

Evidence for platinum(II)–vinylidene complexes and their reactions with water to give hydrocarbons and olefins[☆]

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Abstract

Treatment of the alkynyl complexes *trans*-[Pt(Me)(C≡CR)(PPh₃)₂] (R = *p*-tolyl (**1a**), Ph (**1b**)) at low temperature in a CD₂Cl₂ solution with stoichiometric amounts of the acids HBF₄·Et₂O or CF₃SO₃H affords the corresponding vinylidene derivatives *trans*-[Pt(Me){C=C(H)R}(PPh₃)₂]X (R = *p*-tolyl, X = BF₄ (**2a**BF₄); R = *p*-tolyl, X = CF₃SO₃ (**2a**CF₃SO₃); R = Ph, X = BF₄ (**2b**BF₄)) on the basis of ¹H- and ³¹P{¹H}-NMR data. The reactions of the in situ generated complexes **2** with water, which were followed by ¹H- and ³¹P{¹H}-NMR, lead to the formation of a mixture of the carbonyl complex [Pt(Me)(CO)(PPh₃)₂]X (**3**) and the hydroxo-bridged dinuclear compound [Pt(μ-OH)(PPh₃)₂]₂X₂ (**4**) in a ca. 1:2 ratio. The formation of **3** and **4** is accompanied with the liberation of hydrocarbons R-CH₃ and olefins CH₃CH=CHR (R = *p*-tolyl, Ph), respectively, which arise from the vinylidene ligand likely via an hydroxycarbene intermediate. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Alkynyl; Hydrocarbons; Olefins; Platinum(II) complexes; Vinylidene

1. Introduction

The chemistry of transition metal vinylidene complexes, L_nM=C=C(H)R, has developed rapidly in the last 20 years. Several methods have been employed for the preparation of mononuclear vinylidene complexes, in particular from 1-alkynes via a formal 1,2-hydrogen shift or by addition of electrophiles such as protic acids to metal alkynyl complexes [1]. Early studies on these reactions with platinum(II)–terminal alkyne and –alkynyl complexes have been made by Clark and Chisholm, who suggested the formation from these species of a vinyl carbocation intermediate, Pt–C⁺=C(H)R [2], which would explain the reactions with

alcohols R'OH to afford alkyl(alkoxy)carbene derivatives Pt{C(OR')CH₂R}.

Following our research project on transition metal promoted cyclization reactions of unsaturated ligands such as isocyanides, R–N≡C, [3] carbonyl, C≡O, [4] and nitriles, R–C≡N, [5] by the haloalcohols HO–(CH₂)_n–X (X = Cl, Br; n = 2, 3) and oxirane, $\overline{\text{OCH}_2\text{CH}_2}$, we have recently extended this reaction chemistry to Pt(II)–alkyne and –alkynyl complexes to give carbene [6] or vinyl ether [7] derivatives. The formation of the carbene derivatives has been suggested to proceed via intermediate Pt(II)–vinylidene species, which were not so far detected, but whose implication has been proposed by analogy with the known reactions of vinylidene complexes with nucleophiles to give carbene derivatives [1]. We now report the reactions of the acetylide complexes *trans*-[Pt(Me)(C≡CR)(PPh₃)₂] (R = *p*-tolyl, Ph) with protic acids to give Pt(II)–vinylidene derivatives, which have been characterized by NMR spectroscopy. The reactivity of the in situ prepared Pt(II)–vinylidene species with water is also described. This latter process proceeds with the formation of

[☆] Dedicated to our dear friend and colleague, Professor Alberto Cecon, on the occasion of his 65th birthday.

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hydrocarbons and olefins likely arising from the organic vinylidene group.

