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Reactions of Cationic Isocyanide Platinum(II) Complexes with Water (from Hexafluoroacetone-hydrate): Carboxamido and Isocyanato Complexes

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Abstract. The isocyanide complexes $[Pt(Cl)(C{\equiv}NR)(PPh_3)_2]^+BF_4^-$ (R = CH_2CO_2Et, CH_2Ph, C_6H_{11}, $CH_2SO_2C_6H_4$-*p*-Me) react with hexafluoroacetone-sesquihydrate, $(F_3C)_2CO \cdot 1,5\,H_2O$, in the presence of triethylamine to give the carboxamido (carbamoyl) complexes $[Pt(Cl)\{C(=O)NHR\}(PPh_3)_2]$. Under the same conditions the isocyanoamine complexes *trans*-$[Pt(Cl)(C{\equiv}N\text{-}NR_2)(PPh_3)_2]^+BF_4^-$ (R = Et, Pr^i, 2R = $\overline{CH(Me)(CH_2)_3CH}(Me)$) are transformed into the isocyanato complex *trans*-$[Pt(Cl)(NCO)(PPh_3)_2]$.

Keywords: Platinum; Isocyanides; Carboxamido complexes; Isocyanato complexes

Introduction

From their discovery to this day carboxamido (carbamoyl) complexes $[L_nM\text{-}C(=O)NHR]$ have enjoyed great interest of many research groups. Particularly successful studies have been carried out by *King* [2], *Angelici* [3], and *Behrens* [4] and their coworkers. Various synthetic routes to this kind of complexes have been described

− the addition of amines or ammonia to coordinated CO ligands [3, 4] and the related reaction of Pd^{II} complexes with free CO and amine [3, 5, 6],

− the oxidative addition of carbamoyl chlorides $R_2NC(O)Cl$ to low valent or anionic metal complexes [2, 3, 5],

− the insertion of organic isocyanates into a metal-hydride bond [3, 7],

− the insertion of CO into the rhenium-nitrogen bond of an organometallic imide complex [8],

− the addition of hydroxide to the dicationic isocyanide complex $[Pt(CNMe)_2(PPh_3)_2]^{2+}$ [9],

− the cycloaddition of arylnitrile oxides to the metal-isocyanide in $[CoCp(CNR)(PMe_3)]$ [10],

− the [3+2] cycloaddition between the platinio nitrile ylid $[Pt(Cl)(C{\equiv}N\text{-}CH\text{-}CO_2Et)(PPh_3)_2]$ and salicylic aldehyde and consecutive reactions [11].

The addition of nucleophiles Y-H (Y = NHR, OR, SR) to coordinated isocyanides, first described by *Chatt* et al., provides a rational and often applied route to (bis-heteroatom-stabilized) aminocarbene complexes [12, 13]. Even earlier *Saegusa* et al. had discovered that $\alpha-$additions of the same H-active nucleophiles to isocyanides yielding Y-CH=NR are catalyzed by group 11 and 12 metals in various oxidation states [14], and it was primarily *Bonati* and his group who isolated carbene complexes of these metals thus proving their intermediacy in the catalytic process [13].

Chatt's synthetic access to carbene complexes has been followed in our groups and extended to include CH-acidic nucleophiles (e.g. $CH(CN)_2^-$) as well as functional isocyanides carrying nucleophilic reagents in their side chain [15−18]. In the course of our studies on the chemistry of isocyanide metal complexes we became interested in a method which allows the removal of this ligand under mild conditions. An attractive possibility appeared to us its conversion with OH^-/H_2O into a carboxamido species which is known to be easily cleaved on protonation yielding a CO ligand and free amine (ammonium) [3] (eq. (1)).

$$[L_nM\text{-}CNR] \xrightarrow{OH^-} [L_nM\text{-}C(=O)NHR]^- \xrightarrow{H^+} [L_nM\text{-}CO] + RNH_3^+ \tag{1}$$

Treichel [9] had reported on the reaction of $[Pt(CNMe)_2(PPh_3)_2]^{2+}$ with OH^- which afforded the carboxamido complex $[Pt\{C(=O)NHMe\}(CNMe)(PPh_3)_2]^+$. In our hands, however, the action of hydroxide (KOH/MeCN, NaOH/H_2O/CH_2Cl_2/$(NEt_4)Cl$) on neutral ($[PtCl_2(CNR)(PPh_3)]$) or monocationic platinum complexes ($[PtCl(CNR)(PPh_3)_2]^+$) did not lead to well-characterized products though the isocyanide ligands had disappeared (IR) during the reaction

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[18, 19]. Presumably, any carbamoyl complexes that might have been formed are too labile in the presence of excess hydroxide. With the versatile reagent hexafluoroacetone-hydrate [20] we found a reagent which supplies only the stoichiometric amount of hydroxide necessary for the formation of the carboxamido from the isocyanide ligand.

In this context it may be interesting to note that previously we succeeded in the transformation of carbamoyl back to isocyanide complexes by using the reagent phosgene/triethylamine for the elimination of hydroxide [21].

