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Olefin uptake as tool for linking platinum(II) and iridium(III) in heterobinuclear complexes: Synthesis and characterization of $[PtI_2(Me_2phen)\{(C_5Me_4CH_2CH_2CH{=}CH_2)Ir(Me)(CO)(Ph)\}]$

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Abstract

The ability of $[PtX_2(Me_2phen)]$ (Me_2phen = 2,9-dimethyl-1,10-phenanthroline, X = Cl, Br, I) to act as olefin scavengers, easily giving stable trigonal bipyramidal five-coordinated platinum species $[PtX_2(Me_2phen)(\eta^2\text{-olefin})]$, has been checked toward $[(C_5Me_4CH_2CH_2CH{=}CH_2)Ir(Me)(CO)(Ph)]$, a cyclopentadienyl complex containing an olefinic function introduced by ring methyl activation in the pentamethylcyclopentadienyl iridium(III) complex $[(C_5Me_5)Ir(Me)(CO)(Ph)]$. The reaction of $[PtI_2(Me_2phen)]$ with $[(C_5Me_4CH_2CH_2CH{=}CH_2)Ir(Me)(CO)(Ph)]$ results in the formation of the heterometallic binuclear complex $[PtI_2(Me_2phen)\{(C_5Me_4CH_2CH_2CH{=}CH_2)Ir(Me)(CO)(Ph)\}]$ which is stable and has been completely characterized by elemental analysis, ^1H, ^{13}C, and ^{195}Pt NMR spectroscopy.

Keywords: Platinum; Iridium; Cyclopentadienyl; Five-coordinated platinum complexes; Alkene

1. Introduction

Square planar platinum(II) complexes containing the bidentate heterocyclic ligand neocuproine (Me_2phen, 2,9-dimethyl-1,10-phenanthroline) of general formula $[PtX_2(Me_2phen)]$ (X = Cl, Br, I) are able to readily give uptake of olefins [1], thus forming stable five-coordinated species of the type $[PtX_2(Me_2phen)(\eta^2\text{-olefin})]$. Such a reactivity stems from the steric hindrance due to the 2,9-methyl groups pointing towards the *cis* halide in the square coordination plane of $[PtX_2(Me_2phen)]$ complexes. The tendency to release the intramolecular strain is function of the steric bulk of the halogen ligands (X = I > Br > Cl). A wide range of five-coordinate complexes containing neocuproine or bathocuproine (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) and different alkenes have been obtained through this versatile synthetic pathway [2–4]. In the present work the ability of $[PtI_2(Me_2phen)]$ to give alkene uptake has been successfully tested towards an olefinic function introduced by ring methyl activation in a pentamethylcyclopentadienyl iridium(III) complex.

2. Experimental

2.1. General remarks

Commercial reagent grade chemicals and solvents were used without further purification in the synthesis

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of the platinum compound. $[PtI_2(Me_2phen)]$ [2], $[PtI_2(CH_2{=}CHCH_3)(Me_2phen)]$ [14], and $[(C_5Me_4CH_2CH_2CH{=}CH_2)Ir(Me)(CO)(Ph)]$ [6], were synthesized by previously reported procedures. The synthesis of $[(C_5Me_4CH_2CH_2CH{=}CH_2)Ir(Me)(CO)(Ph)]$ was carried out under nitrogen atmosphere, using standard Schlenk techniques and solvents freshly distilled under nitrogen. Microanalyses were performed by the microanalysis service of the University of Sheffield. 1D and 2D NMR spectra were acquired on a Bruker Avance DPX 400 instrument at 25 °C. Chemical shifts for ^1H and $^{13}C\{^1H\}$ were referenced to residual protic solvent peaks ($CDCl_3$: ^1H, 7.24 ppm; ^{13}C, 77.00 ppm). Chemical shifts for ^{195}Pt were referenced to external $K_2[PtCl_4]$ in D_2O at $\delta = -1615$ ppm. Standard pulse sequences were used for ^1H, $^{13}C\{^1H\}$, $^{195}Pt\{^1H\}$, ^1H *J*-resolved, and ^1H NOESY spectra. The COSY, $[^1H,^{13}C]$-HETCOR, $[^1H,^{13}C]$-LR HETCOR, and $[^1H,^{195}Pt]$-HETCOR experiments were carried out using gradient selected versions of the standard Bruker pulse programs.