2. Experimental

2.1. General procedures and materials

Tetrahydrofuran (THF) and diethyl ether were purified by distillation over sodium/benzophenone under a dinitrogen atmosphere, while dichloromethane under dinitrogen over calcium hydride. All other chemicals were of reagent grade and used as received. All reactions and manipulations were performed under a dry nitrogen atmosphere by using standard Schlenk techniques. The complexes *trans*-[Pt(Me)(C≡C-R)(PPh₃)₂] (R = *p*-tolyl, **1a**; Ph, **1b**) were prepared as described in the literature [6a]. CD₂Cl₂ for NMR experiments was dried over molecular sieves. ¹H-, ¹³C{¹H}- and ³¹P{¹H}-NMR spectra were recorded on a Bruker 200 AC instrument operating at 200.13, 50.32 and 81.01 MHz, respectively. Peak positions are relative to tetramethylsilane and were calibrated against the residual solvent resonance (¹H) or the deuterated solvent multiplet (¹³C). ³¹P chemical shifts were measured relative to external 85% H₃PO₄ with downfield values taken as positive. Infrared spectra were recorded as Nujol mulls on a Perkin Elmer 983 spectrophotometer. GC/MS determinations have been performed on a QMD 1000 instrument: column, PS264, 30 m; from 100 to 280°C, 10° min⁻¹; 1 ml min⁻¹, He flow.

2.2. Reaction of *trans*-[Pt(Me)(C≡C-*p*-tolyl)(PPh₃)₂] (**1a**) with HBF₄·Et₂O and with water in a screw cap with PTFE/silicone septum NMR tube

CD₂Cl₂ (0.8 ml) was transferred under nitrogen in a 5-mm NMR tube containing **1a** (103 mg, 0.12 mmol). Addition at -40°C of 20 μl of a 54% ethereal solution (0.14 mmol) of HBF₄·OEt₂ completely dissolved complex **1a** giving a deep red solution. The tube was introduced into a NMR probe precooled at -20°C. The reaction progress was monitored by variable temperature ¹H- and ³¹P{¹H}-NMR spectroscopy. The ¹H- and ³¹P{¹H}-NMR spectra showed the immediate appearance of signals attributed to the formation of the vinylidene complex *trans*-[Pt(Me){=C=C(H)(*p*-tolyl)}(PPh₃)₂][BF₄] (**2aBF₄**). NMR data for **2aBF₄**. ¹H-NMR (CD₂Cl₂, -20°C): δ 0.77 (t, CH₃, 3H, ³J_{HPt} 6.2, ²J_{HPt} 74.1 Hz); δ 3.92 (s, =CH, 1H, ³J_{HPt} 44.5 Hz). ³¹P{¹H}-NMR (CD₂Cl₂, -20°C): δ 30.8 (s, PPh₃, ¹J_{PPt} 2807 Hz). On warming to 0°C the NMR tube no spectral changes were observed and then H₂O (0.27 mmol, 5 μl) was added. The reaction mixture was allowed to reach room temperature and the ¹H- and ³¹P{¹H}-NMR analyses showed the presence of reso-

nances that could be assigned to the carbonyl *trans*-[Pt(Me)(CO)(PPh₃)₂][BF₄] (**3BF₄**) [6c, 8] and the hydroxo-bridged [Pt(μ-OH)(PPh₃)₂]₂[BF₄]₂ (**4BF₄**) [9] complexes together with other minor unidentified products. Integration of the PPh₃ resonances in the ³¹P{¹H}-NMR spectra showed that **3BF₄** and **4BF₄** were formed in a ca. 1:2 ratio. GC/MS analysis of the reaction mixture after 8 h at room temperature revealed the presence of *p*-xylene (*m/z* 106; r.t. 7.8 min) and CH₃C(H)=C(H)C₆H₄-*p*-CH₃ (*m/z* 132, r.t. 9.2 min) in a ca. 1:2 ratio.

After 24 h the reaction was stopped and the dichloromethane-d₂ solution was worked up as follows. The pale yellow crystals which were formed inside the NMR tube were filtered off and analyzed by IR (Nujol mull: ν(OH) 3550 cm⁻¹) and ³¹P{¹H}-NMR: δ 7.81 (s, PPh₃, ¹J_{PPt} 3744 Hz) [9]. These data agree with those previously reported for **4BF₄** [9]. The CD₂Cl₂ solution was then treated with Et₂O to give a brownish precipitate which was characterized by IR, ¹H- and ³¹P{¹H}-NMR as **3BF₄**. IR (Nujol mull): ν(CO) 2097 cm⁻¹. ¹H-NMR (CD₂Cl₂): δ 0.47 (t, CH₃, 3H, ³J_{HPt} 7.99 Hz, ²J_{HPt} 60.9 Hz). ³¹P{¹H}-NMR (CD₂Cl₂): δ 21.70 (s, PPh₃, ¹J_{PPt} 2624 Hz) [6c,8].

