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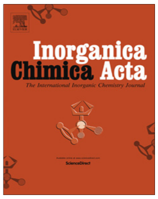

New method for the synthesis of $[PtCl\{\eta^1\text{-}CH_2C(O)R\}(N\text{-}N)]$ ketonyl derivatives starting from the Zeise's salt

Michele Benedetti *, Chiara R. Girelli, Daniela Antonucci, Sandra A. De Pascali, Francesco P. Fanizzi *

Dipartimento di Scienze e Tecnologie Biologiche ed Ambientali, Università del Salento, Via Monteroni, I-73100 Lecce, Italy

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In this work, the reactivity of the Zeise's salt, $K[PtCl_3(\eta^2\text{-}C_2H_4)]$, with ketones, in the presence of strong bases, has been studied. In these conditions the formation of metastable intermediate complexes of the type *trans*-$[PtCl_2\{\eta^1\text{-}CH_2C(O)R\}(\eta^2\text{-}C_2H_4)]^-$, has been demonstrated by NMR spectroscopy. Further reaction with dinitrogen ligands (*N-N*) gives $[PtCl\{\eta^1\text{-}CH_2C(O)R\}(N\text{-}N)]$ complexes. This reactivity of the Zeise's anion can be exploited for the first general synthesis, in a one pot reaction, of σ-carbon Pt(II) ketonyl derivatives with aliphatic or aromatic dinitrogen ligands (even if sterically hindered).

1. Introduction

The reactivity of the Zeise's anion, $[PtCl_3(\eta^2\text{-}C_2H_4)]^-$, with bidentate dinitrogen ligands (*N-N*) has been the main subject of several previous studies on the Pt(II) coordination and organometallic chemistry [1–9]. In particular, it is interesting to note that by direct interaction of a dinitrogen ligand with the Zeise's anion a pentacoordinate intermediate species of the type $[PtCl_2(\eta^2\text{-}C_2H_4)(N\text{-}N)]$ can be formed. Such pentacoordinate complexes are generally unstable and can decay depending on the solvent polarity and temperature, to give unstable square planar cationic species of the type $[PtCl(\eta^2\text{-}C_2H_4)(N\text{-}N)]^+$ and/or stable dichlorido species of the type $[PtCl_2(N\text{-}N)]$, Scheme 1 [2,3]. Only few sterically hindered ligands such as **Me₂phen** (2,9-dimethyl-1,10-phenanthroline) are able to give stable pentacoordinate systems [2,3,10,11].

In previous works we studied the reactivity of the Zeise's anion in basic alcoholic media, discovering that in this case the reactivity of this complex is quite different, giving first low reactive intermediate complexes of the type *trans*-$[PtCl_2(\eta^2\text{-}C_2H_4)(OR)]^-$ (R = H, alkyl), further evolving to reactive species of the type *trans*-$[PtCl_2(OR)(\eta^1\text{-}CH_2CH_2OR)]^{2-}$ [1,4]. These latter complexes can react with dinitrogen ligands, to give organometallic derivatives of the type $[PtCl(\eta^1\text{-}CH_2CH_2OR)(N\text{-}N)]$. The related intermediate complexes *trans*-$[PtCl_2(OH)(\eta^2\text{-}C_2H_4)]^-$, **1**, and *trans*-$[PtCl_2(\eta^1\text{-}CH_2NO_2)(\eta^2\text{-}C_2H_4)]^-$, **2**, Scheme 2, were characterized by NMR spectroscopy and single crystal X-ray diffraction [1]. In the present paper we extend the synthetic application of Zeise's anion reactivity in basic media, in the presence of ketones, to obtain organometallic ketonyl derivatives of the type $[PtCl\{\eta^1\text{-}CH_2C(O)R\}(N\text{-}N)]$.

The chemistry of Pt(II) organometallic ketonyl derivatives is recognized to be important for many potential applications [7,12,13]. Moreover the interaction of ketones with transition metals seem of particular interest [14–17]. However, notwithstanding the efforts made in recent years to develop new synthetic methods for metalated ketones, the number of Pt(II) and Pt(IV) ketonyl complexes seems rather limited. In fact, few examples of Pt(II) ketonyl compounds are known with a variety of ligands, lacking in aliphatic diamine ligands and sterically hindered diimine ligands. In particular previously developed synthetic procedures, giving such complexes, include: (i) the oxidative addition of chloroacetone to Pt(0) complexes [18]; (ii) the reaction of acetone with hydroxo [19–22] or with chloro complexes in the presence of Ag_2O [23] or KOH [24]; (iii) the water-induced reaction of a Pt(0) cyclohexyne complex with acetone [22]; (iv) the reaction of ketones with cationic complexes of the type $[PtCl(\eta^2\text{-}C_2H_4)(N\text{-}N)]^+$ under acidic conditions [25]; the use of $[Hg\{CH_2C(O)Me\}_2]$ or similar complexes as transmetalating agents [26–29]. For these reasons we have exploited the possible use of Zeise's anion, in basic media, to the general synthesis of organometallic ketonyl derivatives of the type $[PtCl\{\eta^1\text{-}CH_2C(O)R\}(N\text{-}N)]$, even in the case of aliphatic diamines and sterically hindered diimine ligands.