2.2. Preparation of $[PtI_2(Me_2phen)\{(C_5Me_4CH_2CH_2CH{=}CH_2)Ir(Me)(CO)(Ph)\}]$

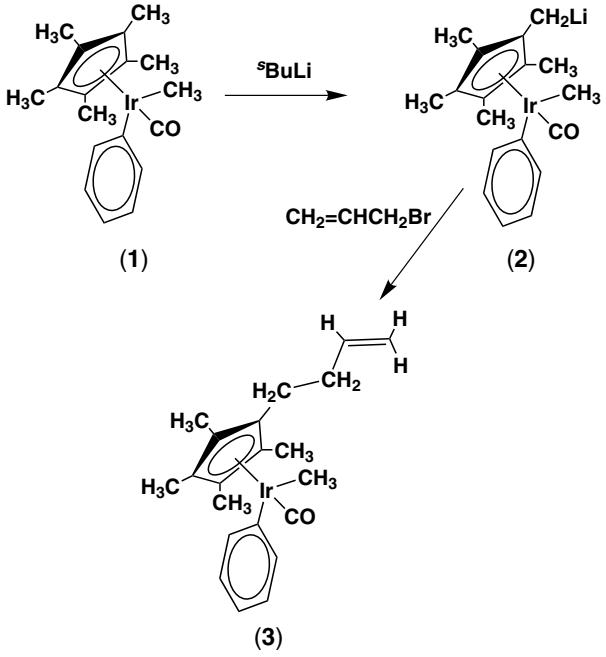
250.2 mg (0.513 mmol) of $[(C_5Me_4CH_2CH_2CH{=}CH_2)Ir(Me)(CO)(Ph)]$ dissolved in chloroform (10 mL) were added to a solution containing 337.3 mg (0.513 mmol) of $[PtI_2(Me_2phen)]$ dissolved in 10 mL of the same solvent. The color of the solution changed instantaneously from deep red to orange. The yellow precipitate of $\{PtI_2(Me_2phen)[(C_5Me_4CH_2CH_2CH{=}CH_2)Ir(Me)(CO)(Ph)]\}$, which was obtained by addition of diethylether to the reaction solution was filtered, washed with diethylether and dried in a flow of dry air (528.5 mg, Yield 90%). $C_{35}H_{39}N_2OI_2IrPt$ Anal. Calc.: C, 36.72; H, 3.43; N, 2.45. Found: C, 36.87; H, 3.44; N, 2.23%.

3. Results and discussion

3.1. General

Complexes containing C_5Me_4R usually have to be prepared starting from the appropriately substituted cyclopentadienyls. Nevertheless, the ring hydrogens of some complexes of general formula $[C_5Me_5ML_n]$ (M = Rh, Ir) are acidic, as demonstrated by their easy exchange for deuterium in D_2O/DO^- [5]. Deprotonation of the ring hydrogens has been used to functionalize pentamethylcyclopentadienyl ligands already bound to a metal.

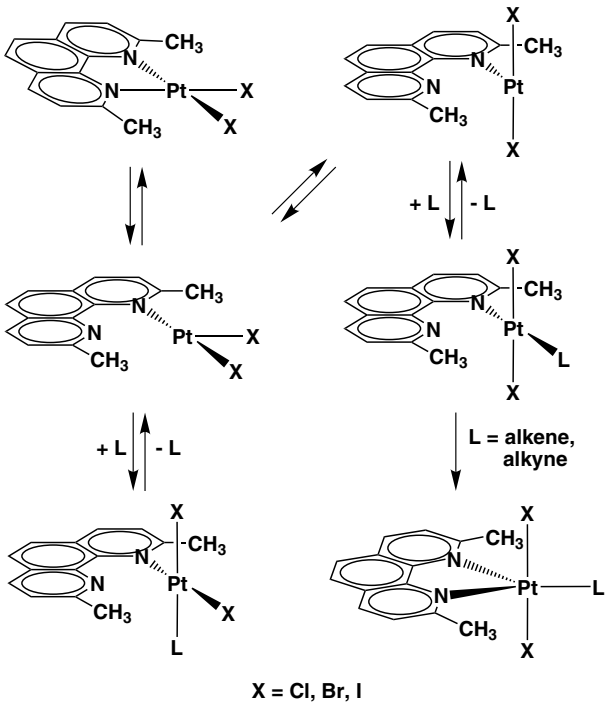
As already reported by some of us, $[C_5Me_4Ir(Me)(CO)(Ph)]$ (**1** in Scheme 1) reacts with ^{S}BuLi to afford a lithiated species (**2**). This intermediate can be then coupled to a variety of electrofiles, allowing a comfortable pathway to obtain a range of substituted cyclopentadienyls [6–8]. By following the synthetic route depicted in Scheme 1, it has been possible to prepare an iridium(III) complex containing a terminal alkene covalently bound to the Cp ring, $[(C_5Me_4CH_2CH_2CH{=}CH_2)Ir(Me)(CO)(Ph)]$ (**3**).



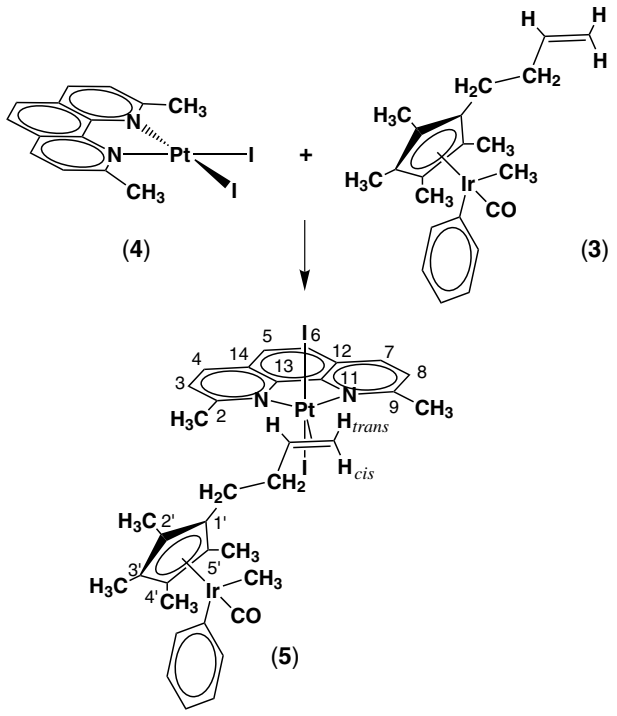
Scheme 1. Synthesis of the complex $[(C_5Me_4CH_2CH_2CH{=}CH_2)Ir(Me)(CO)(Ph)]$ (**3**).

