The Photochemistry of the (Cycloalkene)(hydro)(trispyrazolylborato)iridium Complexes $[Ir(\eta^4\text{-cod})(Tp^{Me2})]$ and $[Ir(\eta^2\text{-coe})H_2(Tp^{Me2})]$: the Formation of $[IrH_4(Tp^{Me2})]$ and $[Ir(CO)H_2(Tp^{Me2})]$

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Photolysis of $[Ir(\eta^2\text{-coe})H_2(Tp^{Me2})]$ (**1**; Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borato, coe = (*Z*)-cyclooctene) in CH_3OH gives a mixture of $[IrH_4(Tp^{Me2})]$ (**4**) and $[Ir(CO)H_2(Tp^{Me2})]$ (**5**) in a *ca.* 1:1 ratio. Mass-spectral analysis of the distillate of the reaction mixture at the end of the photolysis shows the presence of coe. When pure CD_3OD is used as solvent, the deuteride complexes $[IrD_4(Tp^{Me2})]$ ((D_4)-**4**) and $[Ir(CO)D_2(Tp^{Me2})]$ ((D_2)-**5**) are obtained. Also the photolysis of $[Ir(\eta^4\text{-cod})(Tp^{Me2})]$ (**3**) (cod = cycloocta-1,5-diene) gives **4** and **5**. A key feature of this photoreaction is the intramolecular dehydrogenation of cod with formation of cycloocta-1,3,5-triene, detected by mass spectroscopy at the end of the photolysis. Labeling experiments using CD_3OD show that the hydrides in **4** originate from MeOH. When $^{13}CH_3OH$ is used as solvent, $[Ir(^{13}CO)H_2(Tp^{Me2})]$ is formed demonstrating that CH_3OH is the source of the CO ligand. The observation that the photolysis of both **1** and **3** give the same product mixture is attributed to the formation of a common intermediate, *i.e.*, the coordinatively unsaturated $16e^-$ species $\{IrH_2(Tp^{Me2})\}$.

1. Introduction. – The catalytic activation of C–H bonds using soluble metal complexes is a topic of fundamental scientific interest as well as a major unsolved problem in state-of-the-art chemical technology [1]. The photochemical and the thermal activation of alkanes, alkenes, and arenes, starting from organometallic precursors, have been pioneered mainly by *Janowicz* and *Bergman*, *e.g.*, using $[Ir(\eta^5\text{-}C_5Me_5)H_2(PMe_3)]$ [2], and by *Graham* and co-workers, *e.g.*, using $[Ir(CO)_2(\eta^5\text{-}C_5Me_5)]$ [3]. A general approach to C–H bond activation involves an oxidative-addition reaction commonly using a low-valent metal complex containing strong electron donors, *e.g.*, H^-, $\eta^5\text{-}C_5Me_5^-$ and $(alkyl)_3P$ [4][5]. However, more recent studies have led to the recognition that Rh^I complexes with hydrotris(pyrazolyl)borato ions, $Tp^{3R,4R,5R}$[1]), can be used for the thermal and photochemical activation of C–H bonds of alkenes [7]. Thus, the Rh complex $[Rh(CO)_2(Tp^{Me2})]$ activates C–H bonds as irradiation of its solutions in several alkanes (RH), at ambient temperature, produces the corresponding compounds of the type $[Rh(CO)H(R)(Tp^{Me2})]$ and it has been proposed that actual C–H activation occurs at the short-lived $16e^-$ $\{Rh(CO)(Tp^{Me2})\}$

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[1]) The nomenclature used in this publication for the hydrotris(pyrazolyl)borate ligands and their complexes is that proposed by *Trofimenko* [6].

intermediate [8]. Matrix studies by *Bloyce et al.* [9] have confirmed that the most likely primary step is the photo-dissociative loss of CO from the dicarbonyl complex with formation of the above monocarbonyl species.

A detailed study of the C–H activation reaction of alkenes by $[Rh(CO)_2(Tp^{Me2})]$ was recently carried out by *Bromberg et al.* [10] using time-resolved IR experiments to establish the initial femtosecond dynamics and the nano- and microsecond kinetics of the intermediates which lead to the final alkyl hydride products of the type $[Rh(CO)H(R)(Tp^{Me2})]$. They propose the following mechanism for this reaction: *a*) dissociation of CO from $[Rh(CO)_2(Tp^{Me2})]$ and formation of $\{Rh(CO)(\eta^3\text{-}Tp^{Me2})\}$, *b*) addition of R–H to this intermediate to give the 'solvate' $\{Rh(CO)(R{-}H)(\eta^3\text{-}Tp^{Me2})\}$ (**A**), *c*) cleavage of one of the the Rh–N bonds in **A** to give $\{Rh(CO)(R{-}H(\eta^2\text{-}Tp^{Me2})\}$ (**B**), *d*) oxidative addition of R–H to rhodium with formation of $\{Rh(CO)H(R)(\eta^2\text{-}Tp^{Me2})\}$ (**C**), and *e*) the transformation of **C** into $\{Rh(CO)H(R)(\eta^3\text{-}Tp^{Me2})\}$ (**D**).

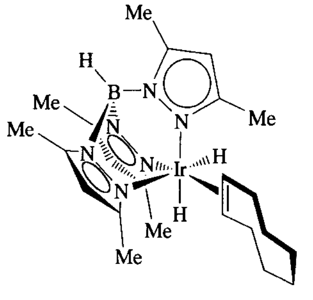
Tanke and *Crabtree* [11], during the reaction of $[Ir_2Cl_2(coe)_4]$ (coe = (*Z*)-cyclooctene) with K[Tp], observe the formation of $[Ir(\eta^3\text{-cyclooctenyl})H(Tp)]$ and postulate that this reaction occurs by way of the intermediate {Ir(coe)Tp} which undergoes intramolecular activation of an allylic C–H bond of the coordinated coe. They also show that $[Ir(C_2H_4)_2(Tp)]$ is photoconverted to the vinyl hydride compound $[Ir(\eta^2\text{-}C_2H_4)H(Tp)(\eta^1\text{-}CH{=}CH_2)]$ and propose that there is intramolecular vinyl C–H bond activation by the intermediate $\{Ir(C_2H_4)Tp\}$ followed by η^2-complexation of the photodissociated ethene [11].