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* Corresponding authors. Tel.: +39 0832 298973; fax: +39 0832 298626 (M. Benedetti) , tel.: +39 0832 298867 (F. P. Fanizzi).

E-mail addresses: michele.benedetti@unisalento.it (M. Benedetti), fp.fanizzi@unisalento.it (F.P. Fanizzi).

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2. Results and discussion

When Zeise's salt, K[$PtCl_3(\eta^2-C_2H_4)$], was dissolved in basic d_6-acetone (by KOD in D_2O addition) new ^1H NMR signals, corresponding to the known hydroxido complex *trans*-[$PtCl_2(OD)(\eta^2-C_2H_4)$]$^-$, **1**, which further reacts to give a new species characterized by a different ethene signal, could be observed, Scheme 2, Fig. 1 [4]. In parallel similar experiments we used as a solvent a basic d_6-acetone/acetone = 90/10 mixture, instead of simple d_6-acetone. In this case the new species, which was detected after a few minutes, could be better characterized for the presence of the η^1-acetonyl signals. Several multinuclear multidimensional NMR experiments were specifically used to fully characterize the new ketonyl species. Collected ^1H, $^1H\{^{13}C\}$ HMBC and $^1H\{^{195}Pt\}$ HSQC NMR spectra, giving signals and cross peaks corresponding to the complex *trans*-[$PtCl_2\{\eta^1-CH_2C(O)CH_3\}(\eta^2-C_2H_4)$]$^-$, **3**, (Schemes 2 and 3) are shown in Figs. 2 and 3.

The assignment of a *trans* geometry to complex **3** stems from the comparison with η^2-olefin ^1H and ^{13}C NMR signals observed in the related previously reported isomers: *trans*-[$PtCl_2(\eta^1-CH_2NO_2)(\eta^2-C_2H_4)$]$^-$, **2** [1], and *cis*-[$PtCl_2\{\eta^1-CH_2C(O)CH_3\}(\eta^2-C_2H_4)$]$^-$, **4** [26–29]. The similar lower η^2-ethene $^2J_{Pt-H}$ and $^1J_{Pt-C}$ values observed are diagnostic of the same *trans* geometry of complexes **2** and **3** (strong *trans* labilizing σ-carbon ligand in *trans* to the olefin in both complexes) as compared to the higher corresponding coupling constants of the *cis* complex isomer **4** (mild *trans* labilizing chlorido ligand in *trans* to the olefin) [26–29], see Table 1. We think that the observed formation of complex *trans*-[$PtCl_2\{\eta^1-CH_2C(O)CH_3\}(\eta^2-C_2H_4)$]$^-$, **3**, is mediated by direct OH^- substitution, in complex **1** (the first formed by the Zeise's anion in the reaction conditions), by the acetonyl $CH_3C(O)CH_2^-$ carbanion, produced in the presence of excess strong base. We can exclude a concerted substitution of coordinated OH^- by acetone in complex **1**, because differently from the formation of complex **2**, by direct interaction between **1** and CH_3NO_2, the reaction of preformed **1** with simple acetone is extremely slow. Last reactivity difference is probably due to the higher acidity of nitromethane, with respect to acetone, able to protonate the platinum bonded hydroxyl of complex **1**, to give complex **2** by a concerted mechanism. On the contrary, in the transmetalation reaction proposed by Vicente et al. [27,28], the interaction of the Zeise's anion with the organometallic derivative [$Hg\{\eta^1-CH_2C(O)CH_3\}_2$] produces the formation of the *cis*-[$PtCl_2\{\eta^1-CH_2C(O)CH_3\}(\eta^2-C_2H_4)$]$^-$, **4**, isomer. This could be explained assuming for the last reaction a mechanism involving a first interaction, in *trans* to the olefin, between Pt(II) of the Zeise's anion and the organometallic [$Hg\{\eta^1-CH_2C(O)CH_3\}_2$] reagent, with migration of an acetonyl in *cis*, to give the observed intermediate **4**.