On the other hand, complexes of the type $[PtX_2(Me_2phen)]$ (X = Cl, Br or I) show an unusual reactivity. The steric interactions between the *ortho* substituents of the phenanthroline ligand and the *cis* halogen atoms in a square planar arrangement favour the reaction with an extra ligand L (L = alkene, alkyne, CO, PPh_3, DMSO, DMS, PhNO, Py or NH_2Pr^n) to give the corresponding addition rather than substitution product [9]. In the case of alkene [2,11] or alkyne [10] ligands, the addition product has a trigonal bipyramidal geometry, with the phenanthroline and the unsaturated ligand in the trigonal plane and the two halogen atoms in axial positions whereas in all other cases the addition product has a square planar geometry with mono-coordinated phenanthroline (Scheme 2) [11–13].

The rate and formation constants for the addition, in the case of alkene, have been found to be strongly dependent upon the bulk of the halogen ligand. In particular, the formation constant of the five coordinate complex increases by a factor of 10 on going from the chloro to the bromo complex, and by a factor of 100 going from the bromo to the iodo species [2]. The availability of $[(C_5Me_4CH_2CH_2CH{=}CH_2)Ir(Me)(CO)(Ph)]$ (**3**), a compound characterized by an olefin function bound to an iridium complex but still suitable for coordination to platinum, triggered our synthetic curiosity.



Scheme 2. Available reaction pathways for $[PtX_2(Me_2phen)]$.



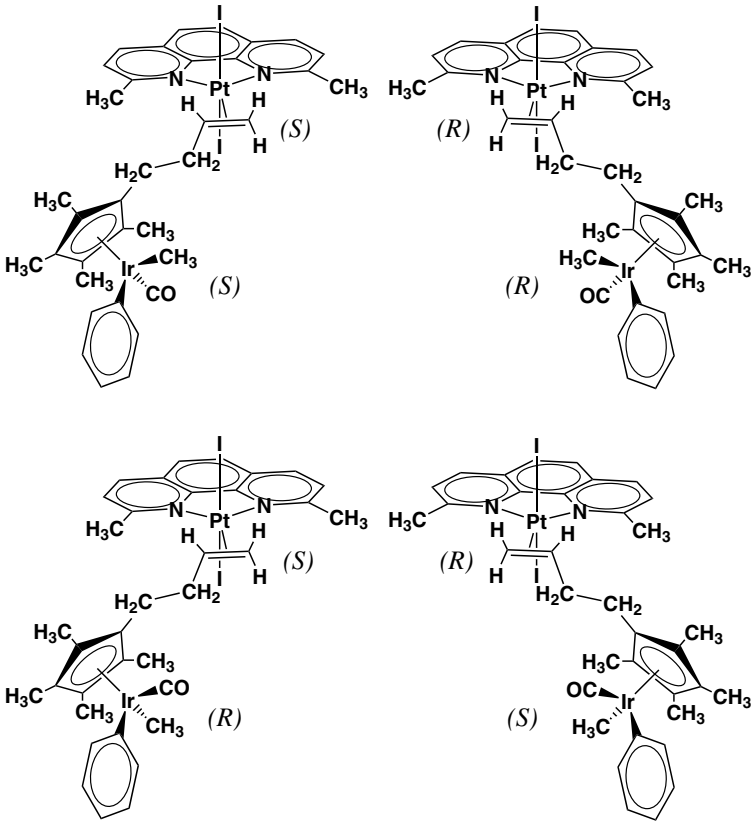
Scheme 3. Synthesis of the complex $[PtI_2(Me_2phen)\{(C_5Me_4CH_2CH_2CH{=}CH_2)Ir(Me)(CO)(Ph)\}]$ (**5**).

We wanted to verify whether the ability of $[PtX_2(Me_2phen)]$ complexes to give olefin uptake could also work toward another metal complex having a pendant olefin function suitable for coordination. As starting platinum complex among the $[PtX_2(Me_2phen)]$ series, we choose $[PtI_2(Me_2phen)]$, the complex we knew to be the most likely to give a thermodynamically stable five-coordinate addition product, due to the higher steric hindrance of the iodo ligands in the square planar geometry. Indeed the complex $[PtI_2(Me_2phen)]$ readily reacts with **3** in chloroform (Scheme 3) to yield the heterometallic binuclear complex $[PtI_2(Me_2phen)\{(C_5Me_4CH_2CH_2CH{=}CH_2)Ir(Me)(CO)(Ph)\}]$ (**5**) containing the expected five-coordinated platinum(II) moiety. The new product could be precipitated by addition of diethylether to the reaction solution and isolated as an air stable yellow solid.

3.2. Stereochemistry

The iridium atom in complexes **1**–**3** has a pseudo-tetrahedral coordination geometry and four different substituents. Therefore, analogously to an sp^3 carbon, it is a chiral centre. Due to the use of the starting iridium complex **1** as unresolved racemic mixture (Scheme 1), also complex **3** was obtained as a racemate. Moreover, the presence in complex **3** of a prochiral alkene leads, upon coordination of the latter to the platinum(II), to the formation of a second chiral centre in the final heterometallic binuclear complex **5**. Consequently, the new species formed, containing a five-coordinated platinum(II) and a pseudo-tetrahedral iridium(III) moieties linked in the same molecule (**5**), consists of four products having different chirality at the two chiral centres (Scheme 4).

