

NUCLEOPHILIC ATTACK ON BIS-(η^5 -CYCLOPENTADIENYL) METAL COMPLEXES: PART II: AMIDINE FORMATION FROM NITRILE COMPLEXES OF W(IV)¹

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Centro de Química Estrutural Complexo I Instituto Superior Técnico Lisboa – Portugal In previous articles [1, 2] we have reported hydride attack on the $\eta^5 - C_5H_5$ rings of cationic and neutral complexes of the type [M ($\eta^5 - C_5H_5$)₂ L₂]^{0,2+} (M = Mo, W; L = Cl, Br, I, 1,2 difenildifosfinoetano). It is also known that complexes [W(Cp)₂ Me(C₂H₄)]⁺²⁺ and [W (Cp)₂ ($\eta^3 - C_3H_5$)]⁺ undergo additions of PR₃ and R⁻ (R = Me, H) to the ethylene and allyl ligands respectively [3, 4], in agreement with recently established rules [5].

In the course of our work we have studied nucleophilic reactions of similar complexes bearing unsaturated, non hydrocarbon, ligands (NCR, CNR, CO, etc.). In this preliminary communication we report the reactions of complexes $[W (Cp)_2 Br (NCR)]^+$ (I; R = Me, Ph) [6] with NH₃ and NHMe₂.

Bubbling dry NH₃ through a MeCN solution of (I; R = Me) produced a slight colour change after 30 min. at 50 °C. Working up of the resulting purple solution gave a purple complex (yield *ca* 70 %) analysing correctly for the amidine addition product [W(Cp)₂ Br { HN:C (Me) NH₂ }] PF₆ (II). Analogous complexes (III-V) were prepared by similar procedure (see scheme).

On the basis of analytical data and of the spectroscopic evidence described below, the following formulation is proposed for complexes (II-V) (see fig. 1).

The ¹H n. m. r. spectra of (II) or (III) (see table) show clearly the presence of two equivalent $\eta^5 - C_5H_5$ rings and of a CH₃ (or C₆H₅) group. Three broad peaks (integrating for one proton each) can be assigned to three magnetically inequivalent N-bonded protons. This feature of the spectra can be understood on the basis of restricted rotation of the C-NH₂ bond of an H₂N(R)

C = N (H)–W bonded acetamidine ligand; in fact 35 % double bond character was found for such a bond in the complex [Pt (NH₃)₂ (HN:C (Me) NH₂)₂]²⁺[7,8]. Upon addition of D₂O to the d⁶Me₂CO solution of (II), two of these broad peaks disappear, but the third one is unaffected. In consistence with this observation, the i.r. spectrum of the sample recovered (II–d) from the d⁶Me₂CO/D₂O solution after forty eight hours at r.t. shows only one band in the N–H stretching region (3315 cm⁻¹). The other N–H stretching frequencies

1 - For part I, see reterence [2]

$$-Cp = \eta^{3} - C_{5}H_{5}$$

 $[W(Cp)_2 Br \left\{ HN : C(Ph) NH_2 \right\} |^+$ (III) [W (Cp)2 Br (NCR)]+ $[W(Cp)_2 B_1 { NH : C (Me) NMe_2 }$ $[W (Cp)_2 Br \left\{ HN : C (Ph) NMe_2 \right\}]^+$ (IV)

ii $NHMe_2$, R = Me, solv = MeCN; NH3, R = Ph, solv. = PhCN;

iii NHMe2, R = Ph, sorv. = PnCN

Scheme



in the i.r. spectrum of (II) moved to the frequency region expected for the N-D vibrations. The presence of bands at $\sim 3500 \text{ cm}^{-1}$ in the i.r. spectrum of (II) assigned to uncoordinated NH2 groups is taken as further support of the formulation of a N-imine bonded amidine [7]. Furthermore, [Mo(Cp)2Br(NH3)]⁺ does not exchange D for H under the same conditions. It was also observed that the band at $\sim 1640 \text{ cm}^{-1}$ in the i.r. spectrum of (II) moves to ~ 1615 cm⁻¹ in (II-d) as was reported for the analogous complex [Pt (NH3)2 $(\text{NH:C (Me) NH}_2)_2]^{2+}$. This shift was explained in terms of the modification of the C = N oscillator due to the heavier D atoms introduced in the amidine [7].

All the observations described are paralleled in (III) and (III-d). The N, N-dimethylamidine complexes (IV) and (V) show two Me signals in their ¹H n.m.r. spectra', again implying restricted rotation of the C-NMe2 bond. Very slow H D exchange was observed for the single broad N-H proton, basic conditions leading to decomposition. However, the samples recovered from d⁶Me₂CO/D₂O did not show any significant change in their i.r. spectra relative to the untreated parent compounds. The only observed N-H stretch in the i.r. spectra of (IV) and (V) is analogous in shape and frequency to the unchanged band in (II-d) and (III-d), apparently supporting the fact that H/D exchange in

Table I

'	Hn	m.r.	. da	ta

Complex	au , multiplicity ^b , <i>relative area</i> , assignement
11	2.07, S (br) ^c , 1, NH ₂ ; 3.77, S (br), 1, NH;
	4.07, S (br), 1, NH2; 4.20, S, 10, Cp;
	7.67, S, <i>3,</i> Me
111	1.63, S (br), 1, NH2; 2.34, M, 5, Ph; 3.19,
	S(br), 1, NH; 3.67, S(br), 1, NH2; 4.06, S,
	<i>10,</i> Cp
IV ^d	4.16, S, 10, Cp; 6.73, S, 3, NMe2; 6.93, S,
	3, NMe ₂ ; 7.69, S, 3, Me
V	2.28, M, 5, Ph; 3.78, S(br), 1, NH; 4.45, S,
	10, Cp; 6.78, S, 3, NMe2; 7.11, S, 3, NMe2

a) in $d^{6}Me_{2}CO;$ b) S singulet, M multiplet; c) br broad; d) at $-30^{\circ}C$ a new peak shows at 3.95 τ ,S, 1, NH

the latter compounds only took place in the uncoordinated NH_2 group.

It is likely that the amidine ligand is formed by direct attack of the amine on the coordinated nitrile in complexes (I) since the $C \equiv N$ stretching frequencies show activation of the electrophilic character of the nitrile carbon [9, 10]. On the other hand, it is known that, apart from NH₃, amines do not add to uncoordinated nitriles NCR unless these carry strong electronwithdrawing R groups [11]. However, this kind of addition to coordinated nitriles is well established in recent literature [12].

Treatment of Me_2CO solutions of (II) with conc. aq. HCl gives crystalline [W (Cp)₂ ClBr] in quantitive yields, presumably leaving the amidine hydrocloride in solution. As the dihalide organometallic complex [W (Cp)₂ X₂] can easily be recovered and recycled, this reaction may prove to be useful for the synthesis of amidines from nitriles and primary or secondary amines; further studies are now in progress to ascertain the synthetic potential use of the work described above.

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