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COMMUNICATION

CIS AND TRANS NUCLEOPHILIC ADDITIONS ON C≡C BONDS ASSISTED BY Pt(II) COMPLEXES. X-RAY CRYSTAL STRUCTURE OF TRANS-{Pt[CIS-(o-NC5H4)CH≡C(Ph)(NEt2)]Cl2(HNEt2)}

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Abstract—The reaction between $PtCl_2(PhCN)_2$ and N,N-dimethyl phenyl propargyl amine (1) affords *trans*-[Pt(N(Me_2)CH_2C=CPh)(NCPh)Cl_2] (3) which formally undergoes *trans*- Cl^- addition onto its C=C bond to give [Pt(C(Ph) = C(Cl)CH_2NMe_2)(NCPh)Cl] (4). On the other hand, the *cis*-nucleophilic addition product *trans*-{Pt[*cis*-(*o*-NC₅H₄) CH=C(Ph)(NEt_2)]Cl_2(HNEt_2)} (6) was obtained quantitatively from the reaction of a large excess of diethylamine with *trans*-[Pt(*o*-NC₅H₄)CH=C(Ph)(SEt_2)Cl_2] (5).

The activation of C=C bonds by transition metal complexes towards intermolecular nucleophilic additions is a well known process.¹ In contrast to metal-olefin complexes, nucleophilic attack on metal-complexed alkynes is relatively rare.¹⁻³ It is assumed that this reaction proceeds through the coordination of the C=C bond with an electrophilic metal centre (usually Pd(II), Fe(II) and Pt(II)). This is then followed by addition of the nucleophile to unsaturation giving rise to a *trans*-

substituted double bond (with respect to the metal centre and the nucleophile).²⁻⁴ However, the coordinated alkyne tends to undergo several competing reactions such as oligomerization or polymerization reactions, insertion reactions into the metal-halogen, -hydride or -carbon bonds usually present in the transition metal complex precursors, or it might be displaced by the incoming nucleophile.⁵ We reasoned that it would be possible to limit these "undesired" reactions by holding the C=C bond in close proximity to the metal coordination sphere, using acetylenes substituted by potentially coordinating groups.

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We present here our preliminary results concerning the behaviour of such ligands, namely N,Ndimethyl phenyl propargyl amine (1) and phenyl-2-pyridinyl acetylene (2), in the presence of Pt(II) compounds and nucleophiles.



RESULTS AND DISCUSSION

The phenyl propargyl amine (1) and phenyl-2pyridinyl acetylene (2) ligands were easily prepared in 85–90% yield by the reaction of phenyl iodide with N,N-dimethyl propargyl amine and 2-bromopyridine with phenyl acetylene, respectively, in the presence of catalytic amounts of $PdCl_2(PPh_3)_2$ and CuI.⁶

The addition of equimolar amounts of the acetylene (1) to $PtCl_2(PhCN)_2$ in THF afforded compound 3 together with 4 in 93% overall yield, after 8 h at room temperature (Scheme 1). The coordination of 1 to the Pt centre via its nitrogen group only in 3 is based upon the presence of ${}^{3}J_{Pt-H}$ (29.2 Hz) for the N(CH₃)₂ protons in the ¹H NMR spectra and the characteristic resonances of acetylenic carbons (88.7 and 80.8 ppm) in the ¹³C NMR spectra. Attempts to obtain 3 in pure form failed since this compound was not stable in solution and after 12 h it was completely transformed into compound 4. The absence of the acetylenic resonances and the appearance of characteristic of C=C bond resonances at 117.0 and 110.1 ppm in the ¹³C NMR spectra are good evidence for the formation of **4**.

The observed *trans*-stereochemistry in **4** is a strong indication that this reaction should proceed via the coordination of the C=C bond to the Pt(II) centre in **3**, leading to the displacement of the Cl^- . Nucleophilic addition of this chloride anion onto the activated C=C unit affords them the more stable five-membered platinacycle.

The substitution of one SEt₂ ligand in the reaction of alkyne (2) with *trans*-PtCl₂(SEt₂)₂ proceeds smoothly in THF at reflux temperature to produce 5 as yellow crystals in 97% yield (Scheme 2). The assignment of the structure of 5 is deduced straightforwardly from its IR, ¹H and ¹³C NMR spectrum. Compound 5 is very stable and did not rearrange in solution, as observed for compound 3, even in THF refluxing for several days. However, compound 5 affords quantitatively 6 as light yellow crystals through reaction with diethylamine in chloroform at reflux temperature for 3 days.