Two diastereoisomeric pairs of enantiomers, *R*-(η^2-olefin), *R*-(Ir); *S*-(η^2-olefin), *S*-(Ir); and *R*-(η^2-olefin), *S*-(Ir); *S*-(η^2-olefin), *R*-(Ir), respectively, should be observed, which are expected to give two different NMR spectra. Indeed the NMR data discussed below show that **5** consists of two diastereoisomers characterized by very similar ^1H and $^{13}C\{^1H\}$ spectra. In the ^1H NMR spectrum (Fig. 1) the small differences in the chemical shifts of the two diastereoisomers could only be observed for the vinylic $=CH_2$ of the junction, for some of the hydrogens in the closest proximity of the olefinic junction (e.g., the phenanthroline 2,9-methyl groups), and for one of the methyl substituents of the cyclopentadienyl ring. In the $^{13}C\{^1H\}$ NMR spectrum only the signals of the Ir moiety are split but the chemical shift difference, which in most cases does not exceed 0.1 ppm for the two diastereoisomers, reaches values of 0.15, 0.47 and 0.75 for the allylic, the C5′ and the C2′ carbons respectively. According to NMR data, the two diastereoisomeric forms of complex **5** are present in 1:1 ratio, therefore no significant induction of chirality is observed when complex **3**, which contains the prochiral olefin, is reacted with **4** to afford the heterometallic binuclear complex **5**.



Scheme 4. The four possible stereoisomers of **5**.

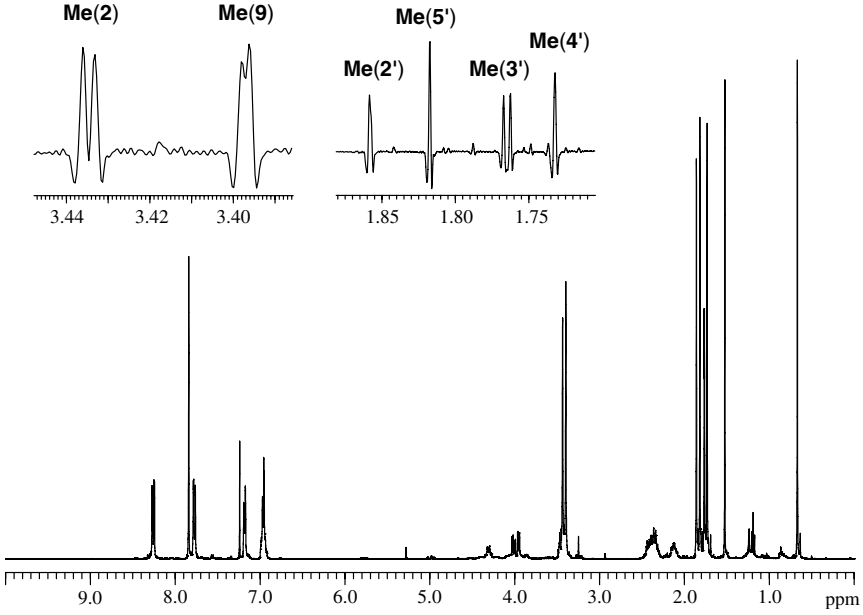


Fig. 1. ^{1}H NMR spectrum of **5**. Inset showing the expansion relative to neocuproine methyl signals (left) and cyclopentadienyl methyl signals (right). Expansions are not shown on the same scale.

3.3. NMR spectroscopy

^{1}H, ^{13}C, and ^{195}Pt NMR data for the Pt–Ir bridge are reported in Table 1, together with those of $[PtI_2(\eta^2\text{-}CH_2{=}CHCH_3)(Me_2phen)]$ (**6**). The latter is the simplest five-coordinate neocuproine iodo complex containing an asymmetric olefin η^2-coordinated to platinum [2], which we also synthesized and used

Table 1
^{1}H, ^{13}C, and ^{195}Pt NMR chemicals shifts[a] for **5** and **6**

	5				**6**	
	^{1}H		^{13}C		^{1}H	^{13}C
Me(2)	3.437s	3.434s	29.22		3.494s	29.19
Me(9)	3.399s	3.397s	28.55		3.416s	28.38
H3	7.776d (8.3)		125.78		7.787d (8.3)	125.78
H8	7.774d (8.3)		126.13		7.760d (8.3)	126.04
H4	8.263d (8.3)		137.94		8.252d (8.3)	137.79
H7	8.255d (8.3)		137.77		8.239d (8.3)	137.62
H(5,6)	7.841s		126.18, 126.05		7.831s	126.12, 125.98
C2	–		161.01		–	161.07
C9	–		161.72		–	161.67
C11,C13	–		144.68, 144.45		–	144.65, 144.39
C12	–		128.66		–	128.58
C14	–		128.54		–	128.49
$=CH_2$						
trans	3.956d (7.5, 1.0)	3.951d (7.5, 1.0)	31.57	31.53	4.051d (7.7)[78]	32.76
Cis	4.016d(10.8, 1.0)	4.004d(10.8, 1.0)			4.142d (10.9)[66]	
$=CH$–R	4.310m (7.5, 10.8) [76]		45.77		4.444m (7.7, 10.9, 6.4) [76]	43.61
$=CH–CH_{2(3)}$	2.362m		39.65	39.50	1.711d (6.4) [48]	24.25
	2.130m					
$-CH_2-(1')$	2.388m		9.26		–	–
Me(2′)	1.859s		9.09	9.07	–	–
Me(3′)	1.768s	1.764s	8.62		–	–
Me(4′)	1.733s		9.05	9.02	–	–
Me(5′)	1.818s		8.66		–	–
IrMe	0.669s		−22.34	−22.33	–	–
C1′	–		100.57	100.47	–	–
C2′	–		99.13	98.88	–	–
C3′	–		97.94	97.92	–	–
C4′	–		98.10	98.01	–	–
C5′	–		99.77	99.30	–	–
CO	–		172.84	172.82	–	–
o-Ph	7.186m		139.89		–	–
m-Ph	6.962m		127.89		–	–
p-Ph	6.951m		122.67		–	–
i-Ph	–		130.68	130.60	–	–
^{195}Pt	−3889.14, −3888.86				−3893.10	

[a] When two values are reported for complex **5**, they refer to the two diastereoisomers. ($J_{H–H}$) and [$J_{Pt–H}$] couplings are given when observable.

as reference compound to compare with the new species.