Particularly interesting is the recent demonstration by *Perez et al.* [12] that the complex $[Ir(C_2H_4)_2(Tp^{Me2})]$ undergoes thermal rearrangement to the hydrido-allyl complex $[Ir(\eta^3\text{-}C_3H_4Me)H(Tp^{Me2})]$ through the intermediacy of the hydrido-vinyl complex $[Ir(\eta^2\text{-}C_2H_4)H(Tp)(\eta^1\text{-}CH{=}CH_2)]$. Propene and but-1-ene undergo similar transformations, while allylic activation of an sp^3-type C–H bond is found with the internal alkene (*Z*)-but-2-ene [13]. Such transformations are uncommon even though several studies have shown that coordinated alkenes will undergo a variety of reactions ranging from substitutions to isomerizations [14–17], and skeletal rearrangements [18].

Despite the relatively small number of alkene complexes that have been examined, several aspects concerning their reactivity are becoming better understood. Thus, it is probable that the reactions of alkenes with electron-rich, coordinatively unsaturated transition-metal species, generated either thermally or photochemically, involve either excited-state chemistry or oxidative additions with nucleophilic character [13–19].

The formation of η^3-allylic hydride intermediates is also an attractive mechanism for the activation of C–H bonds in cyclic alkenes. In this case, the role of light could be simply to induce a decrease in alkenes hapticity and open up a coordination site allowing the subsequent reaction with the cycloalkene to occur [10][11][14].

Also relevant in the context of C–H activation is the recent report by *Ferrari et al.* [20] that $[Ir(\eta^2\text{-coe})H_2(Tp^{Me2})]$ (**1**), when photolysed in benzene in the presence of $(MeO)_3P$, gives $[Ir(C_6H_5)H\{(MeO)_3P\}(Tp^{Me2})]$. Mechanistic investigations indicate that the primary photoproduct of the above reaction is the 16e$^-$, five-coordinate Ir^{III} species $\{IrH_2(Tp^{Me2})\}$ (**2**). *Ferrari et al.* also postulate that this intermediate oxidatively adds benzene forming the seven-coordinate Ir^V species $\{Ir(C_6H_5)H_3(Tp^{Me2})\}$ which then reductively eliminates H_2 to yield $\{Ir(C_6H_5)H(Tp^{Me2})\}$. The final product $[Ir(C_6H_5)H\{(MeO)_3P\}(Tp^{Me2})]$ then results from the addition of the phosphite to $\{Ir(C_6H_5)H(Tp^{Me2})\}$ [20].



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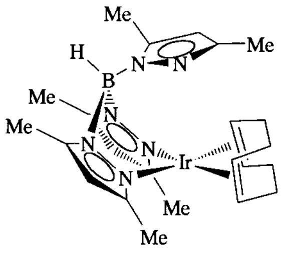

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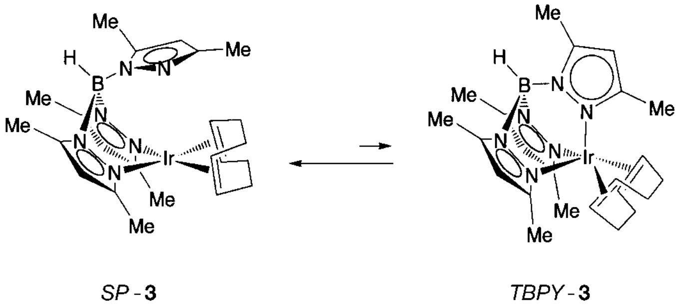
The studies mentioned above indicate that it would be worthwhile to investigate the photoreactivity of organometallic complexes such as $[Ir(\eta^4\text{-cod})(Tp^{Me2})]$ (**3**) (Tp^{Me2} = hydrotris(3,5-dimethylpyrazolyl)borato, cod = cycloocta-1,5-diene) as they are promising candidates for the formation of electron-rich fragments by virtue of their electronic charge-transfer excitations which are of low-energy and, at times, of high intensity [19]. Indeed, electronic properties of this kind can be taken as characteristic of molecules potentially capable of forming coordinatively unsaturated, electron-rich fragments by photoinduced decrease of the dialkene hapticity, *i.e.*, $\eta^4 \rightarrow \eta^2$ which, in the case of **3**, would give $\{Ir(\eta^2\text{-cod})(\eta^x\text{-}Tp^{Me2})\}$ ($x = 2$ or 3) [21]. Such fragments are particularly interesting because both triplet and singlet states are available for them [22].

Studies of the complex $[Ir(\eta^4\text{-cod})(Tp^{Me2})]$ (**3**), which contains an η^4-bonded dialkene, have shown that, while in the solid state the Tp^{Me2} anion is η^2-bonded, in solution it undergoes fast exchange between the η^2- and the η^3-bonded form giving rise to the four-coordinate, square-planar (*SP*-**3**) and five-coordinate, distorted trigonal bipyramidal (*TBPY*-**3**) complexes, the equilibrium position being predominantly in favor of the former (*Scheme 1*) [21]. However, the 16e$^-$ complex *SP*-**3** does not thermally activate a C–H bond of the η^4-coordinated diene, presumably because the bond to be cleaved cannot move sufficiently close to the metal center because of the rigidity of this η^4-coordinated ligand. Therefore, it is likely that light induces the cleavage of one of the alkene–Ir bonds either in the *SP*-**3** or the *TBPY*-**3** isomer with formation of the coordinatively unsaturated species $\{Ir(\eta^2\text{-cod})(\eta^x\text{-}Tp^{Me2})\}$ ($x = 2$ or 3) and this might activate C–H bonds in alkenes *via* an intra- or intermolecular process.

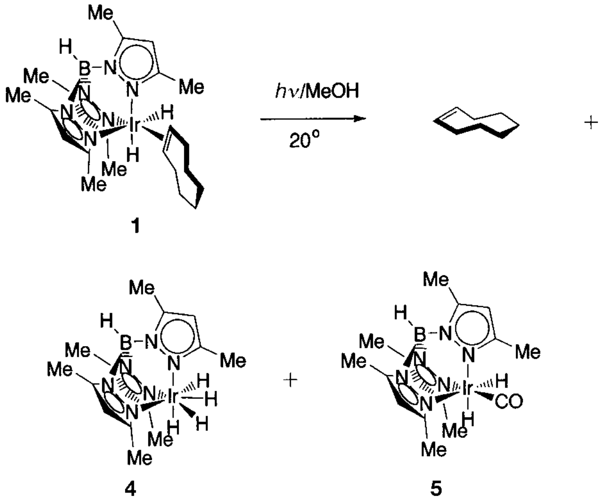
This contribution presents a study of the photo-reactivity of CH_3OH solutions of $[Ir(\eta^2\text{-coe})H_2(Tp^{Me2})]$ (**1**) and of $[Ir(\eta^4\text{-cod})(Tp^{Me2})]$ (**3**).