The disappearance of the $v(C \equiv C)$ bond in the IR spectra of 6 is a strong indication that the amine was added to the C C bond. However, owing to the complexity of its ¹H and ¹³C NMR spectrum, an X-ray diffraction analysis was undertaken in order to determine unambiguously the geometry of this molecule.

The structure of 6 is shown in Fig. 1 together with relevant bond distances and angles. The Pt atom is located in an almost square-planar environment. The two chloride atoms are located *trans* to each other and the coordination sphere is completed by the coordination of the nitrogen lone pairs of the diethylamine and the substituted pyridine



Scheme 2.



Fig. 1. A perspective view of compound **6**. Selected bond distances (Å) : Pt—N(1), 2.009(5); Pt—N(2), 2.050(5); Pt—Cl(1), 2.295(2); Pt—Cl(2), 2.294(2); N(1)—C(5), 1.351(7); C(5)—C(6), 1.460(8); C(6)—C(7), 1.353(8); C(7)—N(3), 1.387(7); C(7)—C(21), 1.496(9); N(3)—C(11), 1.465(8); N(3)—C(9), 1.482(8). Bond angles (°): N(1)—Pt—N(2), 178.1(2); N(1)—Pt—Cl(2), 92.2(2); N(2)—Pt—Cl(2), 89.5(2); N(1)—Pt—Cl(1), 86.8(2); N(2)—Pt—Cl(1), 91.5(2); Cl(2)—Pt—Cl(1), 178.72(7); C(7)—C(6)—C(5), 126.3(6); C(6)—C(7)—N(3), 124.1(5); C(6)—C(7)—C(21), 121.3(5); N(3)—C(7)—C(21), 114.7(5); C(7)—N(3)—C(11), 118.3(5); C(7)—N(3)—C(9), 117.6(5); C(11)—N(3)—C(9), 115.4(6).

ligand. It is at once apparent that the diethyl amine was added to C=C bond in a *syn* manner to produce the *cis* substituted double bond (with respect to the NEt₂ group and the proton). Interestingly, the nitrogen (N3) attached to the vinyl group displayed an almost planar geometry, reflecting the strong electronic delocalization involving the nitrogen lone pair, the vinyl and the phenyl groups.

It is important to note that no reaction took place between the ligand 2 and diethylamine in the absence of the Pt(II) metal. This indicates clearly that the C=C unit of 2 is indeed activated through the coordination of 2 to the metal centre. Whether this activation occurs via direct interaction of the acetylenic unit with the platinum atom or by some electronic delocalization as a result of the coordination of the pyridine unit to Pt is questionable.

Our results show, however, that the anchimeric⁷ assistance of the nitrogen containing units attached to $C \equiv C$ bonds can indeed favour reactions of these

unsaturations with nucleophiles in the presence of a metal centre. The regio- and stereo-selectivity of the observed nucleophilic additions onto these activated C=C bonds depend upon the nature of the anchoring group. In this respect, the flexibility of the CH₂NMe₂ unit in 3 should facilitate the contact between the C=C bond and the metal centre. Therefore the incoming nucleophile (Cl⁻) will be added to the carbon β to NMe₂ group to afford the more stable five-membered platinacycle 4. On the other hand the somewhat rigid geometry of the alkyne 2 in 5 should orient the nucleophilic addition on carbon δ to the N-pyridine atom. This, followed by a concerted intramolecular proton transfer,⁸ affords compound 6.

Work is in progress to demonstrate the generality of these findings to the reactions of related organoplatinum and palladium acetylenic compounds containing several potentially coordinating groups with other nucleophiles.

EXPERIMENTAL

All manipulations were carried out in an atmosphere of dry argon using standart Schlenk techniques. The solvents were distilled from appropriate drying agents under argon. ¹H NMR and ¹³C NMR were recorded on a Varian Gemini 200 MHz. The chemical shifts were measured in ppm relative to TMS as external standard. IR spectra were recorded on a Mattson 3020 FTIR spectrophotometer. Elemental Analyses were carried out by the Central Analítica-UFRGS, Brazil.

