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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)(PPh_3)$_2$] (R = *p*-tolyl (**1a**), Ph (**1b**)) at low temperature in a CD_2Cl_2 solution with stoichiometric amounts of the acids $HBF_4 \cdot Et_2O$ or CF_3SO_3H affords the corresponding vinylidene derivatives *trans*-[Pt(Me){=C=C(H)R}(PPh_3)$_2$]X (R = *p*-tolyl, X = BF_4 (**2aBF$_4$**); R = *p*-tolyl, X = CF_3SO_3 (**2aCF$_3$SO$_3$**); R = Ph, X = BF_4 (**2bBF$_4$**)) on the basis of ^{1}H- and ^{31}P{^{1}H}-NMR data. The reactions of the in situ generated complexes **2** with water, which were followed by ^{1}H- and ^{31}P{^{1}H}-NMR, lead to the formation of a mixture of the carbonyl complex [Pt(Me)(CO)(PPh_3)$_2$]X (**3**) and the hydroxo-bridged dinuclear compound [Pt(μ-OH)(PPh_3)$_2$]$_2$X$_2$ (**4**) in a ca. 1:2 ratio. The formation of **3** and **4** is accompanied with the liberation of hydrocarbons R–CH_3 and olefins CH_3CH=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

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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–$\overset{+}{C}$=C(H)R [2], which would explain the reactions with alcohols R′OH to afford alkyl(alkoxy)carbene derivatives Pt{=C(OR′)CH_2R}.

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–(CH_2)$_n$–X (X = Cl, Br; *n* = 2, 3) and oxirane, $\overline{OCH_2C}H_2$, 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)(PPh_3)$_2$] (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

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☆ Dedicated to our dear friend and colleague, Professor Alberto Ceccon, 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 Schlenck techniques. The complexes *trans*-[Pt(Me)(C≡C–R)(PPh$_3$)$_2$] (R = *p*-tolyl, **1a**; Ph, **1b**) were prepared as described in the literature [6a]. CD$_2$Cl$_2$ for NMR experiments was dried over molecular sieves. ^{1}H-, ^{13}C{^{1}H}- and ^{31}P{^{1}H}-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 (^{1}H) or the deuterated solvent multiplet (^{13}C). ^{31}P chemical shifts were measured relative to external 85% H$_3$PO$_4$ 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)(PPh$_3$)$_2$] (**1a**) with HBF$_4$·Et$_2$O and with water in a screw cap with PTFE/silicone septum NMR tube

CD$_2$Cl$_2$ (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 HBF$_4$·OEt$_2$ 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 ^{1}H- and ^{31}P{^{1}H}-NMR spectroscopy. The ^{1}H- and ^{31}P{^{1}H}-NMR spectra showed the immediate appearance of signals attributed to the formation of the vinylidene complex *trans*-[Pt(Me){=C=C(H)(*p*-tolyl)}(PPh$_3$)$_2$][BF$_4$] (**2aBF**$_4$). NMR data for **2aBF**$_4$. ^{1}H-NMR (CD$_2$Cl$_2$, −20°C): δ 0.77 (t, CH$_3$, 3H, $^3J_{HP}$ 6.2, $^2J_{HPt}$ 74.1 Hz); δ 3.92 (s, =CH, 1H, $^3J_{HPt}$ 44.5 Hz). ^{31}P{^{1}H}-NMR (CD$_2$Cl$_2$, −20°C): δ 30.8 (s, PPh$_3$, $^1J_{PPt}$ 2807 Hz). On warming to 0°C the NMR tube no spectral changes were observed and then H$_2$O (0.27 mmol, 5 μl) was added. The reaction mixture was allowed to reach room temperature and the ^{1}H- and ^{31}P{^{1}H}-NMR analyses showed the presence of resonances that could be assigned to the carbonyl *trans*-[Pt(Me)(CO)(PPh$_3$)$_2$][BF$_4$] (**3BF**$_4$) [6c, 8] and the hydroxo-bridged [Pt(μ-OH)(PPh$_3$)$_2$]$_2$[BF$_4$]$_2$ (**4BF**$_4$) [9] complexes together with other minor unidentified products. Integration of the PPh$_3$ resonances in the ^{31}P{^{1}H}-NMR spectra showed that **3BF**$_4$ and **4BF**$_4$ 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 CH$_3$C(H)=C(H)C$_6$H$_4$-*p*-CH$_3$ (*m*/*z* 132, r.t. 9.2 min) in a ca. 1:2 ratio.