2. Results. – 2.1. *Photolysis of* $[Ir(\eta^2\text{-coe})H_2(Tp^{Me2})]$ (**1**) *in* CH_3OH. The photolysis of this Ir^{III} complex, in CH_3OH at 20°, gives a mixture of $[IrH_4(Tp^{Me2})]$ (**4**) and $[Ir(CO)H_2(Tp^{Me2})]$ (**5**), in the ratio of *ca.* 1:1 (*Scheme 2*). A GC/MS study of the distillate of the reaction mixure at the end of photolysis shows the presence of coe. No other cycloalkene can be detected.

Scheme 1



Scheme 2



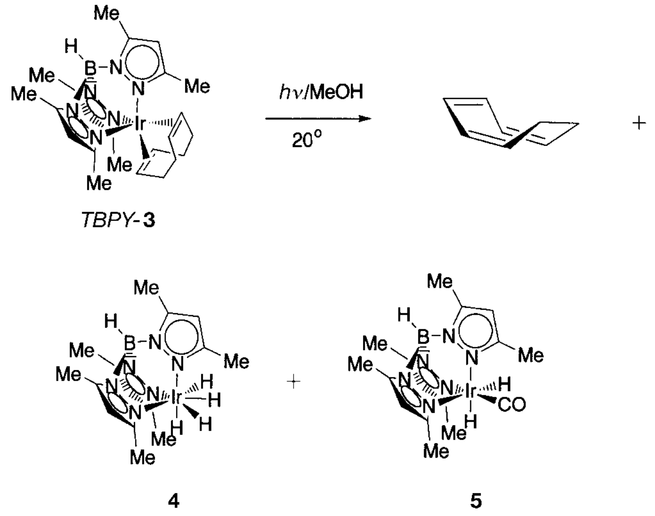
Gradual decomposition of **4** prevents its isolation in the pure state from the reaction mixture, and, therefore, it was characterized in solution by ^{1}H- and ^{13}C{^{1}H}-NMR spectroscopy. Product **4** proves to be the previously reported complex [$IrH_4(Tp^{Me2})$] obtained by other routes by *Paneque et al.* [23] and by *Albinati et al.* [21]. Spectroscopic studies show that **5** is [$Ir(CO)H_2(Tp^{Me2})$] (see later).

Under the same photochemical conditions, complex **4** *does not* react with CO to produce **5** and, *vice versa*, **5** *is not* converted to **4** under an H_2 atmosphere. Thus, neither of them is a precursor for the other.

This photochemical reaction, when carried out in CD_3OD, produces [$IrD_4(Tp^{Me2})$] ((D_4)-**4**) and [$Ir(CO)D_2(Tp^{Me2})$] ((D_2)-**5**). The formation of these deuterides is indicated by *a*) the absence of hydride signals and the presence of the signals for the coordinated Tp^{Me2} ligand in the ^{1}H-NMR spectrum and *b*) the presence of deuteride ligands in (D_2)-**5** at -16.98 ppm in the ^{2}H-NMR spectrum. It is not possible to detect the signal of (D_4)-**4** in its ^{2}H-NMR spectrum recorded in CH_2Cl_2 which has been dried only over a molecular sieve, due H/D exchange with the solvent as shown by the growth of $CHDCl_2$ resonance during the spectral acquisition. The solid-state IR spectrum of (D_2)-**5** shows one band at 1617 cm^{-1}, assigned to the $\tilde{\nu}(Ir-D)$ stretch ($\tilde{\nu}(Ir-H)/\tilde{\nu}(Ir-D) = 1.33$), and another at 2011 cm^{-1} assigned to $\tilde{\nu}(CO)$.

2.2. *Photolysis of [Ir(η^4-cod)(Tp^{Me2})]* (**3**) *in CH_3OH.* Photolysis at $\lambda \geq 335$ nm of a degassed solution of **3**, in CH_3OH at 20° for 4.5 h, results in its complete conversion into the complexes **4** and **5** in the ratio of *ca.* 1 : 1 (*Scheme 3*). GC/MS Studies of the distillate of the reaction mixture, at the end of photolysis, show the presence of cycloocta-1,3,5-triene. No other cycloalkene is detected.

Scheme 3



Spectroscopic studies show that **5**, isolated in 35% yield from the photoreaction mixture, is $[Ir(CO)H_2(Tp^{Me2})]$. This complex is characterized by two IR bands, one at 2152 cm^{-1}, assigned to $\tilde{\nu}(Ir-H)$, as expected for *cis*-dihydrides in which the H-atoms are in *trans*-positions to the same donor groups [24], and another at 2005 cm^{-1} assigned to $\tilde{\nu}(CO)$. It also shows two sets of ligand resonances in the ^1H-NMR spectrum, in a ratio of 2 : 1, due to the pyrazolyl groups and a *singlet* at -17.18 ppm assigned to the hydride. The ^{15}N-NMR spectrum shows two signals at -160.0 and -172.1 ppm, assigned to the coordinated N-atoms of the pyrazolyl ligand [21], in *trans*-positions to H and CO, respectively. Finally, its mass spectrum has main peaks at *m/z* 519.5 (the parent ion $[Ir(CO)H_2(Tp^{Me2})]^{\cdot+}$), 517 ($[M - H_2]^{\cdot+}$) and 491 ($[M - CO]^{\cdot+}$).

Although the preparation of **5** was briefly reported [23], no spectral or other data were published. However, the analogous complex with the unsubstituted hydrotris(pyrazolyl) anion, $[Ir(CO)H_2(Tp)]$, is characterized by $\tilde{\nu}(Ir-H)$ at 2165 and $\tilde{\nu}(C-O)$ at 2020 cm^{-1} [25].

NMR Studies also show that, when the photoreaction of $[Ir(\eta^4\text{-cod})(Tp^{Me2})]$ (**3**) is carried out in CD_3OD it yields $[IrD_4(Tp^{Me2})]$ ((D_4)-**4**) and $[Ir(CO)D_2(Tp^{Me2})]$ ((D_2)-**5**).

