SOME REACTIONS OF DI-μ-CHLOROBIS[3-(DIMETHYLAMINO)-1-FORMYL-2,2-DIMETHYLPROPYL-*C,N*]DIPALLADIUM(II)

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Summary

The preparation of a series of complexes, II–XIII, containing the 1-formylpropylpalladium(II) moiety from di-μ-chlorobis[3-(dimethylamino)-1-formyl-2,2-dimethyl-*C,N*]dipalladium(II) (I) is described, and the structures of these complexes are discussed in terms of their ^{1}H NMR and IR spectra. The relatively low values for ν(C=O) are consistent with the presence of a metal-carbonyl group interaction and the influence of changes in the coordination sphere on this interaction is discussed. Reaction of I with allyl bromide or benzyl chloride gave the η^2-vinyl ether complexes (XV and XVI) while methyl iodide and n-butyl chloride failed to react. I resisted insertions into the Pd–C bond when treated with methyl acrylate, diphenylacetylene, or phenylacetylene. In the last of these, consumption of both acetylene and I was observed, the former by self-condensation and the latter with release of the hydrochloride of 3,3-dimethyl-4-dimethylaminobutanal which exists in the cyclic form XVIII.

Introduction

We have previously reported [1] the synthesis and X-ray structure analysis of di-μ-chlorobis[3-(dimethylamino)-1-formyl-2,2-dimethylpropyl-*C, N*]dipalladium(II) (I) in which there appears to be a direct interaction between the palladium atom and the carbon atom of the formyl group. A number of related compounds, II–XIII, have now been prepared and examined by IR and ^{1}H NMR spectroscopy in order to allow investigation of the influence of changes in the palladium coordination sphere on this interaction. Interactions of this type have been discussed [2] in terms of a direct overlap of metal *d*-orbitals with π-orbitals of the carbonyl function. Alternatively, a σ–π conjugative interaction of the Pd–C bond with the carbonyl group could be invoked to explain the properties of such systems. The latter description has been widely applied [3] in the rationalization of the spectral properties and

reactivities of organometallic derivatives of non-transition metals and also of certain carboxymethylcobalt(III) derivatives [4].

Following our earlier observation [5] that reaction of I with hydrogen chloride gives the corresponding η^2-vinyl alcohol complex XIV we have now found that η^2-vinyl ether complexes can be prepared from I by reaction with benzyl chloride or allyl bromide.

We have also investigated the reactivity of I towards methyl acrylate and acetylenes. Insertion reactions have been observed for certain cyclopalladated species with alkynes [6] and with alkenes [7]. No such reaction is observed in the present case under the conditions used.
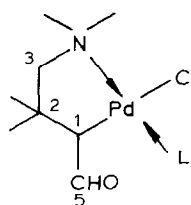
Results and discussion

As mentioned in the introduction, compounds II–XIII were prepared to allow comparison of their IR and ^{1}H NMR spectra. The dimeric derivatives, II–IV, were
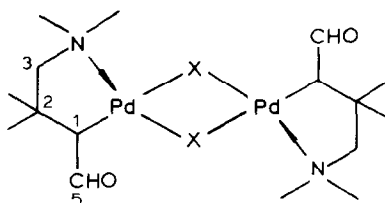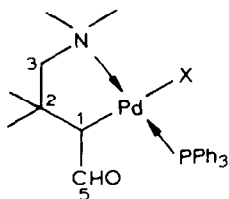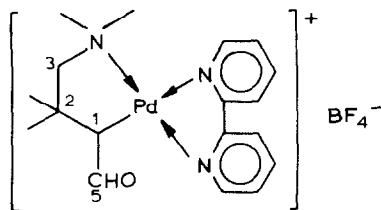
(I , X = Cl ;

II , X = Br ;

III , X = I ;
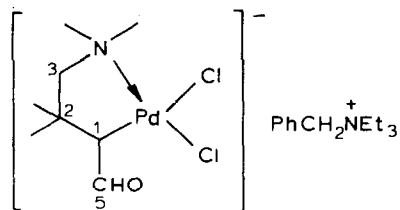
IV , X = SCN)

(V , L = pyridine ;

VI , L = 4-dimethylaminopyridine ;

VII , L = 4-cyanopyridine)

(VIII, X = Cl ;

IX , X = Br ;

X , X = I ;

XI , X = NCS)

(XII)

(XIII)