2.3. Reaction of *trans*-[Pt(Me)(C≡C-*p*-tolyl)(PPh₃)₂] (**1a**) with CF₃SO₃H and with water in a screw cap with PTFE/silicone septum NMR tube

CD₂Cl₂ (0.8 ml) was transferred under nitrogen in a 5-mm NMR tube containing **1a** (103 mg, 0.12 mmol). Addition at -40°C of CF₃SO₃H (10.6 μl, 0.12 mmol) dissolved complex **1a** giving a deep red solution. The tube was introduced into the NMR probe precooled at -20°C. The reaction progress was monitored by variable temperature ¹H- and ³¹P{¹H}-NMR spectroscopy. The ¹H- and ³¹P{¹H}-NMR spectra showed the immediate appearance of signals attributed to the formation of the vinylidene complex *trans*-[Pt(Me){=C=C(H)(*p*-tolyl)}(PPh₃)₂][CF₃SO₃] (**2aCF₃SO₃**). NMR data for **2aCF₃SO₃**. ¹H-NMR (CD₂Cl₂, -20°C): δ 0.76 (t, CH₃, 3H, ³J_{HPt} 6.1, ²J_{HPt} 74.1 Hz); δ 3.72 (s, =CH, 1H, ³J_{HPt} 43.6 Hz). ³¹P{¹H}-NMR (CD₂Cl₂, -20°C): δ 30.63 (s, PPh₃, ¹J_{PPt} 2808 Hz).

On warming to 0°C no spectral changes were observed and then H₂O (0.27 mmol, 5 μl) was added. On warming the NMR tube to room temperature and during a period of time (ca. 8 h) the ³¹P-NMR spectra of the reaction mixture showed resonances which could be attributed to the formation of the carbonyl complex *trans*-[Pt(Me)(PPh₃)₂(CO)][CF₃SO₃] (**3CF₃SO₃**) and [Pt(μ-OH)(PPh₃)₂]₂[CF₃SO₃]₂ (**4CF₃SO₃**) together with other minor unidentified products. GC/MS analysis of the reaction mixture after 8 h at room temperature showed the formation of *p*-xylene (*m/z* 106; r.t. 7.8 min) and CH₃C(H)=C(H)C₆H₄-*p*-CH₃ (*m/z* 132, r.t. 9.2 min).

During this time pale yellow crystals formed in the NMR tube, which were filtered off. IR (Nujol mull): $\nu(\text{OH})$ 3550 cm^{-1} . $^{31}\text{P}\{^1\text{H}\}$ -NMR: δ 7.90 (s, PPh_3 , $^1J_{\text{PPt}}$ 3765 Hz). The compound was identified as $4\text{CF}_3\text{SO}_3$ by comparison with the data reported for 4BF_4 . The CD_2Cl_2 solution was then treated with diethyl ether to give a brownish precipitate which was characterized as $3\text{CF}_3\text{SO}_3$. ^1H -NMR (CD_2Cl_2): δ 0.47 (t, CH_3 , 3H, $^3J_{\text{HPt}}$ 8.10, $^2J_{\text{HPt}}$ 61.2 Hz). $^{31}\text{P}\{^1\text{H}\}$ -NMR: δ 22.16 (s, PPh_3 , $^1J_{\text{PPt}}$ 2609 Hz).