All the new compounds gave satisfactory CHN analysis; selected spectroscopic data are as follows: 3 IR (KBr pellets): 2288 cm⁻¹ [ν (C==N)]. ¹H NMR(CDCl₃): 7.67–7.20 (m, 10H, aromatic); 4.22 (s with Pt satellites, 2H, ${}^{3}J_{Pt-H} = 20.0$ Hz, CH₂); 2.92 (s with Pt satellites, 6H, ${}^{3}J_{Pt-H} = 29.2$ Hz, NMe₂). ¹³C NMR (CDCl₃): 88.7 and 80.8 (C=C); 55.7 (CH₂); 52.3 [N(CH₃)₂]. 4 IR (KBr pellets): 2280 cm^{-1} [v(C=N)]. ¹H NMR (CDCl₃) : 7.60–7.00 (m, 10H, aromatic); 3.80 (s with Pt satellites, 2H, ${}^{3}J_{\text{Pt-H}} = 40.2 \text{ Hz}, \text{ CH}_{2}$; 3.16 (s with Pt satellites, 6H, ${}^{3}J_{Pt-H} = 37.6$ Hz, NMe₂). ${}^{13}C$ NMR (CDCl₃): 120.6 and 110.4 (C=C); 77.9 (CH₂); 54.6 (NMe₂). **5** IR (KBr pellets) : 2221 cm⁻¹ [ν (C==C)]; ¹H NMR (CDCl₃): 8.71 (m, 1H, o-Py); 7.73-7.21 (m, 7H, aromatic); 2.92 and 2.56 (2m, 4H, SCH₂); 1.37 (t, 6H, ${}^{3}J_{HH} = 7.4$ Hz, CH₃). ${}^{13}C$ NMR (CDCl₃): 98.5 and 87.2 (C=C); 30.8 (SCH₂); 12.8 (CH₃). 6 IR (KBr pellets): 3196 cm⁻¹ [v(N-H)]. ¹H NMR (CDCl₃): 8.50 (m, 1H); 7.68-7.18 (m, 5H, Ph); 6.97 (s, 1H, C=CH); 6.80 (t, 1H, ${}^{3}J_{HH} = 6.5$ Hz, aromatic); 6.63 (t, 1H, aromatic); 6.02 (d, 1H, ${}^{3}J_{\rm HH} = 7.9$ Hz, aromatic); 3.65, 3.18, 2.87 and 2.58 (4m, 8H, CH₂), 1.63–1.08 (m, 12H, CH₃).

Crystal structure of 6

 $C_{21}H_{31}Cl_2N_3Pt$, M_r 591.48, monoclinic, $P2_1/c$, a = 15.773(4) Å; b = 10.469(4) Å; c = 14.495(4) $\beta = 92.94(2)^{\circ};$ $\alpha = 90^{\circ};$ $\gamma = 90^{\circ};$ Å; V = 2390.4(13) Å³; Z = 4; $D_x = 1.644$ Mg m⁻³; $F_{000} = 1160$; Mo- K_{α} radiation $\mu = 6.104 \text{ mm}^{-1}$; T = 293(2) K; 8070 measured reflections and 4220 independent reflections [R(int) = 0.021]; ω/θ scans; $2.34^{\circ} < \theta < 25.02^{\circ}$; $-18 \le h \le 18, 0 \le$ $k \leq 12, -17 \leq l \leq 13$; Full-matrix least squares on F^2 ; 257 parameters; R = 0.0258 and $R_w =$ 0.076, $w = 1/\alpha^2$, final *R* indices $[I > 2\sigma > (I)]$; goodness-of-fit on F^2 , S = 0.715; Extinction coefficient: 0.00000(14); Largest difference Fourier peak and hole: 1.335 and $-0.549 \text{ e} \text{ Å}^{-3}$. The structure was solved by direct methods⁹ and subsequent difference Fourier synthesis. The least-squares refinement used anisotropic thermal parameters for non-H atoms. The positions of the H atoms were calculated and only included in the structure-factor calculations. Programs used were SHELXS86 and SHELXL93 (IBM RS/6000 version⁹). Further details of the structure investigation can be obtained from the authors.

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