After 24 h the reaction was stopped and the dichloromethane-d$_2$ 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 ^{31}P{^{1}H}-NMR: δ 7.81 (s, PPh$_3$, $^1J_{PPt}$ 3744 Hz) [9]. These data agree with those previously reported for **4BF**$_4$ [9]. The CD$_2$Cl$_2$ solution was then treated with Et$_2$O to give a brownish precipitate which was characterized by IR, ^{1}H- and ^{31}P{^{1}H}-NMR as **3BF**$_4$. IR (Nujol mull): ν(CO) 2097 cm^{-1}. ^{1}H-NMR (CD$_2$Cl$_2$): δ 0.47 (t, CH$_3$, 3H, $^3J_{HP}$ 7.99 Hz, $^2J_{HPt}$ 60.9 Hz). ^{31}P{^{1}H}-NMR (CD$_2$Cl$_2$): δ 21.70 (s, PPh$_3$, $^1J_{PPt}$ 2624 Hz) [6c,8].

2.3. Reaction of *trans*-[Pt(Me)(C≡C-*p*-tolyl)(PPh$_3$)$_2$] (**1a**) with CF$_3$SO$_3$H and with water in a screw cap with PTFE/silicone septum NMR tube

CD$_2$Cl$_2$ (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 CF$_3$SO$_3$H (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 ^{1}H- and ^{31}P{^{1}H}-NMR spectroscopy. The ^{1}H- and ^{31}P{^{1}H}-NMR spectra showed the immediate appearance of signals attributed to the formation of the vinylidene complex *trans*-[Pt(Me){=C=C(H)(*p*-tolyl)}(PPh$_3$)$_2$][CF$_3$SO$_3$] (**2aCF**$_3$**SO**$_3$). NMR data for **2aCF**$_3$**SO**$_3$. ^{1}H-NMR (CD$_2$Cl$_2$, −20°C): δ 0.76 (t, CH$_3$, 3H, $^3J_{HP}$ 6.1, $^2J_{HPt}$ 74.1 Hz); δ 3.72 (s, =CH, 1H, $^3J_{HPt}$ 43.6 Hz). ^{31}P{^{1}H}-NMR (CD$_2$Cl$_2$, −20°C): δ 30.63 (s, PPh$_3$, $^1J_{PPt}$ 2808 Hz).

On warming to 0°C no spectral changes were observed and then H$_2$O (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 ^{31}P-NMR spectra of the reaction mixture showed resonances which could be attributed to the formation of the carbonyl complex *trans*-[Pt(Me)(PPh$_3$)$_2$(CO)][CF$_3$SO$_3$] (**3CF**$_3$**SO**$_3$) and [Pt(μ-OH)(PPh$_3$)$_2$]$_2$[CF$_3$SO$_3$]$_2$ (**4CF**$_3$**SO**$_3$) 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 CH$_3$C(H)=C(H)C$_6$H$_4$-*p*-CH$_3$ (*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): ν(OH) 3550 cm^{-1}. ^{31}P{^{1}H}-NMR: δ 7.90 (s, PPh$_3$, $^1J_{PPt}$ 3765 Hz). The compound was identified as **4CF$_3$SO$_3$** by comparison with the data reported for **4BF$_4$**. The CD$_2$Cl$_2$ solution was then treated with diethyl ether to give a brownish precipitate which was characterized as **3CF$_3$SO$_3$**. ^{1}H-NMR (CD$_2$Cl$_2$): δ 0.47 (t, CH$_3$, 3H, $^3J_{HP}$ 8.10, $^2J_{HPt}$ 61.2 Hz). ^{31}P{^{1}H}-NMR: δ 22.16 (s, PPh$_3$, $^1J_{PPt}$ 2609 Hz).