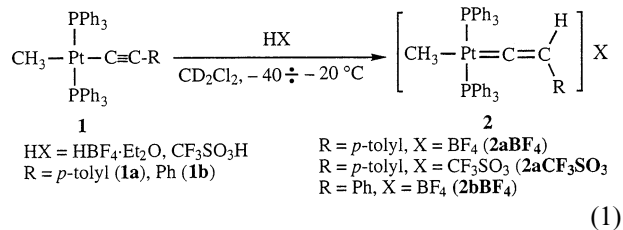
2.4. Reaction of *trans*-[Pt(Me)(C≡C-Ph)(PPh₃)₂] (**1b**) with $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ and with water in a screw cap with PTFE/silicone septum NMR tube

CD_2Cl_2 (0.8 ml) was transferred under nitrogen in a 5-mm NMR tube containing **1b** (106 mg, 0.13 mmol). Addition at -40°C of 20 μl of ethereal solution 54% (0.14 mmol) of $\text{HBF}_4 \cdot \text{OEt}_2$ completely dissolved complex **1b** giving a deep red solution. The tube was introduced into a NMR probe precooled at -20°C . The reaction progress was monitored by variable temperature ^1H - and $^{31}\text{P}\{^1\text{H}\}$ -NMR spectroscopy. The ^1H - and $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra showed the immediate appearance of signals attributed to the formation of the vinylidene complex *trans*-[Pt(Me){=C=C(H)(Ph)}-(PPh₃)₂][BF₄] (**2bBF₄**). NMR data for **2bBF₄**. ^1H -NMR (CD_2Cl_2 , -20°C): δ 0.76 (t, CH_3 , 3H, $^3J_{\text{HPt}}$ 6.4, $^2J_{\text{HPt}}$ 72.1 Hz); δ 3.95 (s, =CH, 1H, $^3J_{\text{HPt}}$ 41.8 Hz). $^{31}\text{P}\{^1\text{H}\}$ -NMR (CD_2Cl_2 , -20°C): δ 30.7 (s, PPh_3 , $^1J_{\text{PPt}}$ 2799 Hz).

On warming the NMR tube to 0°C no spectral changes were observed. At 0°C H_2O (0.27 mmol, 5 μl) was added. On warming to room temperature and within a period of time (ca. 8 h), the ^{31}P -NMR spectra showed the formation of **3BF₄** and **4BF₄** together with other minor unidentified products. GC/MS analysis of the reaction mixture after 8 h at room temperature showed the formation of $\text{CH}_3\text{C}(\text{H})=\text{C}(\text{H})\text{C}_6\text{H}_5$ (m/z 118, r.t. 6.2 min, identified by comparison with an authentic sample) and toluene (m/z 92, r.t. 2.8 min).

3. Results and discussion

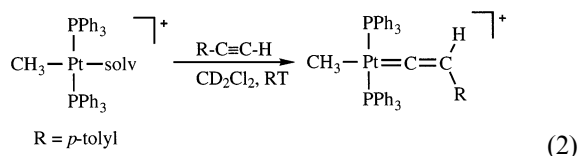
Treatment of the acetylide complexes *trans*-[Pt(Me)(C≡CR)(PPh₃)₂] (R = *p*-tolyl, Ph) (**1**) with stoichiometric amounts of the protic acids HX (HX = $\text{HBF}_4 \cdot \text{OEt}_2$, $\text{CF}_3\text{SO}_3\text{H}$) at low temperature (range from -40 to -20°C) immediately gives rise to deep red solutions. Monitoring the reactions in a screw cap NMR tube (CD_2Cl_2) by spectroscopy (^1H - and $^{31}\text{P}\{^1\text{H}\}$ -NMR) shows the quantitative formation of new species, which can be described as the vinylidene derivatives *trans*-[Pt(Me){=C=C(H)R}(PPh₃)₂]X (**2**) (Eq. 1).