Results and Discussion

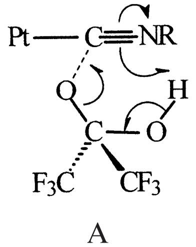
Hexafluoroacetone-hydrate which exists as a geminal diol reacts with cationic isocyanide platinum complexes in the presence of stoichiometric amounts of triethylamine to afford the corresponding carbamoyl complexes **1-4** in high yields (eq. (2)) [22].

$$[\mathrm{Pt(Cl)(C{\equiv}NR)(PPh_3)_2}]^+(\mathrm{BF_4})^- \xrightarrow[\mathrm{(F_3C)_2CO\cdot 1{,}5\,H_2O/NEt_3}]{\mathrm{OH^-}} [\mathrm{Pt(Cl)\{C({=}O)\text{-}NHR\}(PPh_3)_2}] \quad (2)$$

1−4

	R
1	CH_2CO_2Et
2	CH_2Ph
3	C_6H_{11}
4	$CH_2SO_2C_6H_4$-*p*-Me

For the 1,2-addition of OH^- to the isocyano function, a process via a cyclic intermediate of the type A is tentatively suggested. The reactions of the complexes $[Pt(Cl)(C{\equiv}NR)(PPh_3)_2]^+(BF_4)^-$ (R = Me, $CH{=}CH_2$) with $(F_3C)_2CO\cdot 1.5H_2O/NEt_3$ only gave mixtures from which mainly $[PtCl_2(PPh_3)_2]$ was isolated [19]. No reaction at all occurred with the neutral complexes $[PtCl_2L(PPh_3)]$ containing vinylogous isocyanoamine (C≡N-C=C-N<) ligands [18].



A

We also studied the reactions of the *N*-isocyanide complexes *trans*-$[Pt(Cl)(C{\equiv}N\text{-}NR_2)(PPh_3)_2]^+BF_4^-$ (R = Et, Pr^i, 2R = $\overline{CH(Me)(CH_2)_3CH(Me)}$) [24] with $(F_3C)_2CO\cdot 1{,}5\,H_2O/NEt_3$ which should lead to the unknown carbazoyl ligand [M-C(=O)-NH-NR$_2$]. In all three cases, however, an identical product has been obtained and recognized as the isocyanato complex **5** (eq. (3)).

$$\textit{trans}\text{-}[\mathrm{Pt(Cl)(C{\equiv}N\text{-}NR_2)(PPh_3)_2}]^+ \xrightarrow{\text{“}\mathrm{OH^-}\text{”}} <[\mathrm{Pt(Cl)\{C({=}O)\text{-}NH\text{-}NR_2\}(PPh_3)_2}]> \xrightarrow[\mathrm{-HNR_2}]{} \textit{trans}\text{-}[\mathrm{Pt(Cl)(N{=}C{=}O)(PPh_3)_2}] \quad (3)$$

5

This result is in perfect agreement with a related work by *Angelici* [25] who on addition of hydrazine or its mono- and *N,N*-dialkylated derivatives to the CO ligand also observed the formation of isocyanate with elimination of ammonia or amine, respectively. A similar mechanistic sequence − nucleophilic addition to the metal-bonded carbon atom of N-isocyanide complexes, cleavage of the N-N bond and C → N migration of the metal atom − is obviously at work in the reactions of $[M(CO)_5C{\equiv}N\text{-}NR_2]$ (M: Cr, W) with secondary amines (HNR'_2) which (unlike primary amines [17]) give the corresponding cyanamide complexes $[M(CO)_5N{=}C{=}NR'_2]$ [26]. Further reference is made to the analogies with the chemistry of metal carbonyls with N_3^- and vice versa that of azido complexes with free CO [27] as well as − less directly − that of the system azide/isocyanide [28].

The compounds are clearly identified by their characteristic IR absorptions and correct elemental analyses. Of compound **5** all elements were determined with the exception of phosphorus; also the mass spectrum could be recorded which revealed the parent peak (Experimental Part). Two additional weak signals have been assigned to the molecular peaks of $[PtCl_2(PPh_3)_2]$ and $[Pt(NCO)_2(PPh_3)_2]$; as **5** turned out to be pure by thin-layer chromatography, however, the disproportionation must have occurred in the mass spectrometer.

The characteristic IR absorptions of the -C(=O)NH-group in **1-4** appear at 1585−1600 cm^{-1} (νC=O + δNH), in full accordance with the findings in other complexes of the type $[Pt(Cl)\{C({=}O)\text{-}NHR\}(PPh_3)_2]$ which have been prepared by different routes [5]. The isocyanato complex **5** exhibits very characteristic, strong ν_{as}NCO and ν_sNCO IR absorptions at 2244 and 1350 cm^{-1}, respectively. In comparison, for $[Pt(NCO)_2(PPh_3)_2]$ the corresponding IR absorptions were observed at 2234 and 1313 cm^{-1} [23].