TABLE 1

ANALYTICAL, IR, CRYSTALLISATION SOLVENT, AND m.p. DATA FOR THE COMPLEXES

Complex	Analysis (Found (calcd.) (%))			m.p. (°C)	Solvent	ν(C=O) (cm^{-1}) (Nujol mull)
	C	H	N			
I [a]	–	–	–	–	–	1644; 1635 [b]
II	29.26 (29.24)	5.18 (4.92)	4.11 (4.26)	178–178.5 [c]	dichloromethane/acetone	1642
III	25.71 (25.59)	4.36 (4.30)	3.77 (3.73)	182–184 [c]	dichloromethane/acetone	1640
IV	35.57 (35.25)	5.27 (5.27)	9.12 (9.14)	> 200 [c]	acetone	1651
V	42.98 (42.98)	5.87 (5.84)	7.74 (7.72)	176–178 [c]	acetone/light petroleum	1625
VI	44.57 (44.36)	6.47 (6.47)	10.25 (10.35)	178–183 [c]	acetone	1630 [d], 1621
VII	43.28 (43.31)	5.20 (5.21)	10.80 (10.82)	163–166 [c,e]	acetone/light petroleum	1636(sh), 1627
VIII	57.29 (57.16)	5.80 (5.73)	2.65 (2.56)	181–184	acetone/light petroleum	1643, 1634 [f]; 1634 [g]
IX	52.93 (52.84)	5.45 (5.30)	2.28 (2.37)	175–180	acetone/light petroleum	1642, 1635 [f]
X	48.81 (48.97)	4.93 (4.91)	2.22 (2.20)	173–175 [c]	acetone/light petroleum	1625
XI	56.78 (56.98)	5.61 (5.50)	4.89 (4.92)	202–205	dichloromethane/acetone	1630
XII	44.04 (43.97)	4.88 (4.93)	8.65 (8.55)	202–210 [c]	water	1640
XIII	49.00 (49.26)	7.60 (7.50)	5.42 (5.47)	112–117	–	1621

[a] See ref. 1. [b] Solution in CDCl$_3$. [c] Decomp. [d] More intense. [e] Melts and resolidifies at about 108°C. [f] Relative intensities 1/1. [g] Solution in CH$_2$Cl$_2$.

TABLE 2

HYDROGEN-1 NMR DATA (ppm, J(Hz)) FOR COMPLEXES AT AMBIENT TEMPERATURE

Complex	Solvent	CMe	NMe	NCH$_2$	J_{gem}	PdCH	CHO	J(H-1/H-5)	J(H-1/H-3e[a])
I	CDCl$_3$	1.02, 1.60	2.55, 2.71	2.12, 3.66	12.2	3.56	9.40	b	1.8
	(CD$_3$)$_2$CO	1.00, 1.61	2.56, 2.78	2.32, 3.50	12.2	3.53	9.38	1.5	1.7
II	(CD$_3$)$_2$CO	1.01, 1.62	2.62, 2.85	2.33, 3.65	12.2	3.64	9.40	1.5	b
III	CD$_2$Cl$_2$	1.01, 1.56	2.68, 2.89	2.18, 3.72	11.7	3.66	9.31	1.5	b
	(CD$_3$)$_2$CO[d]	1.01, 1.58	–	–	–	–	9.36	–	–
IV	CD$_2$Cl$_2$	0.97, 1.46	2.61, 2.78	2.19, 3.62	12.3	2.75	9.20	1.7	1.7
	(CD$_3$)$_2$CO	0.96, 1.48	2.63, 2.85	2.31, 3.61	12.2	c	9.21	1.7	d
V	CDCl$_3$	1.03, 1.63	2.70, 2.87	2.28, 3.66	12.2	3.08	9.12	3.1	1.6
VI	CDCl$_3$	1.04, 1.60	2.63, 2.80	2.17, 3.61	12.2	3.02	9.03	2.7	1.5
VII	CDCl$_3$	1.07, 1.65	2.80, 2.94	2.37, 3.62	12.2	3.05	9.38	4.3	<1
VIII	CDCl$_3$	0.87, 1.42	2.73, 2.95	2.27, 3.87	12.2	2.54	8.63	1.5	1.2
	(CD$_3$)$_2$CO	0.80, 1.40	2.61, 2.88	2.15, 3.76	12.0	2.44	8.61	b	c
IX	CDCl$_3$	0.85, 1.40	2.71, 2.96	2.23, 3.85	12.2	2.61	8.61	1.5	1.5
X	CDCl$_3$	0.83, 1.39	2.77, 3.05	2.23, 3.89	12.1	2.77	8.61	1.7	1.5
XI	CDCl$_3$	0.82, 1.35	2.63, 2.82	2.21, 3.72	12.2	2.33	8.51	1.5	c
XII	(CD$_3$)$_2$CO	1.11, 1.61	2.92, 3.09	2.65, 3.85	12.0	3.55	9.80	3.6	2.0
XIII	CDCl$_3$	1.00, 1.53	2.49, 2.72	2.03, 3.57	12.0	3.57	9.19	1.6	c