3.4. Iridium moiety of the Pt–Ir bridge complex 5

Coordination of the olefinic side arm of $[(C_5Me_4CH_2CH_2CH{=}CH_2)Ir(Me)(CO)(Ph)]$ to platinum with formation of the heterobimetallic complex is clearly shown by the typical presence of ^{195}Pt satellites for the signals of the alkene protons. As expected in the five-coordinated complexes, the vinylic protons also show the typical shielding with respect to the free olefin, which is usually smaller if compared to the same effect observed in four-coordinate platinum olefin complexes [3]. The complete assignment of the two different vinylic systems for the two diastereoisomers of the heterometallic binuclear complex could be made taking advantage of the 2D ^{1}H COSY and 2D ^{1}H *J*-resolved spectra. In particular, the 2D ^{1}H *J*-resolved spectra allowed to differentiate the splitting of the signals due to couplings from the splitting due to the presence of two different diastereoisomers (Fig. 2). Indeed very little differences were found in the ^{1}H chemical shifts of the coordinated olefinic arm for the two diastereoisomers, being the major observed $\Delta\delta$ 0.012 and 0.004 ppm for the $=CH_2$ vinylic protons *cis* (H_{cis}) and *trans* (H_{trans}) to the double bond susbtituent, respectively. Moreover as already found in the case of **6**, the olefin systems of the two diastereoisomers present in complex **5**, show both very small values (<2 Hz) for the geminal coupling between the $=CH_2$ protons which, in turn, show *cis* and *trans* couplings with the $=CHR$ of 7.6 and 10.7 Hz, respectively. The signals of this latter olefinic proton which overlap at 4.310 ppm for the two isomers, in addition to platinum satellites ($J_{H–Pt} \approx 76$ Hz), show a complex multiplet structure due to significant couplings with the allylic protons, as indicated by the ^{1}H COSY spectrum. Allylic and cyclopentadienyl ring bound CH_2

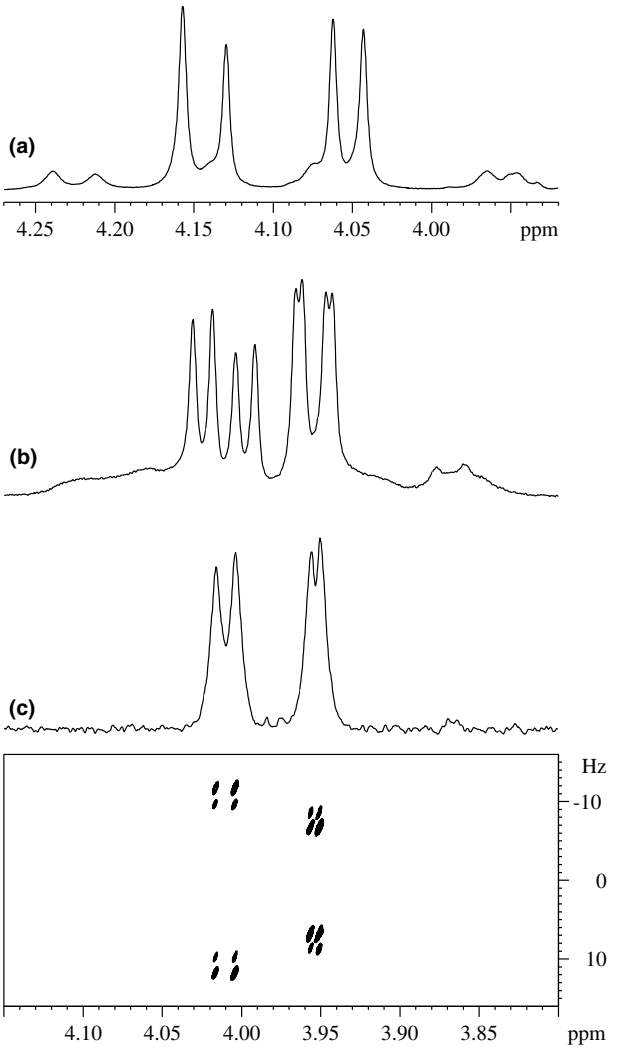


Fig. 2. Expansion of the *J*-resolved spectrum of **5**, showing the olefin methylenic protons: (a) expansion of the ^{1}H NMR spectrum of the corresponding protons of **6**, for comparison; (b) expansion of the ^{1}H NMR spectrum of the corresponding protons of **5**; (c) projection along the ^{1}H (chemical shifts) axis of the *J*-resolved spectrum, showing the presence of two diastereoisomers for complex **5**.

signals could not be differentiated for the two diastereoisomers. The allylic protons undergo significant diastereotopic splitting (2.362 and 2.130 ppm), and one of them overlaps with the proton signals of the CH_2 bound to the cyclopentadienyl ring, observed as a single multiplet at 2.388 ppm. Due to diastereotopic splitting caused by the chiral iridium, up to four different signals could be observed for the four cyclopentadienyl methyls in complex **2** derivatives [8].