2.3. *Photolysis of [Ir(η^4-cod)(Tp^{Me2})]* (**3**) *in* $^{13}CH_3OH$. The photolysis of [Ir(η^4-cod)(Tp^{Me2})] (**3**), dissolved in ^{13}C-enriched CH_3OH (*ca.* 60%), gives a mixtures of [IrH_4(Tp^{Me2})] (**4**), [Ir(CO)H_2(Tp^{Me2})] (**5**), and [Ir(^{13}CO)H_2(Tp^{Me2})] ((^{13}CO)-**5**). The IR spectrum of this mixture, in the solid state, shows bands at 2152, 2005, and 1956 cm^{-1}, assigned to $\tilde{\nu}$(Ir−H), $\tilde{\nu}$(^{12}CO), and $\tilde{\nu}$(^{13}CO), respectively. The decrease in $\tilde{\nu}$(CO) frequency in (^{13}CO)-**5** **^{13}CO**, relative to in **5**, corresponds to that expected from force-field considerations [26]. Also the ^{1}H-, ^{13}C-, and ^{13}C{^{1}H}-NMR spectra of the mixture of **5**/(^{13}CO)-**5**, in CD_2Cl_2, are in agreement with the above structural assignment (see *Exper. Part*). Thus, CO in **5** is derived from CH_3OH.

2.4. *H/D Exchange between* CD_3OD *and [IrH$_4$(Tp^{Me2})]* (**4**) *and [Ir(CO)H$_2$(Tp^{Me2})]* (**5**). ^{1}H-NMR Studies of this exchange in CD_2Cl_2 show that the signal due to **4**, a *singlet* at −15.21, weakens upon addition of a small amount of CD_3OD while the isotopomers [$IrD_nH_{(4-n)}$(Tp^{Me2})] ((D_n)-**4**; $n = 1-3$) are formed, as shown by appearance of the corresponding signals at −15.04, −14.88, and −14.75 ppm. The rate of H/D exchange appears to be relatively rapid in the system compared with that occurring in C_6D_6 [23]. No H/D exchange between **5** and CD_3OD occurs under these conditions. Control experiments show that, in the case of [IrH_4(Tp^{Me2})] (**4**), H/D scrambling occurs exclusively at the hydride sites, and that there is no incorporation of D into the coordinated Tp^{Me2} ligand even after 24 h in the dark.

2.5. *H/D Exchange between* H_2O *and [IrD$_4$(Tp^{Me2})]* ((D_4)-**4**) *and [Ir(CO)D$_2$(Tp^{Me2})]* ((D_2)-**5**). To confirm occurrence of H/D isotope exchange between adventitious water, present despite very careful workup, the reverse experiment was also performed, *i.e.*, a mixture [IrD_4(Tp^{Me2})] ((D_4)-**4**)/[Ir(CO)D_2(Tp^{Me2})] ((D_2)-**5**), in strictly anhydrous CD_2Cl_2, was treated with traces of H_2O and the reaction monitored by ^{1}H-NMR. While there is no signal in the hydride region of the ^{1}H-NMR spectrum of the freshly prepared solution, after the addition of trace amounts of H_2O, the gradual incorporation of H-atoms occurs, and the mixture of isotopomers [$IrD_nH_{(4-n)}$(Tp^{Me2})] ((D_n)-**4**; $n = 1-3$) is produced. However, also in this experiment there is no evidence of incorporation of H-atoms in (D_2)-**5**.

2.6. *Photolysis of [Ir(CO)H$_2$(Tp^{Me2})]* (**5**) *in* CH_3OD. When this complex, dissolved in CH_3OD, was irradiated at $\lambda > 335$ nm for 4.5 h, [Ir(CO)D_2(Tp^{Me2})] ((D_2)-**5**) was formed quantitatively. As, there is photochemical exchange between the D-atoms of CH_3OD and the hydride ligands of **5**, it is not possible to experimentally establish whether the hydrides in **5**, formed during the photochemical reaction described in *Scheme 2*, originate from the cycloalkene or CH_3OH.

2.7. *Spectroscopic Studies of [Ir(η^4-cod)(Tp^{Me2})]* (**3**). The electronic absorption spectrum of this complex was measured to assign its ligand-field and charge-transfer bands and to elucidate the nature of the photochemically active excited states. As the square planar isomer [Ir(η^4-cod)(η^2-Tp^{Me2})] (*SP*-**3**) predominates in solution [21], the features observed are assigned to transitions within this form. This complex shows an intense absorption system between 350 and 450 nm characterized by one band at 370.5 nm ($\varepsilon = 2010$), another at 430.5 nm ($\varepsilon = 2655$), and a shoulder at 491.2 nm ($\varepsilon = 543$). No absorptions with intensities characteristic for ligand-field bands are observed. As absorptions of comparable intensities are not present either in the spectrum of the uncomplexed Tp^{Me2} anion or of free cod, these features are assigned to transitions involving one or more metal orbitals.

The molar absorptivity values and the solvent independence of the energies of the above bands suggest that they originate from metal-to-ligand charge transfer (MLCT). It is noteworthy that the spectra of the complexes $[IrX(CO)(PR_3)_2]$ (X = Cl and Br) in this region show analogous absorption features which have been assigned to be MLCT transitions [27]. As such states are extremely short-lived [19b], a rapid relaxation to a longer lived chemically active, ligand field (LF) state is expected to occur.