[a] Pseudoequatorial proton. [b] Broadened. [c] Obscured. [d] Very dilute solution.

prepared by metathesis of I with lithium bromide, sodium iodide and sodium thiocyanate, respectively. The monomeric species V–XI were obtained by cleavage of I–IV with the appropriate ligand, while XIII was prepared by reaction of I with benzyltriethylammonium chloride and XII by successive treatment of the same substrate with 2,2'-bipyridyl and silver tetrafluoroborate. Analytical, IR, crystallisation solvent, and m.p. data for all thirteen compounds are collected in Table 1 and ^{1}H NMR assignments are summarised in Table 2. The ^{1}H NMR spectrum of VII contained additional peaks arising from I and free ligand showing that, in this single instance, dissociation of ligand is taking place.

Structures of the complexes

The ^{1}H NMR spectra of the dimers, I–IV, are all very similar (see Table 2) and compounds II–IV are therefore assumed to have structures similar to that determined [1] for I. We have been unable to determine the mode of bonding of the thiocyanate group unambiguously. Thus, although its IR spectrum indicates [8] (ν(CN) 2140 cm^{-1}) that bridging involves both sulphur and nitrogen, it is not possible to decide which ligand atom is *trans* to the Pd–C bond. However, studies [9] of monodentate thiocyanate complexes suggest that the ligand tends to bond through nitrogen when bulky substituents are present in the *cis* position and a ligand of high *trans* influence occupies the *trans* position. Thus if similar criteria may be applied to bridging thiocyanate one would anticipate that IV would have the thiocyanate nitrogen *cis* to the bulkier NMe$_2$ group which places it *trans* to the Pd–C bond. Significantly, the PdCH proton resonance in the NMR spectrum of IV appears markedly upfield (ca. 0.8 ppm) of the positions found for this signal in the spectra of the remaining dimers I–III, presumably due to the diamagnetic anisotropy of the thiocyanate group. Bearing in mind that shielding zones would be expected at the ends of the thiocyanate group and the anticipated [10] geometries of Pd–S–C–N vs. Pd–N–C–S (see Fig. 1), a Pd–S bond *cis* to the Pd–C bond would more readily explain the large upfield shift observed.

In the monomeric complexes V–XI the added ligand takes up the position *cis* to the Pd–C bond as found [8,11] for related systems. This is most clearly demonstrated for the phosphine-containing complexes VIII–XI which all show a ^4J(P–Pd–N–CH$_3$) coupling of about 3 Hz in their ^{1}H NMR spectra indicating [12] a *trans* disposition of the Pd–P and Pd–N bonds. In addition, the introduction of the triphenylphosphine induces marked upfield shifts of the PdCH resonance in comparison with I, presumably because of shielding by phenyl rings. Upfield shifts of
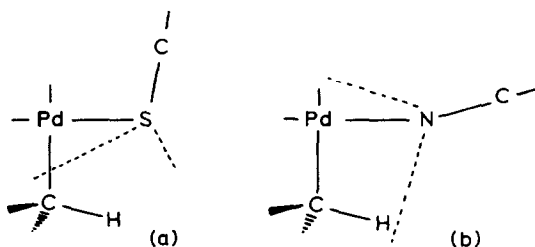

Fig. 1. Comparison of anticipated shielding regions for a bridging thiocyanate group (a) Pd–S *cis* to Pd–C, (b) Pd–N *cis* to Pd–C.

this resonance, although smaller in magnitude, are also observed for the pyridine-containing complexes V–VII for a similar reason. The configuration of VI has been established unambiguously by an X-ray study [13], which confirms that the dimethylaminopyridine moiety is bonded via the pyridine nitrogen and is *cis* to the Pd–C bond. Using the arguments outlined above, one would anticipate bonding of the SCN moiety through nitrogen in XI. IR evidence is consistent [14] with this conclusion since it shows a very strong band at 2080 cm^{-1} and a very weak one at 819 cm^{-1}. Compounds XII and XIII are assumed to be ionic [15].