In the ^{1}H NMR spectrum of complex **5**, which consists of two diastereoisomers, five out of the eight expected separate signals are observed for the four methyl groups of the cyclopentadienyl ligand (1.859, 1.818, 1.768 and 1.764, and 1.733 ppm), two of them (1.768 and 1.764 ppm) integrate together as one of the others. This is a clear indication that at the instrument field used (400 MHz) the signals for three of the four cyclopentadienyl methyl overlap for the two diastereoisomers. The signals at 1.768 and 1.764 ppm were attributed to the Me(3′) groups of the two different diastereoisomers on the basis of 2D ^{1}H NOESY and 2D [^{1}H,^{13}C]-HETCOR spectra which also allowed sequential assignment for all the cyclopentadienyl methyls. On the other hand, the methyl group directly bound to the iridium atom shows, in the ^{1}H spectrum, a single resonance at 0.669 ppm for both diastereoisomers. Also the ^{1}H signals of the phenyl group bound to the iridium moiety could not be differentiated for the two diastereoisomers. In the aromatic region one multiplet integrating for two hydrogens at 7.186 ppm, assigned to the *ortho* protons, and a broad multiplet integrating for three hydrogens, assigned to the overlapping *meta* and *para* protons, were separately assigned (6.962 and 6.951 ppm, respectively) on the basis of the [^{1}H,^{13}C]-HETCOR spectrum. 2D [^{1}H,^{13}C]-HETCOR, [^{1}H,^{13}C]-Long Range HETCOR, and the ^{13}C{^{1}H}spectrum, together with the 2D ^{1}H NOESY spectra, allowed almost complete assignment for the ^{13}C signals which, for the two diastereoisomers, could be differentiated all but the vinylic =CHR, the *ortho*, *meta*, and *para* carbons of the phenyl system together with the Me(3′) and Me(5′) of the cyclopentadienyl ligand (Table 1). The quaternary carbon were assigned on the basis of the [^{1}H,^{13}C]-Long Range HETCOR spectrum. The biggest differences in ^{13}C shifts between the two diastereoisomers were observed for the quaternary carbons C2′, C5′, and C1′ $\Delta\delta$ = 0.75, 0.47 and 0.10 ppm, respectively. The most significant differences for the ^{13}C shifts in the iridium moiety of the Pt–Ir bridge **5** (given as average for the two diastereoisomers) with respect to the simple Ir complex **3** are those found for the alkene carbons, which undergo a strong shielding upon coordination to platinum (=CH_2 and =CHR are 31.5 and 45.8 ppm, and 115.4 and 137.5 ppm for **5** and **3**, respectively) [8]. Other significant differences for the ^{13}C shifts are observed for the allylic carbon (39.6 and 34.8 for **5** and **3**, respectively) and for the CH_2 bound to the cyclopentadienyl ring (26.1 and 23.7 for **5** and **3**, respectively). Much smaller $\Delta\delta$ were measured for all the other carbon atoms of the iridium moiety of **5**.

3.5. Platinum moiety of the Pt–Ir bridge complex 5

Five-coordinate complexes containing an asymmetric olefin, due to the slow rotation about the platinum–alkene bond [14], are expected to give two different sets of NMR signals, corresponding to the two halves of the neocuproine ligand [2]. The $\Delta G^{\#}$ value for the olefin rotation, obtained for **6** by lineshape analysis of the ^{1}H NMR variable temperature spectra (82.2 ± 0.8 kJ mol^{-1}, with a coalescence temperature of 110 °C) indicates that, at room temperature, there is no signal