The ^1H -NMR spectra at low temperature (-20°C) of complexes **2** show the methyl resonance at 0.76–0.77 ppm (ca. 1 ppm downfield compared to that found for the alkynyl species **1** [6a]), which shows up as a triplet due to coupling with the two magnetically equivalent phosphorous atoms and flanked by ^{195}Pt satellites ($^2J_{\text{HPt}}$ ca. 72–74 Hz). This latter coupling constant value is significantly higher than that found for the acetylide complexes **1** ($^2J_{\text{HPt}}$ ca. 53 Hz [6a]) and also higher than those found in the carbene *trans*-[Pt(Me){=C-(OCH₂CH₂X)CH₂R}(PPh₃)₂][BF₄] (X = Cl [6a]; Br, I, OH [6c]; $^2J_{\text{HPt}}$ ca. 45 Hz), carbonyl *trans*-[Pt(Me)(CO)(PPh₃)₂][BF₄] ($^2J_{\text{HPt}}$ ca. 61 Hz [6c]) and chloro derivative *trans*-[Pt(Me)(Cl)(PPh₃)₂] ($^2J_{\text{HPt}}$ 43.5 Hz [10]). The $^2J_{\text{HPt}}$ values of the Me-resonance of **2** may also be compared with those found in the isocyanide complex *trans*-[Pt(Me)(CNC₆H₄-*p*-OMe)(P-MePh₂)₂][BF₄] ($^2J_{\text{HPt}}$ 61.2 Hz [11]) and the vinyl compound *trans*-[Pt(Me){C(OCH₂CH₂Cl)=CH(*p*-tolyl)}-(PPh₃)₂] ($^2J_{\text{HPt}}$ 46.9 Hz [6c]). On the other hand the $^2J_{\text{HPt}}$ values of **2** fit well with those found for the nitrile complexes *trans*-[Pt(Me)(NCR)(PPh₃)₂][BF₄] (R = Me, $^2J_{\text{HPt}}$ 78.1 Hz; R = Ph, $^2J_{\text{HPt}}$ 77.7 Hz, [13]). Thus, based on $^2J_{\text{HPt}}$ values of the methyl resonance in platinum(II) complexes, the following order of NMR *trans* influence [12] is found: R–C≡N (R = Me, Ph) \approx =C=C(H)R (R = *p*-tolyl, Ph) < CO \approx C≡N–C₆H₄–*p*-OMe < $^-\text{C}\equiv\text{C}-\text{R}$ (R = *p*-tolyl, Ph) < $^-\text{C}(\text{OCH}_2\text{CH}_2\text{Cl})=\text{CH}(\textit{p}\text{-tolyl}) \approx =\text{C}(\text{OCH}_2\text{CH}_2\text{X})\text{CH}_2\text{R}$ (X = Cl, Br, I, OH). The presence of vinylidene ligands in **2** is shown by ^1H -NMR resonances at ca. 3.7–3.9 ppm due to the vinylidene hydrogen [14] which appear as singlets flanked by ^{195}Pt satellites ($^3J_{\text{HPt}}$ 41.8–44.5 Hz).

The $^{31}\text{P}\{^1\text{H}\}$ -NMR spectra run at -20°C of **2** show a single resonance at ca. 30 ppm flanked by ^{195}Pt satellites ($^1J_{\text{PPt}}$ ca. 2800 Hz) due to the two magnetically equivalent *trans*-PPh₃ ligands. No other signals were present. The $^{13}\text{C}\{^1\text{H}\}$ -NMR spectrum of **2aBF₄** recorded at -40°C does not show the resonance due to the α -carbon atom of the vinylidene group, while that due to the β -carbon is clearly evident at 71.9 ppm ($^2J_{\text{CPt}}$ 28.3 Hz). The resonance at 5.42 ppm (t, $^2J_{\text{CP}}$ 4.4 Hz, $^1J_{\text{CPt}}$ 619 Hz) is attributed to the carbon atom of the methyl group bound to Pt and the singlet at 21.57 ppm to the CH_3 -Ph carbon. The IR spectrum of the CD_2Cl_2 solution of **2aBF₄** shows a medium-intensity absorption at 1620 cm^{-1} attributable to the vinylidene C=C bond [14].

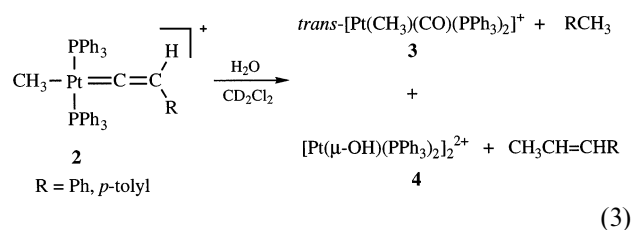
It is interesting to note that resonances analogous to those of **2aBF₄** are observed in the ¹H-NMR spectra of the reaction mixtures between the solvento cationic complex *trans*-[Pt(Me)(PPh₃)₂(solv)][BF₄], which is prepared from the corresponding chloro derivative by treatment with AgBF₄, and the terminal alkyne H–C≡C-*p*-tolyl (Eq. 2).