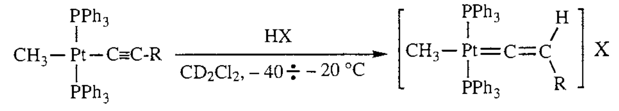
2.4. Reaction of trans-[Pt(Me)(C≡C-Ph)(PPh$_3$)$_2$] ***(1b)*** *with HBF$_4$·Et$_2$O and with water in a screw cap with PTFE/silicone septum NMR tube*

CD$_2$Cl$_2$ (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 HBF$_4$·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 ^{1}H- and ^{31}P{^{1}H}-NMR spectroscopy. The ^{1}H- and ^{31}P{^{1}H}-NMR spectra showed the immediate appearance of signals attributed to the formation of the vinylidene complex *trans*-[Pt(Me){=C=C(H)(Ph)}-(PPh$_3$)$_2$][BF$_4$] (**2bBF$_4$**). NMR data for **2bBF$_4$**. ^{1}H-NMR (CD$_2$Cl$_2$, −20°C): δ 0.76 (t, CH$_3$, 3H, $^3J_{HP}$ 6.4, $^2J_{HPt}$ 72.1 Hz); δ 3.95 (s, =CH, 1H, $^3J_{HPt}$ 41.8 Hz). ^{31}P{^{1}H}-NMR (CD$_2$Cl$_2$, −20°C): δ 30.7 (s, PPh$_3$, $^1J_{PPt}$ 2799 Hz).

On warming the NMR tube to 0°C no spectral changes were observed. At 0°C H$_2$O (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 **3BF$_4$** and **4BF$_4$** together with other minor unidentified products. GC/MS analysis of the reaction mixture after 8 h at room temperature showed the formation of CH$_3$C(H)=C(H)C$_6$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)(PPh$_3$)$_2$] (R = *p*-tolyl, Ph) (**1**) with stoichiometric amounts of the protic acids HX (HX = HBF$_4$·OEt$_2$, CF$_3$SO$_3$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$_2$Cl$_2$) by spectroscopy (^{1}H- and ^{31}P{^{1}H}-NMR) shows the quantitative formation of new species, which can be described as the vinylidene derivatives *trans*-[Pt(Me){=C=C(H)R}(PPh$_3$)$_2$]X (**2**) (Eq. 1).



1
HX = HBF$_4$·Et$_2$O, CF$_3$SO$_3$H
R = *p*-tolyl (**1a**), Ph (**1b**)

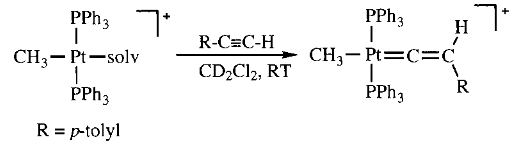
2
R = *p*-tolyl, X = BF$_4$ (**2aBF$_4$**)
R = *p*-tolyl, X = CF$_3$SO$_3$ (**2aCF$_3$SO$_3$**
R = Ph, X = BF$_4$ (**2bBF$_4$**)

(1)

The ^{1}H-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 ($^2J_{HPt}$ ca. 72–74 Hz). This latter coupling constant value is significantly higher than that found for the acetylide complexes **1** ($^2J_{HPt}$ ca. 53 Hz [6a]) and also higher than those found in the carbene *trans*-[Pt(Me){=C-(OCH$_2$CH$_2$X)CH$_2$R}(PPh$_3$)$_2$][BF$_4$] (X = Cl [6a]; Br, I, OH [6c]; $^2J_{HPt}$ ca. 45 Hz), carbonyl *trans*-[Pt(Me)(CO)(PPh$_3$)$_2$][BF$_4$] ($^2J_{HPt}$ ca. 61 Hz [6c]) and chloro derivative *trans*-[Pt(Me)(Cl)(PPh$_3$)$_2$] ($^2J_{HPt}$ 43.5 Hz [10]). The $^2J_{HPt}$ values of the Me-resonance of **2** may also be compared with those found in the isocyanide complex *trans*-[Pt(Me)(CNC$_6$H$_4$-*p*-OMe)(P-MePh$_2$)$_2$][BF$_4$] ($^2J_{HPt}$ 61.2 Hz [11]) and the vinyl compound *trans*-[Pt(Me){C(OCH$_2$CH$_2$Cl)=CH(*p*-tolyl)}-(PPh$_3$)$_2$] ($^2J_{HPt}$ 46.9 Hz [6c]). On the other hand the $^2J_{HPt}$ values of **2** fit well with those found for the nitrile complexes *trans*-[Pt(Me)(NCR)(PPh$_3$)$_2$][BF$_4$] (R = Me, $^2J_{HPt}$ 78.1 Hz; R = Ph, $^2J_{HPt}$ 77.7 Hz, [13]). Thus, based on $^2J_{HPt}$ 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) ≈ =C=C(H)R (R = *p*-tolyl, Ph) < CO ≈ C≡N–C$_6$H$_4$ - *p*-OMe < $^-$C≡C–R (R = *p*-tolyl, Ph) < $^-$C(OCH$_2$CH$_2$Cl)=CH(*p*-tolyl) ≈ =C(OCH$_2$CH$_2$X)CH$_2$R (X = Cl, Br, I, OH). The presence of vinylidene ligands in **2** is shown by ^{1}H-NMR resonances at ca. 3.7–3.9 ppm due to the vinylidene hydrogen [14] which appear as singlets flanked by ^{195}Pt satellites ($^3J_{HPt}$ 41.8–44.5 Hz).