The magnitudes of both the J(H-1/H-3e) (″W″) and J(H-1/H-5) couplings found for most of the complexes suggest that they have similar average conformations in solution and further that the preferred conformations are probably the same as those found for I and VI in the solid state. However, the relatively large values of J(H-1/H-5) found for V, VI, VII and XII presumably reflect changes in the average H-1/H-5 dihedral angle which perhaps result from a favourable interaction of the oxygen atom of the carbonyl group with an α-carbon atom in the adjacent pyridine ring. Such an interaction would be expected to become less important through the series VII → V → VI because of the progressive reduction in electron densities in the pyridine rings.

Infrared spectra in the carbonyl region

As Nujol mulls, all compounds display strong absorption in the range 1620–1650 cm^{-1} (see Table 1). As discussed previously [1] for I these represent unusually low values compared with those normally found for aliphatic aldehydes. In the majority, a single, relatively symmetrical, band is observed. However the phosphine adducts VIII and IX both show a pair of sharp symmetrical bands of similar intensities while in the dimethylaminopyridine adduct, VI, which also shows two bands, the one at higher energy is significantly stronger. In addition, for the cyanopyridine adduct VII this band has a shoulder on the higher energy side. In the last case this may reflect the presence of more than one preferred rotamer (cf. NMR discussion above). However, our X-ray study indicates that in VI only one rotamer is present with all aldehyde groups in an identical environment in the crystal. Thus, splitting of the carbonyl absorption must be due to Fermi resonance or the presence of disorder in the surface of the crystals. In the case of the phosphine adducts, VIII and IX, site symmetry may cause the observed splitting since the former shows a single band in dichloromethane solution.

The most obvious conclusion that results from a study of Table 1, is that cleavage of the dimers with monodentate ligands leads to a displacement of the carbonyl bands to lower energies as a result of increased electron density on palladium. Further, among the halide bridged dimers I–III, there is a very small apparent decrease in energy of the carbonyl stretching frequency on going from chloride to iodide. This presumably reflects the expected increase in σ-electron donation to palladium in passing from chloride to iodide. The stronger *trans* influence of iodide vs. chloride or bromide shows up clearly when the values of ν(C=O) for the phosphine halides VIII–X are compared. The influence of having a relatively good π-acceptor ligand *cis* to the Pd–C bond may be reflected in the observation that the (average) band position for the phosphine chloride VIII appears at higher energy than for the pyridine V and substituted pyridine adducts, VI and VII. It is, however, impossible to rationalise the relative band positions found for V–VII on this basis.

In the bipyridyl complex XII the σ-donating tendency of the nitrogen atoms is presumably offset by the π-accepting properties of the aromatic rings while for the anionic species XIII where the ligands are expected to have little or no π-accepting tendency, $\nu(C=O)$ has the lowest value found in the series studied.

Reactions of I with organic halides

If I were to react with organic halides, one might expect either *C*-alkylation via oxidative addition to give a palladium(IV) intermediate [16] or *O*-alkylation (cf. *O*-protonation on reaction with HCl [5]). The latter reaction could be taken as evidence that the interaction of the formyl group with the Pd atom involves [1] a contribution from the resonance structure XVII. Excess of methyl iodide failed to
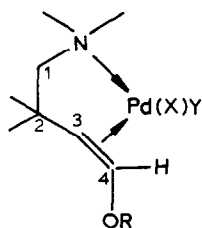
(XIV , R = H ; X = Y = Cl ;

XV , R = CH$_2$CH=CH$_2$; X = Br ; Y = Cl ;

XVI , R = CH$_2$Ph ; X = Y = Cl)
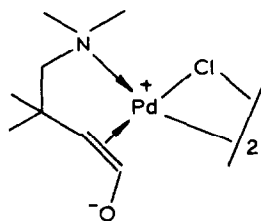
(XVII)

undergo significant reaction with I upon heating in CDCl$_3$ at 50°C for 3 days although traces of a dark insoluble material precipitated. With allyl bromide, on the other hand, a slow reaction with I took place at ambient temperature in CDCl$_3$. With excess of allyl bromide, in the absence of solvent, this reaction was complete within 2 days, a ^{1}H NMR spectrum of the residue after removal of unreacted allyl bromide showing it to be largely the allyl enol ether complex XV. Benzyl chloride did not react with I at ambient temperature but formed the corresponding enol ether derivative XVI on heating with I at 100°C in the absence of solvent. I was recovered after heating in refluxing 1-chlorobutane for 20 h.

