitable crystals were obtained by slow diffusion of ethyl ether in a solution of compound 2 in dichloromethane. The molecule exhibits a three-legged piano-stool geometry with the iridium atom attached to the chloride ligand, the pentaethylcyclopentadienyl ring, and the alkenylidyphosphinite ligand through the phosphorus and the carbon atoms of the $\kappa^2$ coordinated olefin. Therefore, the bond distances between the iridium center and the olefin are 2.217(12) and 2.228(11) Å. In addition, the carbon-carbon distance of 1.4013(18) Å is larger than that found for similar complexes such as $[\text{Ir}(\kappa^2$-$\text{C}_5\text{Me}_3\text{Cl}(\text{CO})(\kappa^3$-$\text{P}$-$\text{Ph}_2$-$\text{POCH}_2$-$\text{CH}_2$-$\text{CH}_2$)$(\text{BF}_4)$) (1.2677(7) Å) [22], rhenium complexes bearing the same ligand [ReX(CO)$_3$(P-$\text{Ph}_2$-$\text{OCH}_2$-$\text{CH}_2$)$_2$] (X = Cl, Br) (around 1.32 Å) [23] or the DFT optimized structure of complex 1 (1.3353 Å) (see SI) due to the lower $sp^2$ character of the carbon atoms upon coordination to the metal (see Fig. 1 for distances and angles). In addition, the solid-state structure also shows a parallel orientation of the olefin with respect to the pentamethylpentadienyl ring. Notably, in solution the NMR data also support the parallel orientation of the olefin with a relative large difference between the chemical shifts of the geminal protons of the olefin ($\Delta\delta = 0.57$ ppm) and a small difference between the cis protons ($\Delta\delta = 1.05$ ppm). This two facts are consistent with complexes bearing an alkenylphosphane ligand [21,26].

In order to observe synthesized metalloxa phospholanes, the electrophilicity of the olefinic moiety at the phosphinite ligand was considered and confirmed by the NMR spectroscopic data. Thus, in the $^1$H NMR spectrum of each complex two doublets with coupling constants around $5\text{–}6$ Hz are observed, one at around 123 ppm corresponding to the phosphinite ligand and the others at 17.3, 15.9 and –48.3 ppm for the positively charged $\text{PPh}_3^+$, $\text{PPh}_2\text{Me}$ and PTA groups, respectively. In the $^1$H NMR spectra, as happened in complex 2, the protons in both CH$_2$ groups are diastereotopic. While the OCH$_2$ moiety is not very influenced by the change in the coordination mode, the hybridization switch from $\text{Csp}^2$ to $\text{Csp}^3$ in the CH moiety...
produces a 2 ppm shift from 5.76 in complex 2 to around 3.45 ppm for complexes 3. In addition, the protons of the CH₂ group bonded to the phosphane, present a doublet of doublet of doublets multiplicity in all cases with an extra coupling, compared to complex 2, of around 15 Hz with the corresponding phosphine. Finally, the ¹³C(¹H) NMR spectra show, not only a high field shift of the former olefinic carbons to the aliphatic region of the spectrum, but also a different multiplicity. Thus, the carbon directly bonded to the phosphine substituent appears at 27.5 ppm for 3c as a broad signal and at 30.1 ppm for both 3a and 3b as doublet of doublets with couplings of around 30 Hz to the adjacent phosphorus atom and 3 Hz to the distant phosphorus nucleus. Similarly, the CH₂ groups, now bonded to the iridium atom, show two-bond couplings of around 14 Hz for the phosphinite ligand and 5 Hz for the positively charged phosphine.

Again, the analysis in solution was further confirmed with the solid-state structure obtained by X-ray diffraction analysis of the three iridaoxaphospholanes 3 (Fig. 2 for complex 3b and SI for the rest). The structures display a three piano legged stool geometry due to the presence of the pentamethylcyclopentadienyl and chloride ligands as well as the metallocyclic five-membered ring. Thus, the Ir–P and Ir–C distances of the iridacycle (around 2.2 and 2.1 Å respectively) shorten by 0.1 Å with respect to complex 2, probably due to the formation of the cycle, and the former C=Ir–C bond now present a distance usual of single bonds (1.537(4)). The rest of the iridaoxaphospholane moiety present similar distances and angles in comparison with other 1,2-oxaphospholane rings [16,17]. Finally, the positively charge phosphine is bonded to the iridooxaphospholane ring through a similar P=Ir–C bond of around 1.80 Å than the P=C distances to the phosphine substruates which are in the range of 1.7 to 1.9 Å (See Fig. 2 and Table S2 for distances and angles).

Mechanistically, complexes 3 can be obtained by the nucleophilic attack of the phosphane on the terminal carbon of the olefin with the concomitant intramolecular coordination of the inner Csp² carbon to the metal center. This reaction leads to the formation of a five-membered ring complex instead of six-member ring, and therefore, the obtaining of the 1,2-iridaoxaphospholane derivative. Interestingly, nucleophilic addition of phosphines to allyl or alklenyphosphane ligands at transition metals have been previously observed, however, it had always taken place at the inner carbon of the olefin [19–22].

In order to shed light on the reactivity difference between the iridium (III) allylphosphine intermediate cation complex reported by Martínez de Salinas et al. [Ir(η⁵-C₅Me₅)Cl(κ²P,C,C-PPh₂CH₂CH—CH₂)]⁺ [22] and cation complex 2, the atomic charges of both complexes were determined by DPT calculations. Thus, the olefin of complex 2, with a phosphinite ligand, present atomic charges of −0.07 and −0.06 au for the inner and the terminal carbon respectively, while similar values of −0.05 and −0.06 au were found for the literature described complex bearing a phosphinite ligand. These results indicate that the charges have no effect in the reactivity outcome, while energy might play a role on it.