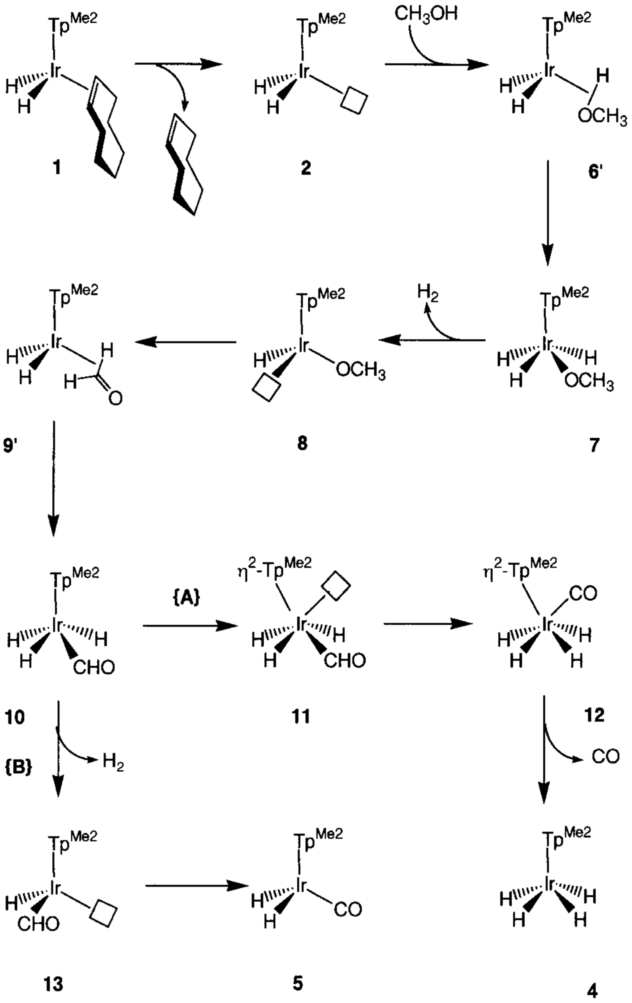
3. Discussion. – 3.1. *Photolysis of* $[Ir(\eta^2\text{-coe})H_2(Tp^{Me2})]$ (**1**) *in* CH_3OH. This reaction (see *Scheme 2*) will be discussed first as it is likely to be related to that of the same complex dissolved either in benzene or Et_2O studied earlier by *Ferrari et al.* [20]. As these authors established that the most likely primary photoproduct formed during the photolysis of **1** is the Ir^{III} five-coordinate fragment $\{IrH_2(Tp^{Me2})\}$ (**2**), it is proposed here that **2** is the primary photoproduct also when the photolysis of **1** is carried out in CH_3OH.

A possible reaction pathway leading to the formation of the tetrahydrido complex $[IrH_4(Tp^{Me2})]$ (**4**) is shown in *Scheme 4*. It is proposed that, after the coe dissociation from the **1** [20], CH_3OH occupies the vacant site on the metal with the formation of the intermediate $[Ir(CH_3OH)H_2(Tp^{Me2})]$ (**6**). Although, in its ground state, CH_3OH will be bonded to Ir through the O-atom, it is likely that the oxidative addition of an O–H bond, postulated as the next step, will occur at the short-lived photoexcited isomer **6′** where the O–H bond interacts with the metal center [10]. The product of this reaction should be the Ir^V intermediate $\{IrH_3(OCH_3)(Tp^{Me2})\}$ (**7**). Similar hydrido-alkoxy complexes are known as *Yoshida* and *Otsuka* report that $[Pt(PEt_3)_3]$ reacts with CH_3OH giving $[PtH(PEt_3)_3](OCH_3)$ which, however, cannot be isolated [28], and *Gotzig et al.* have spectroscopically identified *cis*-$[OsH(OCH_3)(PMe_3)_4]$ and its subsequent decomposition to *cis*-$[OsH_2(PMe_3)_4]$ [29].

It is further postulated that photoinduced loss of H_2 from **7** produces a monohydrido-alkoxo complex $\{IrH(OCH_3)(Tp^{Me2})\}$ (**8**) whose coordinative unsaturation will induce a β-H-abstraction reaction from the CH_3O group giving the Ir^{III} dihydrido intermediate $\{Ir(H_2CO)H_2(Tp^{Me2})\}$ (**9**) which contains coordinated CH_2O. While the latter ligand, in the 'static' form of **9**, is expected to be bonded to Ir through its O-atom, it is likely that the next step will occur at a photoactivated isomeric form of this intermediate in which the metal interacts with a C–H bond of the aldehyde **9′**. Such a species could then undergo an oxidative addition reaction with formation of the formyl intermediate $\{Ir(CHO)H_3(Tp^{Me2})\}$ (**10**). It is also proposed here that this intermediate will react further by two pathways. One of them ({**A**}; see *Scheme 4*) involves the loss of CO from the CHO ligand. As this reaction requires a vacant coordination site for the outgoing CO, it is proposed that this vacant site is produced by the photochemically induced Ir–N bond cleavage (→**11**) whereby the Tp^{Me2} ligand becomes η^2-bonded. *Bromberg et al.* [10] have detected a process of this type during a photochemical study of C–H activation by $\{Rh(CO)(\eta^3\text{-}Tp^{Me2})\}$. Finally, it is proposed that photoinduced loss of CO from $\{Ir(CO)H_4(\eta^2\text{-}Tp^{Me2})\}$ (**12**) produces $[IrH_4(Tp^{Me2})]$ (**4**) with the pyrazolylborate ligand coordinated to Ir in an η^3-mode.

As $[Ir(CO)H_2(Tp^{Me2})]$ (**5**) is formed together with $[IrH_4(Tp^{Me2})]$ (**4**) during the photolysis of **3**, it is conceivable that **5** is formed from **4** as, during this reaction, CO is evolved. However, this is unlikely as *a*) the ratio **4**/**5** is unchanged when the

Scheme 4



photolysis of **3** is carried out in a stream of CO, and *b*) *Paneque et al.* [23] report that the formation of $[IrH_2(L)(Tp^{Me2})]$ (L = CO and PMe_3) from **4** requires 'forcing conditions', and *c*) the tetrahydride **4** is photochemically stable. Thus, it is proposed here that the formyl-trihydrido intermediate **10** can also undergo reductive elimination of dihydrogen with formation of $\{IrH(CHO)(Tp^{Me2})\}$ (**13**) ({**B**}; see *Scheme 4*). Its decarbonylation would then yield the corresponding carbonyl hydride $[Ir(CO)H_2(Tp^{Me2})]$ (**5**). This process is an established decomposition pathway for a metal formyl complex [30].

Precedents for the reactions postulated above have been established by several groups which have shown that transition-metal halides in the presence of phosphines react with CH_3OH to give CH_2O, which then acts as a source of CO [31–34].

Most of the steps postulated in *Scheme 4* were formulated as involving intermediates that contain η^3-bonded Tp^{Me2} ligands. However, the photochemical studies by *Bromberg et al.* [10] on $[Rh(CO)_2(Tp^{Me2})]$ indicate that several of the reactions shown in *Scheme 4* might instead occur at short lived intermediates with η^2-bonded Tp^{Me2} ligands. Thus, in the absence of more detailed spectroscopic studies, the hapticity of the Tp^{Me2} ligands in most of the intermediates shown in *Scheme 4* had not been specified.