The ^{31}P{^{1}H}-NMR spectra run at −20°C of **2** show a single resonance at ca. 30 ppm flanked by ^{195}Pt satellites ($^1J_{PPt}$ ca. 2800 Hz) due to the two magnetically equivalent *trans*-PPh$_3$ ligands. No other signals were present. The ^{13}C{^{1}H}-NMR spectrum of **2aBF$_4$** 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 ($^2J_{CPt}$ 28.3 Hz). The resonance at 5.42 ppm (t, $^2J_{CP}$ 4.4 Hz, $^1J_{CPt}$ 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$_2$Cl$_2$ solution of **2aBF$_4$** shows a medium-intensity absorption at 1620 cm^{-1} attributable to the vinylidene C=C bond [14].

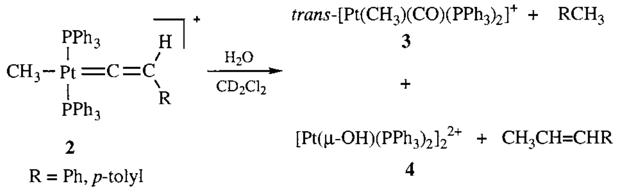
It is interesting to note that resonances analogous to those of **2aBF**$_4$ are observed in the ^{1}H-NMR spectra of the reaction mixtures between the solvento cationic complex *trans*-$[Pt(Me)(PPh_3)_2(solv)][BF_4]$, which is prepared from the corresponding chloro derivative by treatment with $AgBF_4$, and the terminal alkyne H–C≡C-*p*-tolyl (Eq. 2).



(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 η^2-alkyne intermediate *trans*-$[Pt(Me)(PPh_3)_2(\eta^2\text{-}R\text{–}C{\equiv}C\text{–}H)][BF_4]$ which was not clearly detected by low temperature ^{1}H-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 $[RuCl_2(PH_3)_2(HC{\equiv}CH)]$ to $[RuCl_2(PH_3)_2({=}C{=}CH_2)]$ [15b]. The Re-assisted η^2-alkyne to vinylidene isomerization via the 1,2-H shift mechanism has been suggested by Bianchini et al. who characterized the π-alkyne complex $[(triphos)Re(CO)_2(\eta^2\text{-}H\text{–}C{\equiv}C\text{–}H)][BF_4]$ which spontaneously transforms into the vinylidene complex $[(triphos)Re(CO)_2({=}C{=}CH_2)][BF_4]$ [14b]. In conclusion, we suggest that as for $[(triphos)Re(CO)_2]^+$, also for the *trans*-$[Pt(Me)(PPh_3)_2]^+$ 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.