The mechanism of the 1-alkyne to vinylidene conversion at a Pt(II) center is not known, although it most likely proceeds by initial formation of the η²-alkyne intermediate *trans*-[Pt(Me)(PPh₃)₂(η²-R–C≡C–H)][BF₄] which was not clearly detected by low temperature ¹H-NMR spectroscopy and eventually tautomerizes to the vinylidene group possibly via a 1,2-hydrogen shift as proposed, on the basis of EHMO calculations, by Silvestre and Hoffmann [15a] and recently supported by ab initio studies on the conversion of [RuCl₂(PH₃)₂(HC≡CH)] to [RuCl₂(PH₃)₂(=C=CH₂)] [15b]. The Re-assisted η²-alkyne to vinylidene isomerization via the 1,2-H shift mechanism has been suggested by Bianchini et al. who characterized the π-alkyne complex [(triphos)Re(CO)₂(η²-H–C≡C–H)][BF₄] which spontaneously transforms into the vinylidene complex [(triphos)Re(CO)₂(=C=CH₂)] [14b]. In conclusion, we suggest that as for [(triphos)Re(CO)₂]⁺, also for the *trans*-[Pt(Me)(PPh₃)₂]⁺ fragment the alternative 1,3-hydrogen shift mechanism [16] to vinylidene via oxidative addition of the alkyne C–H bond is hardly accessible due to its low electron-richness.

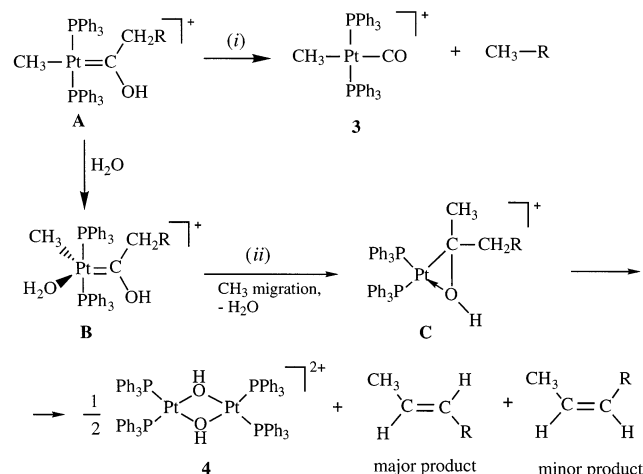
The reactions of the in situ prepared vinylidene species **2** in CD₂Cl₂ with stoichiometric amounts of water were followed by ¹H- and ³¹P{¹H}-NMR initially at 0°C and then at room temperature for an additional 8 h. The NMR data revealed the formation from the reaction mixture of mainly two species, i.e. the carbonyl complex **3** and the hydroxo-bridged dinuclear compound **4** (Eq. 3) accompanied with the parallel formation of hydrocarbons RCH₃ (i.e. *p*-xylene from **2aBF₄** and **2aCF₃SO₃** and toluene from **2bBF₄**) and olefins of the type CH₃CH=CHR (R = *p*-tolyl, Ph)¹ in a ca. 1:2 ratio, which were identified by GC/MS analysis (see Experimental).

¹ Both olefins are formed as *cis* and *trans* stereoisomers in about a 2:10 ratio. CH₃–CH=CH–C₆H₅ has been identified on the basis of a comparison with an authentic sample, and its mass spectrum recognized in the NBS data base [*M*⁺], *m/z* 118. CH₃–CH=CH–C₆H₄-*p*-CH₃ has been identified on the basis of its mass spectrum recognized in the NBS data base [*M*⁺], *m/z* 132.