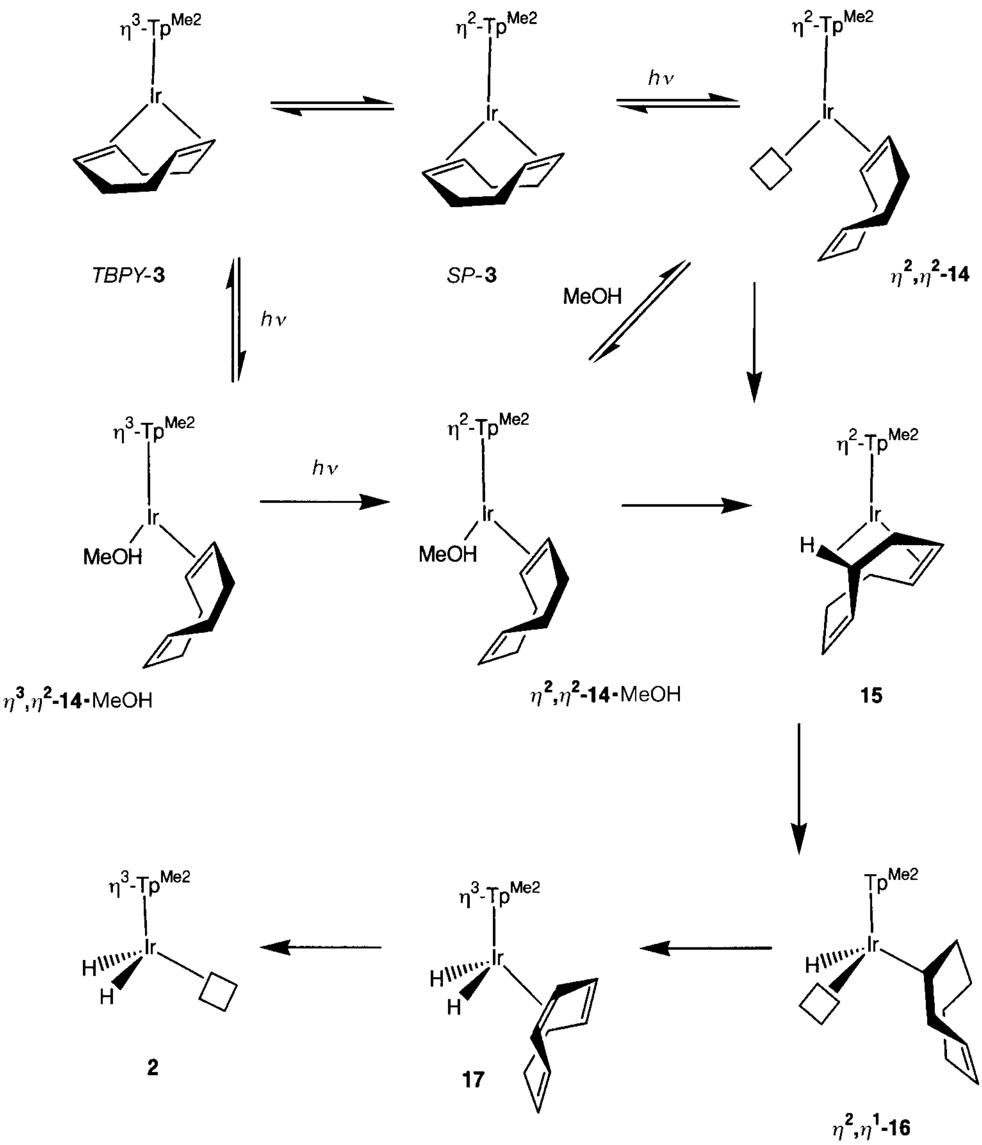
Furthermore, it is also conceivable that the oxidative addition of CH_3OH to Ir in **2** occurs though a C–H instead of an O–H bond as postulated in *Scheme 4*. In such case, instead of **7**, the intermediate formed would be $\{IrH_3(CH_2OH)(Tp^{Me2})\}$ (**7′**) which might react further with elimination of H_2, as proposed for **7**, giving $\{IrH(CH_2OH)(Tp^{Me2})\}$ (**8′**). As the rearrangement of a fragment such as '$MH(CH_2OH)$' to '$MH_2(H_2CO)$' appears to be unprecedented, preference has been given to the oxidative addition of an O–H bond.

3.2. *Photolysis of* $[Ir(\eta^4\text{-cod})(Tp^{Me2})]$ (**3**) *in* CH_3OH. As the photolysis of $[Ir(\eta^4\text{-cod})(Tp^{Me2})]$ (**3**) (see *Scheme 2*), like that of $[IrH_2(\eta^2\text{-coe})(Tp^{Me2})]$ (**1**) in the same medium (see *Scheme 3*), leads to the simultaneous formation of $[IrH_4(Tp^{Me2})]$ (**4**) and $[Ir(CO)H_2(Tp^{Me2})]$ (**5**) in a similar ratio, it is proposed that the two reactions have a common intermediate, *i.e.*, **2**, and the pathway proposed for its formation from **3** is summarized in *Scheme 5*. Mention was made earlier that solutions of **3** contain mixtures of $[Ir(\eta^4\text{-cod})(\eta^2\text{-}Tp^{Me2})]$ (*SP*-**3**) and $[Ir(\eta^4\text{-cod})(\eta^3\text{-}Tp^{Me2})]$ (*TBPY*-**3**) in rapid equilibrium (see *Schemes 1* and *5*), and the question arises here whether the photoinduced cleavage of one of the Ir–alkene bond occurs at the former or the latter isomer.

If this cleavage occurs in the five-coordinate species *TBPY*-**3**, it is expected that the resulting coordinatively unsaturated intermediate $[Ir(\eta^2\text{-cod})(\eta^3\text{-}Tp^{Me2})]$ (η^2,η^3-**14**) would add a solvent molecule with formation of η^3,η^2-**14** · MeOH which would be isolobal with intermediate **A** of *Bromberg et al.* [10]. It should also be noted that, in the present case the four-coordinate form *SP*-**3** predominates in solution and has the required spectral characteristics for photo-excitation. Also here the cleavage of one of the iridium–alkene bonds would occur as a consequence of an active CT transition, which depopulates an Ir–cod, and populates an antibonding molecular orbital and, consequently, reduces the cod hapticity from η^4 to η^2. The resulting intermediate, $\{Ir(\eta^2\text{-cod})(\eta^2\text{-}Tp^{Me2})\}$ (η^2,η^2-**14**), is also expected to interact with the solvent giving η^2,η^2-**14** · MeOH which would be isolobal with intermediate **B** of *Bromberg et al.* [10]. As the reaction pathway formulated by these authors includes the photochemical transformation of **A** into **B**, it is possible that, in the present case, η^2,η^3-**14** · MeOH reacts further with formation of η^2,η^2-**14** · MeOH. However, as discussed earlier, this intermediate can also be formed directly from *SP*-**3**.