Therefore, assuming a concerted mechanism for the reaction of cation complex 2 with PPh₂Me, the energies for the attack at both possible carbon atoms of the double bond were calculated (Fig. 3). Interestingly, the attack of the phosphine to the terminal carbon atom presents not only a lower barrier (ΔE = 8.4 kcal/mol) compared to the attack to the inner carbon atom (ΔE = 15 kcal/mol) but also, the cationic iridooxaphospholane 3b⁺ appears to be 5.2 kcal/mol more stable than the theoretical six membered ring cationic complex 3b⁺.

3. Conclusions

The capability of the alkenylidiphenylphosphinite ligand to coordinate in both κ¹P and κ²P(C, C) modes has allowed the synthesis of complexes [Ir(η⁵-C₅Me₅)Cl(κ¹P-PPh₂OCH₂CH—CH₂)] (1) and [Ir(η⁵-C₅Me₅)Cl(κ²P,C,C-PPh₂OCH₂CH—CH₂)](PF₆) (2). Nucleophilic attack of different phosphines to the terminal carbon of the alkene moiety of the phosphinite ligand gave rise to a new family of metallacycles, the iridooxaphospholane complexes [Ir(η⁵-C₅Me₅)Cl(κ²P,C,C-PPh₂OCH₂CH—CH₂(PR₃)](PF₆) (PR₃ = PPh₂ (3a), PPh₂Me (3b), PTA (3c)). DFT calculations have determined that this reaction takes place through a lower energy barrier than a possible attack to the inner carbon as happened when using alkylphosphane ligands.

4. Experimental section

4.1. General procedures

All synthetic procedures were performed under a dry argon atmosphere by following conventional Schlenk techniques. Solvents were purified by distillation from the appropriate drying agents and degassed before use. All reagents were obtained from commercial sources and used as received. The allylidenyphosphinite PPh₂OCH₂CH—CH₂ and the complex [Ir(η⁵-C₅Me₅)Cl(κ¹P)] were prepared following previously published methods [24,27]. Unless stated, NMR spectra were recorded in CD₂Cl₂ or CDCl₃ at room temperature on Bruker ARX-400 instrument, with resonating frequencies of 400 MHz (¹H), 161 MHz (¹³P (¹H)) and 100 MHz (¹³C(¹H)) using the solvent as the internal lock. ¹H and ¹³C(¹H) signals are referred to internal TMS and those of ¹³P(¹H) to 85 % H₃PO₄, downfield shifts (expressed in ppm) are considered positive. ¹H and ¹³C(¹H) NMR signal assignments were confirmed by ¹H, ¹³C) COSY, (¹H, ¹³C) HSQC and (¹H, ¹³C) HMBC experiments. Coupling constants are given in hertz. C and H analyses were carried out with a Carlo Erba 1108 analyzer.

4.2. X-ray methodology

Crystallographic data for complexes 2, 3a, 3b-2CH₂Cl₂ and 3c was collected on a Bruker D8 Venture Photon 100 CMOS diffractometer at 100 K using Mo-Kα radiation (λ = 0.71073 Å). The frames were
4.2. \([\text{Ir}(\eta^5-C_2Me_5)Cl_2(\eta^4-PPh_2OCH_2CH=CH_2)]\) [PF_6] (2)

A suspension of complex 1 (0.10 g, 0.15 mmol) and TlPF_6 (0.082 g, 0.23 mmol) in MeCN (8 mL) was stirred at room temperature for 1 h. The suspension obtained was filtered through Celite® and the filtrate was concentrated under reduced pressure giving a yellow oil that was treated with Et_2O (2 x 3 mL). The yellow solid obtained was recrystallized from a CH_2Cl_2 solution. Yield: 96 mg (85%).

**Elem. Anal.:** Calc. for C_{28}H_{42}Cl_2O_2P_2: C, 62.50; H, 4.18; N (CdCl_2) & 8.16–8.02 (m, 4H, C_{para}H, Ph), 7.42–7.34 (m, 6H, C_{ortho}H + C_{meta}H, Ph), 5.90 (ddd, δ_{HH} = 17.2, δ_{HH} = 10.4, δ_{HH} = 4.7, δ_{HH} = 0.8 Hz, 1H, CH_2 = CH), 5.39 (dq, δ_{HH} = 17.2, δ_{HH} = 4.7, δ_{HH} = 1.8 Hz, 1H, ≈CH_2, H_{trans}), 5.20 (dq, δ_{HH} = 10.6, δ_{HH} = 4.8, δ_{HH} ≈ 1.7 Hz, 1H, ≈CH_2, H_{cis}).

4.4.3. \([\text{Ir}(\eta^5-C_2Me_5)Cl_2(\eta^4-PPh_2OCH_2CH=CH_2)]\) [PF_6] (3a, 3b, 3c)

A solution of the complex 2 (0.050 g, 0.06 mmol) in CH_2Cl_2 (6 mL) the corresponding phosphine was added (0.06 mmol) and the mixture stirred at room temperature for 30 min (3a, 3b) or 24 h (3c). Then, the solution was concentrated under reduced pressure giving a yellow oil that was treated with Et_2O (3 x 3 mL). The yellow solid obtained...
for the report worked in this paper.

Data availability

Data will be made available on request.

Acknowledgments

AMG thanks Xunta de Galicia for financial support through the project GRC2019/24. We thank the University of Vigo CACIT services for recording the NMR spectra and collecting X-ray data.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2022.116193.

References

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