averaging for the two halves of the neocuproine ligand due to fast rotation of the olefin on the NMR timescale [2,14]. Interestingly, the $\Delta G^{\#}$ for the rotation of the unsaturated ligand in these five-coordinate systems is lower for palladium alkene or platinum alkyne neocuproine complexes ($\Delta G^{\#} = 56.9 \pm 0.8$ and 71.5 ± 0.8 kJ mol^{-1} for $[PdBr_2(Me_2phen)(\eta^2\text{-}CH_2{=}CHCH_3)]$ [2] and $[PtI_2(Me_2phen)(\eta^2\text{-}CH{=}CCH_3)]$ [14], respectively). Indeed, also in the case of complex **5** rotation around the Pt–olefin bond must be a high energy process, since two different sets of NMR signals, corresponding to the two halves of the neocuproine ligand, are found. The sequence of ^{1}H and ^{13}C signals related to the two halves of the neocuproine ligand was assigned on the basis of the 2D ^{1}H NOESY and 2D [^{1}H,^{13}C]-HETCOR spectra. Due to the presence of two diastereoisomers, a further splitting for the signals was expected also for the neocuproine ligand. ^{1}H and ^{13}C NMR data of **5** show that at the instrument field used (400 MHz) the only signals of the neocuproine ligand showing different chemical shift for the two diasteroisomers are those of the 2,9 methyls in the ^{1}H NMR spectrum (two close signals with an approximate 1:1 ratio at 3.437 and 3.434 ppm for Me(2), 3.399 and 3.397 ppm for Me(9), respectively). No doubling of the signals (^{1}H, ^{13}C) due to the presence of the two diastereoisomers was observed for ^{1}H resonances other than those of the neocuproine methyls, most probably because of the distance of the chiral Ir centre from the phenanthroline ring system. The 1:1 integral ratio observed for the two diastereoisomers both for the neocuproine 2,9 methyl and the Me(3′) cyclopentadienyl signals, indicate that the presence of a chiral center on the iridium atom does not give a significant induction of chirality upon coordination of the olefin to platinum. Due to the hindered rotation of the olefin bound to platinum, the 2D ^{1}H NOESY spectrum was particularly useful to assign the two halves of the phenanthroline ligand, since dipolar couplings are clearly and selectively seen between the Me(2) and Me(9) with the =CHR and $=CH_2$ vinylic protons, respectively. In particular, the most shielded methyl group of neocuproine (3.40 ppm, Me(9) average value), has NOE cross peaks only with $=CH_2$ terminal protons (4.012 and 3.955 ppm), while the deshielded signal (3.43 ppm, Me(2) average value) has cross peaks only with the =CHR terminal of the olefin (4.310 ppm) (Fig. 3). The attribution of the neocuproine methyl signals allowed to assign the H3, H8 (7.776 and 7.772 ppm, respectively) and the H4, H7 protons (8.254 and 8.263 ppm, respectively) of the phenanthroline (J_{H3-H4} and $J_{H7-H8} = 8.3$ Hz). The H5,6 protons (7.841 ppm) gave a single resonance at the field used to acquire the spectra. As for the iridium moiety, the ^{13}C{^{1}H} NMR spectrum of the neocuproine ligand in complex **5** was assigned on the basis of the 2D [^{1}H,^{13}C]-HETCOR and [^{1}H,^{13}C]-Long Range HETCOR spectra after the sequential ^{1}H assignment. In order to complete the NMR characterization of compound **5**, 1D ^{195}Pt{^{1}H} NMR and [^{1}H,^{195}Pt]-HETCOR spectra were acquired. Due to the large chemical shift range typical for ^{195}Pt NMR, diastereoisomeric platinum atoms often show separate resonances [15]. Due to the quadrupole effect of the chelate nitrogen ligand, the 1D ^{195}Pt{^{1}H} spectrum of **5** shows, for the two diastereoisomers, a broad peak at $\delta = -3889$ ppm, which could be partially resolved in the [^{1}H,^{195}Pt]-HETCOR spectrum in two peaks only 0.28 ppm apart from each other. The ^{195}Pt chemical shift values of the two diastereoisomers of **5** compare well with the chemicals shift at $\delta = -3893.10$ ppm obtained for **6**, suggesting a very similar platinum coordination sphere for the two compounds, which in the case of **5** does not seem to be affected by the presence of the iridium moiety.

3.6. Conformation of the Pt–Ir bridge complex 5

The 2D ^{1}H NOESY spectrum also allowed to get some information about the relative conformation in solution for the two moieties of the Pt–Ir bridge complex **5**. In particular, among the two diastereotopic allylic protons, one (H_a) seems to interact selectively with the most deshielded of the two vinylic $=CH_2$

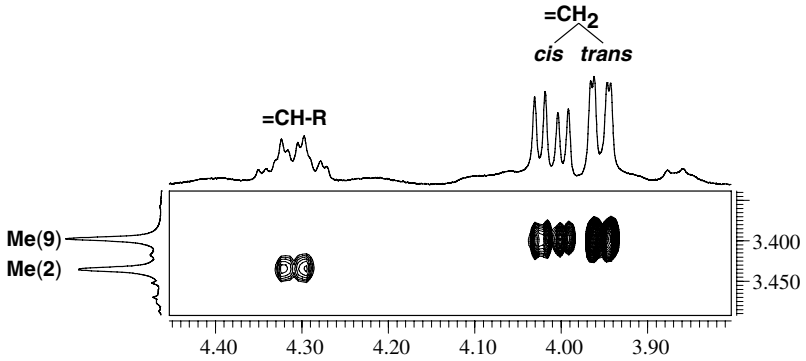


Fig. 3. 2D ^{1}H NOESY spectrum of **5**, expansion relative to the neocuproine methyl cross peaks with the vinylic protons of the iridium moiety.

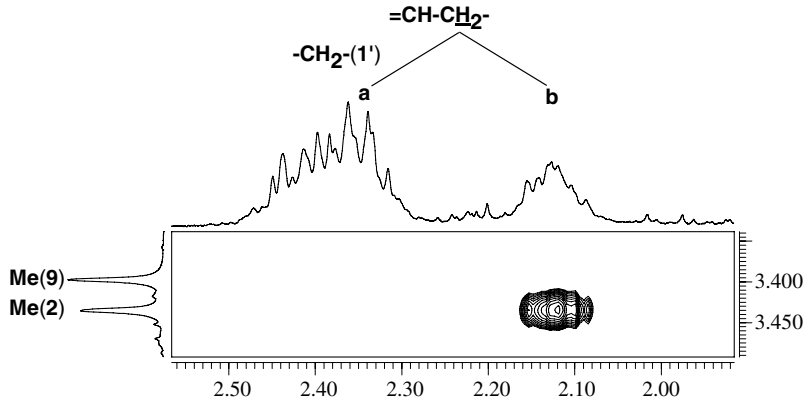


Fig. 4. 2D ^{1}H NOESY spectrum of **5**, expansion relative to the neocuproine methyl cross peaks with the aliphatic protons of the iridium moiety.

protons while the other (H_b) shows NOESY cross peaks with the =CHR vinylic proton and the Me(2) of the neocuproine (Figs. 4 and 5), strongly suggesting a preferential orientation of the aliphatic side chain which links the olefin and the cyclopentadienyl system (Scheme 5). Among the two vinylic $=CH_2$ protons, the one showing NOESY cross peak with the allylic proton H_a has the larger $^3J_{H-H}$ (*trans* coupling) with the =CHR vinylic proton, and therefore is the one in *cis* position (H_{cis}) with respect to the aliphatic side chain which links the olefin and the cyclopentadienyl system.