The Ir system described here differs from that of *Bromberg et al.* [10] as, in this case, after the photochemical cleavage of one of the cod double bonds, the other remains coordinated to Ir. Therefore, one of the C–H bonds of the CH_2 groups of the dialkene could get sufficiently close to the metal atom, displace the coordinated solvent and enter into an agostic interaction with the metal center (**15**). This interaction could then induce the oxidative addition of this C–H bond with formation of the hydrido η^1-alkenyl intermediate $\{Ir(\eta^1\text{-}C_8H_{10})H(\eta^2\text{-}Tp^{Me2})\}$ (η^1,η^2-**16**). While it is likely that a complex of this composition, in its ground state, will be present as the hydrido-η^3-allyl

Scheme 5



isomer $\{Ir(\eta^3\text{-}C_8H_{10})H(\eta^2\text{-}Tp^{Me2})\}$ (η^3,η^2-**16**), its photoexcitation is expected to transform it into η^1-**16**.

It is further postulated that intermediate η^2-**16** undergoes a hydride-transfer reaction to give the corresponding complex $\{Ir(\eta^2\text{-}C_8H_{10})H_2(Tp^{Me2})\}$ (**17**) and that the latter, as proposed for **1**, under photochemical conditions, will form $\{IrH_2(Tp^{Me2})\}$ (**2**) with liberation of the cycloocta-1,3,5-triene detected in the mass spectrum of the solution at the end of the photolysis. By analogy with the related reactions described above, it is proposed that $\{IrH_2(Tp^{Me2})\}$ (**2**) will further react with CH_3OH as depicted in *Scheme 4*.

It is noteworthy that the intramolecular photo-dehydrogenation of cod in a complex such as **3** appears to be unprecedented. Furthermore, while polyhydrido complexes possessing four or more hydride ligands usually are extremely reactive species, $[IrH_4(Tp^{Me2})]$ (**4**) is *photochemically stable* under the reaction conditions used in this study. Finally, although the thermal formation of carbonyl-hydrido complexes from reactions carried out using an alcohol as a solvent has been known for many years [35], to our knowledge, the photochemical equivalent of this type of reaction with (pyrazolylborate)iridium complexes is new. Furthermore, it occurs at the surprisingly low temperature of 20°, which is unprecedented for such a process.

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Experimental Part

General. The solvents CH_3OH and CD_3OD (*Fluka*) were purified by refluxing them in the presence of dry Mg turnings and I_2, and distilling them off, excluding moisture from the system. The CH_2Cl_2 (*Fluka*) was refluxed over CaH_2 and then distilled. The hexane (*Fluka*) was dried by refluxing it over Na/benzophenone and distilled under Ar prior to use. The deuterated solvents CD_2Cl_2 and C_6D_6 were obtained from *Fluka* and dried over molecular sieves (3 Å). The $^{13}CH_3OH$ (^{13}C, atom 60%) was obtained from the *Cambridge Isotope Laboratories*. The gases used in synthesis were *Aldrich* standard grade (H_2 99.99%, CO 99.95 purity). IR Spectra: *Bruker IFS 88* FT-IR spectrometer. NMR Spectra: *Bruker AC 200* instrument and, in part, *Bruker AMX 500*, operating at 200.13 (500.13), 30.7 (76.6), 50.2 (125.6) MHz for ^1H, ^2H, and ^{13}C, respectively. The chemical shift scales are relative to internal TMS for ^1H, ^2H, and ^{13}C, and external $MeNO_2$ for ^{15}N. As the ^{15}N-NMR data (50.7 MHz) were obtained using $^{15}N,^1H$-correlation spectroscpy, they provided only the N(2) resonance. MS: *Varian MAT CH7* instrument (70 eV). The photochemical reactions were performed with the output of a 500-W *Oriel* Hg lamp fitted with an IR blocking filter and a water filter to remove excess heat. All preparations and photochemical experiments were carried out under dry Ar using standard *Schlenk* techniques. The complexes $[Ir(\eta^4\text{-cod})(Tp^{Me2})]$ [21] (**3**) and $[Ir(\eta^2\text{-coe})H_2(Tp^{Me2})]$ [36] (**1**) were prepared as described in the appropriate references.

Photolysis of $[Ir(\eta^4\text{-cod})(Tp^{Me2})]$ (**3**) *in* CH_3OH. A soln. of **3** (7.8 mg, 0.013 mmol) in CH_3OH (4 ml) was prepared by distilling CH_3OH directly into the quartz cuvette in which the photochemical reaction was to be carried out. The cuvette was sealed with a septum cap and the soln. stirred by an Ar flow (this stirring is very important to ensure that the reaction goes to completion and to prevent any build-up of precipitate on the walls of the cuvette). The soln. was irradiated at $\lambda \geq 335$ nm at 20°. The photolysis was stopped when ^1H-NMR monitoring of the mixture showed that the cod signals of **3** at 3.87, 1.92, and 1.35 ppm had disappeared (*ca.* 270 min). Removal of the solvent under vacuum at r.t. gave a pinkish-white residue. The ^1H-NMR spectrum of the crude residue, dissolved in CD_2Cl_2, showed the presence of two complexes $[IrH_4(Tp^{Me2})]$ (**4**) and $[Ir(CO)H_2(Tp^{Me2})]$ (**5**) in a 1:1 ratio (see below). The MS of the filtrate, after reduction to a small volume under vacuum, shows the presence of cycloocta-1,3,5-triene. Larger amounts of **4** and **5** were obtained by repeating the above photolysis 15 times. Spectral data for **4** obtained from the mixture of the two complexes: FT-IR (KBr): 2155*s* ($\tilde{\nu}$(Ir–H)). ^1H-NMR (CD_2Cl_2): 5.86 (*s*, 3 H, H–C(4)); 4.71 (*s*, 1 H, BH); 2.38 (*s*, 9 H, Me–C(5)); 2.16 (*s*, 9 H, Me–C(3)); –15.21 (*s*, 4 H, IrH). ^{15}N-NMR (CD_2Cl_2): –164.6 (N(2)).