Experimental Part

The starting materials $[Pt(Cl)(CNR)(PPh_3)_2](BF_4)$ (R = CH_2Ph, $CH_2SO_2C_6H_4$-*p*-Me) [15] and $[Pt(Cl)(CNNR_2)(PPh_3)_2](BF_4)$ [24] were prepared from $[(Ph_3P)_2Pt(\mu\text{-}Cl)_2Pt(PPh_3)_2](BF_4)_2$ [29] and the respective isocyanide according to published procedures. The experimental data of **2** and **4** were already reported in [15].

$[Pt(Cl)(CNCH_2CO_2Et)(PPh_3)_2](BF_4)$: A solution of 1.33 g (11.76 mmol) of $CNCH_2CO_2Et$ in 30 ml of chloroform is added dropwise with stirring to a suspension of 9.90 g (5.88 mmol) of $[(Ph_3P)_2Pt(\mu\text{-}Cl)_2Pt(PPh_3)_2](BF_4)_2$ in 50 ml of the same solvent. In the end the suspension has largely cleared up and is filtered through Celite. The pale yellow filtrate is concentrated in vacuum to about half the volume, layered carefully with 40 ml of diethylether and cooled to 0 °C. The compound separates as colourless rod-shaped crystals which are washed with ether and dried in high vacuum. Yield 10.0 g (89 %). M.P. 194 °C; $C_{41}H_{37}BClF_4NO_2P_2Pt$ (955.04): Found C 50.93, H 3.79, N 1.40; Calc. C 51.56, H 3.90, N 1.47 %.

IR (KBr, cm^{-1}): 3070 sh, 3055 w, 2985 w, 2940 vw (νCH), 2266 s (νCN), 1756 vs ($\nu_{as}CO_2$), 1215 s ($\nu_s CO_2$), 1055 vs, br ($\nu_{as}BF_4$), 342 w (νPtCl); – **^{1}H NMR** (δ, $CDCl_3$): $\delta = 2.2$ (t, 3H, C_2H_5), 3.74 (t, 2H, CH_2), 3.9 (9, 2H, C_2H_5), 7.47 (m, 30H, Ph).

General procedure for **1-4**: To a solution of 1.0 mmol of $[Pt(Cl)(CNR)(PPh_3)_2](BF_4)$ in 10 ml of dichloromethane are added 1.2 mmol (121 mg) of triethylamine and 1.1 mmol (212 mg) of hexafluoroacetone-sesquihydrate. The mixture is allowed to stand in the dark for 1 d after which time the solvent is removed in vacuum and the residue recrystallized from dichloromethane/acetone and diethylether. Yield 80 %.

1: M.P. 174 °C (dec.); $C_{41}H_{38}ClNO_3P_2Pt$ (885.25): Found C 55.73, H 4.02, N 1.60; M 877.5 in $CHCl_3$; Calc. C 55.65, H 4.33, N 1.58 %.

IR (KBr, cm^{-1}): 3435 sh, 3390 m (νNH), 3075 sh, 3050 m, 2985, 2930, 2895 w (νCH), 1735 sh, 1724 s ($\nu_{as}CO_2$), 1594 vs, 1585 sh (νC=O and δNH), 1224 sh, 1178 s ($\nu_s CO_2$), 1156 sh.

3: M.P. 194 °C (dec.); $C_{43}H_{42}ClNOP_2Pt$ (881.30): Found C 58.03, H 4.50, N 1.44; Calc. C 58.60, H 4.80, N 1.59 %.

IR (KBr, cm^{-1}): 3425 m (νNH), 3075 sh, 3055 m, 2925 s, 2850 m (νCH), 1600 s, 1586 sh, 1570 sh (νC=O and δNH), 1188 sh, 1157 m-s.

***trans*-$[Pt(Cl)(NCO)(PPh_3)_2]$ (5)**: To a solution of 1.0 mmol of *trans*-$[Pt(Cl)(CNNR_2)(PPh_3)_2](BF_4)$ in 20 ml of dichloromethane are added 1.1 mmol of triethylamine and 1.1 mmol of hexafluoroacetone-sesquihydrate. The mixture is stirred and after 10 min pale yellow crystals start to separate. The mixture is concentrated to about 5 ml, and the solid is filtered off and recrystallized several times from dichloromethane. Yield 86 %.

M.P. 242 °C; $C_{37}H_{30}ClNOP_2Pt$ (797.13): Found C 55.42, H 3.83, N 1.80, O 2.38, Cl 4.17, Pt 23.04; Calc. C 55.75, H 3.79, N 1.76, O 2.01, Cl 4.45, Pt 24.47 %.

IR (KBr, cm^{-1}): 2244 vs (ν_{as}NCO), 1350 vs (ν_sNCO); the absence of any IR bands about 550 cm^{-1} points to *trans*-configuration as in the starting complex [30]. – **MS** (*m/z* (%)): 797 (3) [M^+], 755 (10) [M^+-NCO], 719 (26) [M^+-NCO-Cl].

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