A proposed mechanism for the reaction products observed in Eq. 3 is given in Scheme 1. This entails initial formation of the unstable hydroxycarbene species **A** derived by nucleophilic attack of H₂O on the vinylidene group. The ¹H-NMR spectra of the 1:1 reaction mixtures of **2aBF₄**, **2aCF₃SO₃** or **2bBF₄** and H₂O show new resonances at ca. 0.33–0.34 ppm (t, ³J_{HPt} ca. 6.7–6.4 Hz, ²J_{HPt} ca. 86–89 Hz), respectively, which were tentatively assigned to the CH₃–Pt group of species **A**. The hydroxycarbene OH resonance could not be located. The corresponding ³¹P-NMR spectra showed singlets at 24.8 ppm (¹J_{PPt} 3268 Hz for R = *p*-tolyl) and 24.9 ppm (¹J_{PPt} 3256 Hz for R = Ph). These latter signals slowly decrease in intensity and after 8 h two main resonances are detected in the spectrum: a singlet at 7.8 ppm (¹J_{PPt} 3744) and a singlet at 21.7 ppm (¹J_{PPt} 2624 Hz) attributed to the dinuclear hydroxo-bridged species [Pt(PPh₃)₂(μ-OH)]₂²⁺ (**4**) [9] and the carbonyl complex *trans*-[Pt(Me)(CO)](PPh₃)₂⁺ (**3**) [6c,8], respectively.

The formation of the carbonyl complex *trans*-[Pt(Me)(CO)](PPh₃)₂⁺ and *p*-xylene or toluene (route *i* of Scheme 1) parallels the behaviour reported for the Ru- and Re-assisted C≡C bond cleavage of terminal alkynes by water, which has been shown to proceed via hydroxycarbene intermediates to give the metal carbonyl and hydrocarbons [14,17]. The formation of the carbonyl ligand as a result of the nucleophilic attack by water on the vinylidene α-carbon atom and subsequent carbon–carbon cleavage has been confirmed by reaction of **2aBF₄** with H₂¹⁸O. In this case the reaction leads



Scheme 1.

to the formation of *trans*-[Pt(Me)(PPh₃)₂(C¹⁸O)][BF₄] as shown by the red-field shift exhibited by the stretching vibration of the carbonyl group [$\nu_{\text{C}=\text{O}}^{\text{18}} = 2054 \text{ cm}^{-1}$]. The frequency change $\Delta\nu_{\text{CO}} = \nu_{\text{C}=\text{O}}^{\text{16}} - \nu_{\text{C}=\text{O}}^{\text{18}} = 2098 - 2054 \text{ cm}^{-1} = 44 \text{ cm}^{-1}$ is in good agreement with the value that may be calculated from the change in reduced mass ($\Delta\nu_{\text{CO}} = 47 \text{ cm}^{-1}$) [18].

The formation of **4** and the olefins of the type CH₃CH=CHR (route *ii* of Scheme 1) can be explained by a migratory process of the methyl group on the carbene carbon of the hydroxycarbene complex promoted by water whose coordinating ability leads to the formation of the required *cis*-hydrido-carbene intermediate, possibly a pentacoordinate species of the type **B**. This latter rearranges to the unstable species **C**, which eventually decomposes to afford **4** and the olefin. Although we have no spectroscopic evidence for **B** and **C**, such a mechanism agrees well with previous studies reported on the hydride to carbene migration catalyzed by acetonitrile for the hydrido-dithiocarbene complex *trans*-[Pt(H)(=C(SCH₂CH₂S))(PPh₃)₂][BF₄]. This latter affords the migratory-insertion product *cis*-[Pt{C(H)SCH₂CH₂S}(PPh₃)₂][BF₄], which was isolated and structurally characterized [19] showing a metallacyclopropane structure of the Pt–C–S moiety, via the pentacoordinate intermediate [Pt(H)(=C(SCH₂CH₂S))(PPh₃)₂(MeCN)][BF₄], which could be detected by a FAB/MS study [20]. Migration of an alkyl ligand to a transition metal coordinated carbene is a known process and it has been recently demonstrated to be the basis for the catalytic formation of tetrahydrofuranlydene esters via alkyl migration in Pt(II)–carbene complexes [21].

Acknowledgements

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