Attempted reactions of I with methyl acrylate and alkynes

No change was observed (^{1}H NMR) when I was heated at 50°C in CDCl$_3$ or CD$_3$CN for several days with methyl acrylate. Indeed, I was stable to heating in neat methyl acrylate at reflux for several hours. I also remained unchanged on heating with diphenylacetylene in the same two solvents at 50°C. However, yellow solutions of I, in these solvents, slowly darkened in colour in the presence of phenylacetylene at ambient temperature. When successive molar equivalents of this compound were added and the reaction was monitored by ^{1}H NMR loss of the resonances due to the aldehyde I lagged well behind loss of the acetylenic proton resonance at 50°C. The signals for I only disappeared after reaction with about five molar equivalents (per Pd) of the acetylene. The ligand in I appears to have been converted into a single product which lacks an aldehyde proton resonance and displays a sharp singlet for the C-methyl protons. This product was extracted into D$_2$O and identified as the hydrochloride of 3,3-dimethyl-4-dimethylaminobutanal which rather surprisingly
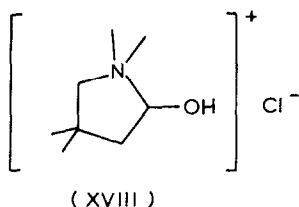
(XVIII)

exists in the cyclic form XVIII in both $CDCl_3$ and D_2O. This and related systems are discussed in a separate paper [17].

Experimental

Melting points were determined on the Kofler block and are uncorrected. Infrared spectra were recorded on a Beckman IR-12 spectrophotometer. Hydrogen-1 NMR spectra were obtained on a Bruker WP-60 or WH-400 (Southwestern Ontario NMR Centre) or Varian EM360L spectrometers with tetramethylsilane as internal standard. Microanalyses were performed by Mr. S.H. McKinnon of this department or by Galbraith Laboratories, Inc., Knoxville, Tennessee. Compounds I–XI were purified by preparative TLC on Kieselgel G (Merck) using dichloromethane/ methanol (99/1 or 199/1) followed by crystallisation from the appropriate solvent (see Table 1).

Preparation of di-μ-chlorobis[3-(dimethylamino)-1-formyl-2,2-dimethylpropyl-C,N]di-palladium(II) (I)

This compound was most conveniently prepared via dichloro[4-methoxy-2,2,N,N-tetramethylbut-(Z)-3-enylamine]palladium(II) [18] which was generated by mixing dichloromethane solutions of 4-methoxy-2,2,N,N-tetramethylbut-3-en-ylamine (0.8635 g, 5.50 mmol) [18] and bis(benzonitrile)dichloropalladium (1.8478 g, 5.00 mmol). A solution containing water (2 cm³) and N,N-dimethylaniline (1.2118 g, 10.0 mmol) in acetone (25 cm³) was then added, and the resulting solution was allowed to stand at ambient temperature overnight. Evaporation of the solvent, and preparative TLC of the residue gave I (1.1890 g, 83.7%).

Preparation of the dimeric species II–IV

A solution of I in acetone was treated with 2.2 equivalents of lithium bromide or sodium iodide or sodium thiocyanate in the same solvent. After standing at ambient temperature for 5 minutes the solutions were evaporated and the material which was recovered by extraction of the residues with dichloromethane was then purified by preparative TLC.

Preparation of the phosphine and pyridine adducts V–XI

The appropriate dimer in dichloromethane was treated with triphenylphosphine (2.2 equiv.) or the appropriate pyridine (4 equiv.). The adducts were obtained by preparative TLC of the resulting solutions. In the case of adducts V–VII a few drops of the appropriate pyridine was added to the solvent used (see Table 1) for crystallisation.