As already discussed, both the vinylic $=CH_2$ protons (H_{cis} and H_{trans}) show two different ^{1}H NMR signals for

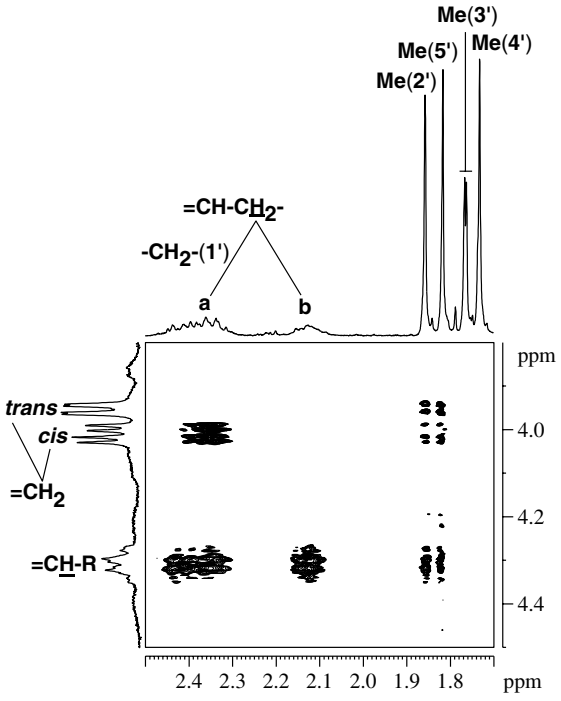
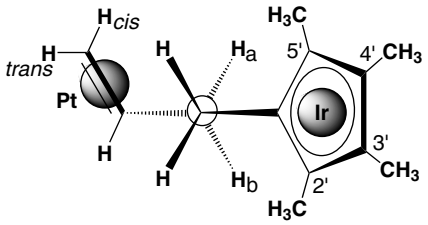


Fig. 5. 2D ^{1}H NOESY spectrum of **5**, showing the cross peaks of the vinylic protons with the Me(2′), Me(5′), allylic CH_2, and homoallylic CH_2.



Scheme 5. Preferential orientation of the iridium moiety side chain as suggested by NOE contacts. H_a: low field allylic proton (2.362 ppm); H_b: high field allylic proton (2.130 ppm). Platinum ligands other than olefin, and iridium substituents other than cyclopentadyenil ring are not shown for clarity.

the two diastereoisomeric forms of **5**. Interestingly, H_{cis}, which occupies in the asymmetric η^2-olefin the position *cis* to the aliphatic side chain carrying the cyclopentadienyl-Ir chiral system, shows also the larger observed $\Delta\delta$ between the ^{1}H signals for the two diastereoisomers of **5**. Among the methyl substituents of the cyclopentadienyl ring, only Me(2′) and Me(5′) show NOESY cross peaks with the olefin containing side arm.

Different volume integrals, observed in the 2D ^{1}H NOESY spectrum for these specific cross peaks allowed to differentiate between Me(2′) and Me(5′), the former being on the average closer to the =CHR and the latter closer to $=CH_2$ protons. No other long range contacts between the platinum and iridium moieties were observed, indicating that while the coordinated olefin and the allylic protons have low mobility, the rest of the cyclopentadienyl iridium moiety tends to move in solution, still remaining far away from the neocuproine ligand.

4. Conclusions

The results reported herein show that the ability of $[PtX_2(Me_2phen)]$ (X = Cl, Br or I) complexes to give olefin uptake, leading to five-coordinated platinum(II) species $[PtX_2(Me_2phen)(\eta^2\text{-olefin})]$, can be used for the

preparation of binuclear heterometallic compounds, provided that olefinic function is covalently bound to another metal complex and available for coordination to platinum. The high degree of destabilization of the starting square planar iodo complex [$PtI_2(Me_2phen)$] can be used to force the addition reaction toward the five-coordinate species. In the present case the huge size of the olefinic susbtituent in [$(C_5Me_4CH_2CH_2CH{=}CH_2)Ir(Me)(CO)(Ph)$] (**3**) does not decrease the thermodynamic stability of the five-coordinated addition complex [$PtI_2(Me_2phen)\{(C_5Me_4CH_2CH_2CH{=}CH_2)Ir(Me)(CO)(Ph)\}$] (**5**) which results an air and solution stable compound, completely characterized by ^{1}H, ^{13}C, and ^{195}Pt NMR spectroscopy. Interestingly, although the Pt–Ir bridge compound, formed by connecting in the same complex a racemic chiral iridium(III) complex and a platinum bound prochiral η^2-olefin, consists of two diastereoisomers, the observed spectroscopic differences between the two species are minimal. Moreover, spectroscopic data show 1:1 integral ratio for the two diastereoisomers, indicating that the presence of a chiral center on the iridium atom does not give a significant induction of chirality upon coordination of the olefin to platinum. Most probably, this is a consequence of the spatial separation between the two chiral centres (prochiral η^2-olefin and asymmetric iridium) provided by the two methylene groups connecting the cyclopentadienyl ring to the olefinic moiety in the binuclear heterometallic complex. The conformational analysis of the Pt–Ir bridge complex, based on 2D ^{1}H NOESY experiments shows that the coordinated olefin and the allylic protons have low mobility, while the cyclopentadienyl iridium and platinum neocuproine moieties, although they can undergo dynamic motion in solution, still remain far away from each other.

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