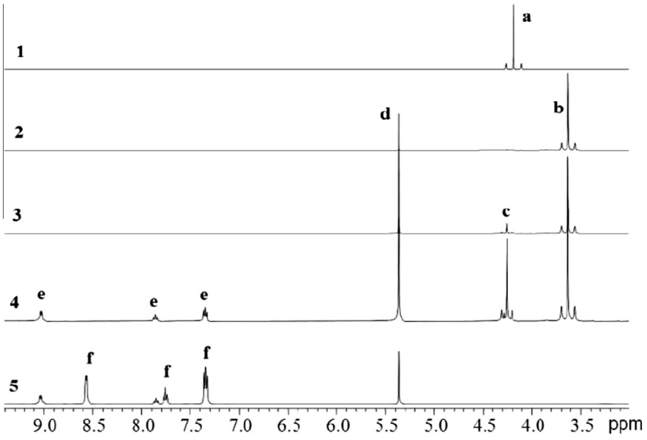
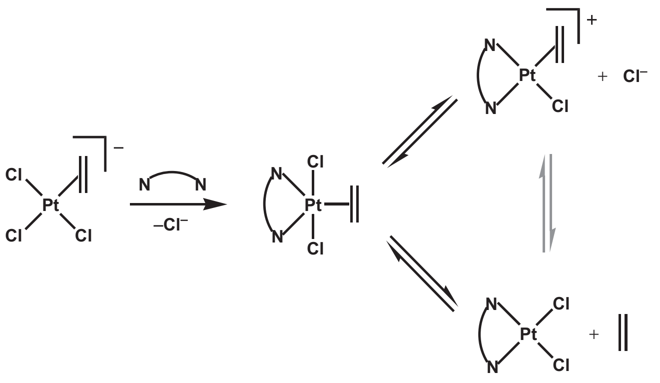


Fig. 1. ^1H NMR spectra, collected at 5 °C, showing initially (spectra 1-3), the hydrolysis of the Zeise's salt, K[$PtCl_3(\eta^2-C_2H_4)$], in basic d_6-acetone, (presence of KOD, previously dissolved in the minimum amount of D_2O), and afterward the addition product of pyridine (spectra 4-5). 1) Zeise's ion NMR signals (a); 2) formation of *trans*-[$PtCl_2(OD)(\eta^2-C_2H_4)$]$^-$, **1** (b), after addition of KOD; 3) gradual transformation of complex *trans*-[$PtCl_2(OD)(\eta^2-C_2H_4)$]$^-$ into *trans*-[$PtCl_2\{\eta^1-CD_2C(O)CD_3\}(\eta^2-C_2H_4)$]$^-$, **3** (c) (the formation reaction was followed for about 10 min); 4) immediate formation of free ethene (d) and complex *trans*-[$PtCl_2\{\eta^1-CD_2C(O)CD_3\}(\mathbf{py})$]$^-$, **5** (e), after addition of pyridine (**py**); 5) addition of excess **py** (f). The reaction of **1** with acetone, to give **3**, was followed for about 10 min, instead reaction with **py** was followed for about 15 min [27].



Scheme 1. Schematic representation of the formation of pentacoordinate complexes, by direct interaction of the Zeise's anion with dinitrogen (N-N) ligands. Pentacoordinate complexes can decay to cationic species and/or dichlorido species.

trans-[$PtCl_2(OH)(\eta^2-C_2H_4)$], **1**.

trans-[$PtCl_2(\eta^1-CH_2NO_2)(\eta^2-C_2H_4)$], **2**.

trans-[$PtCl_2\{\eta^1-CH_2C(O)CH_3\}(\eta^2-C_2H_4)$], **3**.

cis-[$PtCl_2\{\eta^1-CH_2C(O)CH_3\}(\eta^2-C_2H_4)$], **4**.

Scheme 2. Schematic representation of the chemical structure of complexes **1**-**4**, derived from the Zeise's salt in different experimental conditions.

It is to be underlined that *trans*-[$PtCl_2(\eta^1-CH_2NO_2)(\eta^2-C_2H_4)$]$^-$, **2**, reported in a previous work and obtained with a similar reaction, by using nitromethane instead of acetone, was also characterized by single crystal X-ray diffraction. Unfortunately in the case of complex **3** all attempts to obtain crystals suitable for X-ray diffraction failed, even with different counterions and at low temperature, for the intrinsic low kinetic stability of such complex. On the other hand the reactivity of **3** with nitrogen ligands (*N*) was found similar to that exhibited by **2** [1], giving similar *trans* derivatives of the type *trans*-[$PtCl_2\{\eta^1-CH_2C(O)CH_3\}(N)$]$^-$. In the case of pyridine, **py**, formation of *trans*-[$PtCl_2\{\eta^1-CH_2C(O)CH_3\}(\mathbf{py})$]$^-$, **5**, analogous to the previously described *trans*-[$PtCl_2\{\eta^1-CH_2NO_2\}(\mathbf{py})$]$^-$, **5′** [1], was observed, Fig. 1 and Table 1. Moreover complex **3** is able to give, by reaction with dinitrogen ligands (*N-N*), olefin loss and formation of square planar derivatives of the type [$PtCl\{\eta^1-CH_2C(O)CH_3\}(N-N)$], Scheme 3 and Table 1.

We focused our attention on the synthesis of complexes of the type [$PtCl\{\eta^1-CH_2C(O)R\}(N-N)$] with different classes of dinitrogen ligands. In particular we used as model ligands sterically unhindered or hindered amine or imine dinitrogen ligands, i.e., **en** (ethylenediamine), **tmen** (*N,N,N′,N′*-tetramethyl-ethylenediamine),