Preparation of 2,2'-dipyridyl[3-(dimethylamino)-1-formyl-2,2-dimethylpropyl-C,N]palladium(II) tetrafluoroborate (XII)

An acetone solution containing I and 2,2'-dipyridyl (2 equiv.) was treated with a solution of silver tetrafluoroborate (2 equiv.) in the same solvent. The precipitated silver chloride was filtered off and the filtrate concentrated, whereupon XII crystallised upon standing.

Preparation of benzyltriethylammonium dichloro-[3-dimethylamino)-1-formyl-2,2-dimethylpropyl-C,N]palladate(II) (XIII)

A dichloromethane solution containing stoicheiometric amounts of I and benzyltriethylammonium chloride was allowed to evaporate to dryness. Trituration of the resulting gum with diethyl ether gave XIII as a yellow powder.

Treatment of I with organic halides

I was recovered essentially unchanged from the following attempted reactions: with methyl iodide (6 equiv.) in $CDCl_3$ at 50°C for 3 days; with benzyl chloride (2 equiv.) in $CDCl_3$ at 20°C for 7 days; with 1-chlorobutane (neat) at reflux for 20 h. I did react slowly (^{1}H NMR monitoring) with allyl bromide (2 equiv.) in $CDCl_3$ at 20°C. Much more rapid reaction was observed in the absence of solvent. A solution of I (35 mg) in allyl bromide (1.5 cm^3) was left at room temperature for 2 days. Excess allyl bromide was then evaporated off under vacuum and the residue identified as essentially pure allyl enol ether complex XV; NMR: δ($CDCl_3$) (ppm) 1.17 (s, C–CH$_3$), 1.74 (s, C–CH$_3$), 2.29 (d, J 12.5 Hz, N–CH), 2.63 (s, N–CH$_3$), 3.04 (s, N–CH$_3$), 3.46 (d, J 12.5 Hz, N–CH), 4.59 (d, J 4.8 Hz, H(3)), 4.84 (d, J 6 Hz,O–CH$_2$), 5.3–6.5 (m, 3 vinyl H's), 7.67 (d, J 4.8 Hz, H(4)). This pale red-brown oil failed to crystallize, even after preparative TLC from which it was recovered largely unchanged (^{1}H NMR).

I (55 mg) was heated at 100°C for 15 h in benzyl chloride (4 cm^3) and unreacted chloride was then removed under vacuum. The residue was essentially pure benzyl enol ether complex XVI; NMR: δ($CDCl_3$) (ppm) 1.14 (s, C–CH$_3$), 1.71 (s, C–CH$_3$), 2.21 (d, J 13 Hz, N–CH), 2.24 (s, N–CH$_3$), 2.90 (s, N–CH$_3$), 3.30 (d, J 13 Hz, N–CH), 4.54 (d, J 4.6 Hz, H(3)), 5.36 (d, J 10 Hz, O–CH), 5.38 (d, J 10 Hz, O–CH), 7.2–7.6 (m, aromatic H's), 7.64 (d, J 4.6 Hz, H(4)). This pale yellow oil failed to crystallize and on preparative TLC was reconverted into I.

Treatment of I with methyl acrylate and alkynes

I was resistant to reaction (^{1}H NMR evidence) under the following conditions: with methyl acrylate (2 equiv.) in $CDCl_3$ or CD_3CN at 50°C for 1 week; in refluxing methyl acrylate for 5 h; with diphenylacetylene (2 equiv.) in $CDCl_3$ or CD_3CN at 50°C for 1 week.

The yellow solutions resulting from dissolving I and phenylacetylene (1 equiv. per Pd) in $CDCl_3$ or CD_3CN gradually darkened over several hours at ambient temperature and the acetylenic proton resonance gradually disappeared while the aldehyde proton resonance suffered a reduction in intensity. Similar changes were noted (over several minutes) when further equivalents of the acetylene were added and the solution was then warmed to 50°C. After 5 equiv. of the acetylene had reacted, the resonance of the aldehyde proton was absent and the two resonances arising from the C-methyl protons in I had been replaced by a single resonance (δ 1.23 ppm in

CDCl$_3$). The reaction solvents were evaporated, the residues dissolved in CH$_2$Cl$_2$ and extracted with D$_2$O. The resulting extracts contained the hydrochloride of 3,3-dimethyl-4-dimethylaminobutanal; AgNO$_3$ test and NMR comparison with an authentic sample prepared [17] from 4-methoxy-2,2,N,N-tetramethylbut-3-en-ylamine [18].

Acknowledgement

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