The residue containing the products **4** and **5** was dissolved in CH_2Cl_2. The resulting soln. was reduced to a small volume in vacuum and the residue was recrystallized twice from hexane at 0°. This gave anal. pure **5**, as white product in 35% yield. FT-IR (KBr): 2152*s* ($\tilde{\nu}$(Ir–H)), 2005*s* ($\tilde{\nu}$(CO)) [16]. ^1H-NMR (CD_2Cl_2): 5.88 (*s*, 2 H, H–C(4)); 5.84 (*s*, 1 H, H–C(4′)); 4.68 (*s*, 1 H, BH); 2.39 (*s*, 6 H, Me–C(5)); 2.34 (*s*, 3 H, Me–C(5′)); 2.24 (*s*, 6 H, Me–C(3)); 2.20 (*s*, 3 H, Me–C(3′)); –17.18 (*s*, 2 H, IrH). $^{13}C\{^1H\}$-NMR (CD_2Cl_2): 151.94 (*s*, 1 C, C(3′)); 151.39 (*s*, 2 C, C(3)); 139.31 (*s*, 1 C, C(5′)); 139.28 (*s*, 2 C, C(5)); 106.18 (*s*, 2 C, C(4)); 106.15 (*s*, 1 C, C(4′)); 17.66 (*s*, 1 C, *Me*–C(3′)); 16.04 (*s*, 2 C, *Me*–C(3)); 13.05 (*s*, 1 C, *Me*–C(5′)); 12.87 (*s*, 2 C, *Me*–C(5)).

^{15}N-NMR (CD_2Cl_2): – 160.0 (*s*, 2 N, N(2) (*trans*-H)), – 172.1 (*s*, 1 N, N(2)(*trans*-CO)). MS (peaks are quoted for ^{193}Ir isotopomer): 519.5 ($M^{+\bullet}$), 517 ($[M - H_2]^{+\bullet}$), 491 ($[M - CO]^{+\bullet}$).

Photolysis of **3** *in CD_3OD.* A soln. of **1** (7.8 mg; 0.013 mmol) in CD_3OD (4 ml) was prepared and irradiated as described above. Removal of the solvent under vacuum yielded (D_4)-**4** and (D_2)-**5** in a 1 : 1 ratio. The residue was crystallized twice from hexane at 0° yielding the anal. pure complex [Ir(CO)D_2(Tp^{Me2})]. FT-IR (KBr): 1617*s* ($\tilde{\nu}$(Ir–D)), 2011*s* ($\tilde{\nu}$(CO)). ^{2}H-NMR (CH_2Cl_2): – 16.98 (*s*, IrD). The ^{1}H-NMR for (D_4)-**4** and (D_2)-**5** is silent in the hydride region. All the signals of the Tp^{Me2}-coordinated in (D_4)-**4** and (D_2)-**5** are present (see the last paragraph of the above section).

Photolysis of **3** *in $^{13}CH_3OH$.* The compounds **4**, **5**, and ^{15}CO-**5** were obtained as described above replacing CH_3OH with *ca.* 60% enriched $^{13}CH_3OH$. Spectroscopic data for ^{13}CO-**5**: FT-IR (KBr): 2152*s* (ν(Ir–H)), 1956*s* ($\tilde{\nu}$(CO)). ^{13}C-NMR (CD_2Cl_2): 170 (*t*, ^2J(^{13}C, ^{1}H) = 7.4, CO). ^{13}C{^{1}H}-NMR (CD_2Cl_2): 170 (*s*, CO).

Experiments under a CO or H_2 Atmosphere. These were carried out using **3** in CH_3OH, as described above, but H_2 or CO was passed through the solns. during photolysis. The results were identical with those of the reaction carried out under Ar.

Photolysis of [Ir(η^2-coe)(Tp^{Me2})] (**1**) *in CH_3OH.* A soln. of **1** (5.5 mg, $9.14 \cdot 10^{-3}$ mmol) in CH_3OH (4 ml) was prepared and irradiated as described for **3**. Removal of the solvent under vacuum yielded a residue, which was washed with CH_3OH and dried under vacuum. The ^{1}H-NMR spectrum of the residue showed the presence of **4** and **5**, in the ratio of *ca.* 1 : 1, and coe.

Photolysis of [Ir(CO)H_2(Tp^{Me2})] (**5**) *in CH_3OD and CD_3OD.* The photolysis was carried out using quantities as described above replacing CH_3OH with the deuterated solvents. The NMR spectra of the reaction mixture show the presence of (D_2)-**5** and a new hydride at – 20.75 ppm. The identity of this hydride is the subject of further investigation.

H/D Exchange between Solutions [IrH_4(Tp^{Me2})] (**4**) *and [Ir(CO)H_2(Tp^{Me2})]* (**5**) *in CD_2Cl_2 and CD_3OD.* A 1 : 1 mixture **4/5** (3 mg) in CD_2Cl_2 (0.5 ml) was placed in an NMR tube fitted with a *Teflon* stopcock for facile closure. After addition of 0.25 µl of CD_3OD (0.003 mmol), the ^{1}H-NMR spectrum shows the gradual disappearance of the signal at – 15.21 ppm due to **4** and growth of the resonances due to the isotopomers (D_n)-**4** (n = 1 – 3), *i.e.*, at – 15.04 (^1J(H,D) = 2.45 ((D_1)-**4**)); – 14.88 (^1J(H,D) = 2.7 ((D_2)-**4**)); – 14.75 (^1J(H,D) = 2.7 ((D_3)-**4**)). No H/D exchange between CD_3OD and is observed.

The same results were obtained using a soln. of **4** and **5** in pure C_6D_6. The conditions and quantities used were similar to those described above. After 16 h, the ^{1}H-NMR spectrum of the soln. showed that intensity of the signal of **4** had weakened and that the isotopomers (D_n)-**4** (n = 1 – 3) had formed, as reported by *Paneque et al.* [23].

*H/D Exchange between (D_4)-**4** and (D_2)-**5**, and H_2O.* The procedure and quantities of reagents used were similar to those described above. After addition of 0.2 µl (0.013 mmol) of H_2O, the ^{1}H-NMR spectrum reveals the appearance of peaks at – 15.21 ppm typical of complex **4** and resonances at – 15.04, – 14.88, and – 14.76 corresponding to the signals of the isotopomers (D_n)-**4** (n = 1 – 3), respectively. The exchange was almost complete after 24 h as indicated by the total absence of the signals due to (D_4)-**4** in ^{2}H-NMR spectrum.

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