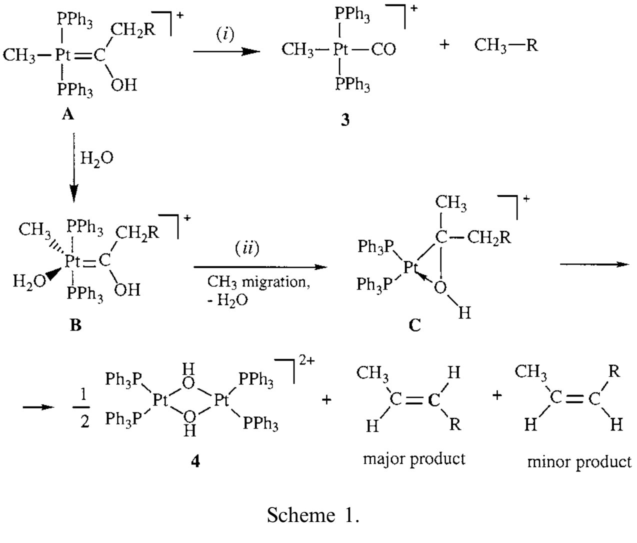
The reactions of the in situ prepared vinylidene species **2** in CD_2Cl_2 with stoichiometric amounts of water were followed by ^{1}H- and $^{31}P\{^1H\}$-NMR initially at 0°C and then at room temperature for an additional 8 h. The NMR data revealed the formation from the reaction mixture of mainly two species, i.e. the carbonyl complex **3** and the hydroxo-bridged dinuclear compound **4** (Eq. 3) accompanied with the parallel formation of hydrocarbons RCH_3 (i.e. *p*-xylene from **2aBF**$_4$ and **2aCF**$_3$**SO**$_3$ and toluene from **2bBF**$_4$) and olefins of the type $CH_3CH{=}CHR$ (R = *p*-tolyl, Ph)[1] in a ca. 1:2 ratio, which were identified by GC/MS analysis (see Experimental).



(3)

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 H_2O on the vinylidene group. The ^{1}H-NMR spectra of the 1:1 reaction mixtures of **2aBF**$_4$, **2aCF**$_3$**SO**$_3$ or **2bBF**$_4$ and H_2O show new resonances at ca. 0.33–0.34 ppm (t, $^3J_{HP}$ ca. 6.7–6.4 Hz, $^2J_{HPt}$ ca. 86–89 Hz), respectively, which were tentatively assigned to the CH_3–Pt group of species **A**. The hydroxycarbene OH resonance could not be located. The corresponding ^{31}P-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 $[Pt(PPh_3)_2(\mu\text{-}OH)]_2^{2+}$ (**4**) [9] and the carbonyl complex *trans*-$[Pt(Me)(CO)](PPh_3)_2]^+$ (**3**) [6c,8], respectively.

The formation of the carbonyl complex *trans*-$[Pt(Me)(CO)](PPh_3)_2]^+$ 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 **2aBF**$_4$ with $H_2^{18}O$. In this case the reaction leads



Scheme 1.

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[1] Both olefins are formed as *cis* and *trans* stereoisomers in about a 2:10 ratio. $CH_3\text{–}CH{=}CH\text{–}C_6H_5$ has been identified on the basis of a comparison with an authentic sample, and its mass spectrum recognized in the NBS data base [$M^{+\cdot}$], *m*/*z* 118. $CH_3\text{–}CH{=}CH\text{–}C_6H_5\text{-}p\text{-}CH_3$ has been identified on the basis of its mass spectrum recognized in the NBS data base [$M^{+\cdot}$], *m*/*z* 132.

to the formation of *trans*-[Pt(Me)$(PPh_3)_2$($C^{18}O$)][BF_4] as shown by the red-field shift exhibited by the stretching vibration of the carbonyl group [$\nu^{18}_{(CO)} = 2054$ cm^{-1}]. The frequency change $\Delta\nu_{(CO)} = \nu^{16}_{(CO)} - \nu^{18}_{(CO)} = 2098 - 2054$ cm^{-1} $= 44$ cm^{-1} is in good agreement with the value that may be calculated from the change in reduced mass ($\Delta\nu_{(CO)} = 47$ cm^{-1}) [18].

The formation of **4** and the olefins of the type $CH_3CH{=}CHR$ (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)(=$CSCH_2CH_2S$)$(PPh_3)_2$][BF_4]. This latter affords the migratory-insertion product *cis*-[Pt{C(H)SCH_2CH_2S}$(PPh_3)_2$][BF_4], which was isolated and structurally characterized [19] showing a metallacyclopropane structure of the Pt–C–S moiety, via the pentacoordinate intermediate [Pt(H)(=$CSCH_2CH_2S$)-$(PPh_3)_2$(MeCN)][BF_4], 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 tetrahydrofuranylidene esters via alkyl migration in Pt(II)–carbene complexes [21].

Acknowledgements

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