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FOUR-MEMBERED CHELATE AMINOALKENYL COMPLEXES OF PLATINUM(II). SYNTHESIS, CARBONYLATION AND OXIDATION TO AMINOACIDATO COMPLEXES

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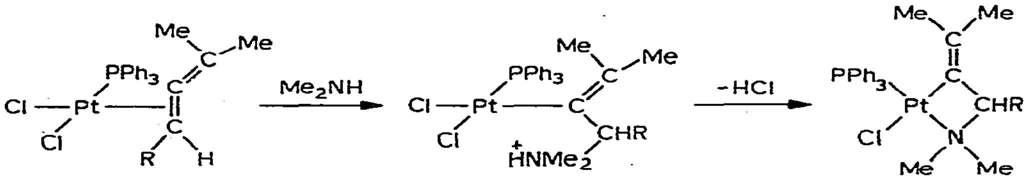
Summary

Amination of Pt^{II}-allene complexes of the type *cis*-$[\text{PtCl}_2(\text{Me}_2\text{C=C=CHR})(\text{PPh}_3)]$ gives the new four-membered C, N chelate aminoalkenyl complexes $[\overline{\text{PtC(=CMe}_2\text{)CHRN}}\text{Me}_2(\text{PPh}_3)\text{Cl}]$. These undergo ready insertion of carbon monoxide into the C—Pt σ-bond; the resulting acyl complexes are oxidized by hydrogen peroxide to aminoacidato complexes, and the free unsaturated β-aminoacids can be recovered in good yield by ligand displacement.

In previous papers [1] we described the first examples of platinum(II) complexes containing the four-membered $\overline{\text{Pt—C—C—N}}$ ring *, obtained by amination of co-ordinated mono-olefins [3]. We now report that analogous aminoalkenyl complexes (3) can be obtained by amination of Pt(II) coordinated allenes [4], and subsequent dehydrohalogenation of the resulting zwiterrionic β-ammonioalkenyl complexes, according to Scheme 1.

SCHEME 1



(1) (2) (3)

(a, R = H; b, R = Me)

The cyclization reaction can be performed at 0°C in chloroform in the pre-

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* Other workers, unaware of our papers, reported as new the synthesis and NMR spectral properties of one of these aminoalkyl complexes [2].

sence of an equimolar amount of aqueous base (NaOH or Me_2NH). The products have been characterized by elemental analysis, MW determination, and IR and ^{1}H NMR spectroscopy (in $CDCl_3$).

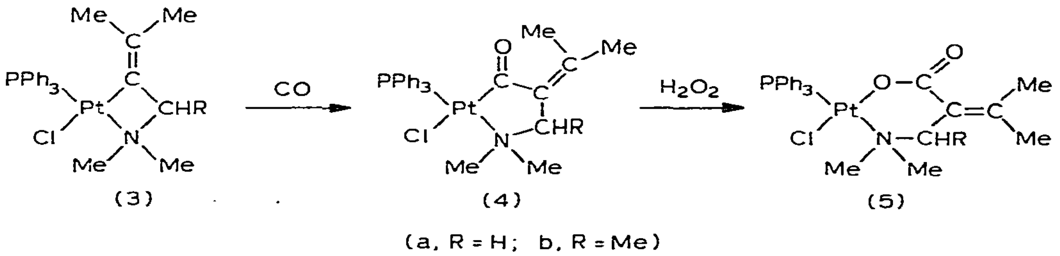
3a, NMR (δ, ppm): 0.69 t (*Me*, ^5J(H—H) 2 Hz, ^4J(H—Pt) 9 Hz), 1.37 s (*Me*, ^4J(H—Pt) 7 Hz), 2.87 d (N*Me*$_2$, ^4J(H—P) 4 Hz, ^3J(H—Pt) 33 Hz), 4.86 bs (CH_2, ^3J(H—Pt) 55 Hz).

3b, NMR (δ, ppm): 0.70 s (*Me*, ^4J(H—Pt) 9 Hz), 1.38 s (*Me*, ^4J(H—Pt) 8 Hz), 1.68 d (CH—*Me*, ^4J(H—Pt) 5 Hz), 2.67 d (N*Me*, ^4J(H—P) = 4 Hz, ^3J(H—Pt) 35 Hz), 2.87 d (N*Me*, ^4J(H—P) = 3 Hz, ^3J(H—Pt) = 29 Hz), 5.03 q (CH, ^3J(H—Pt) = 91 Hz).

We selected the carbonylation reaction as the starting point for the study of the reactions of compounds such as **3** and their previously reported [1] saturated analogues, $[\overline{PtCH_2CHRN}Me_2(PPh_3)Cl]$.

The insertion of carbon monoxide into simple alkyl [5,6] or alkenyl [7] complexes of platinum(II) usually requires rather drastic conditions [5,6] and may not take place at all [5,7]. On the other hand, cyclic aminoaryl complexes were reported to react with CO under fairly mild conditions [8]. We find for the Pt^{II} aminoalkyl and alkenyl complexes that unsaturation at the σ-bonded carbon atom can be a determining factor in promoting the insertion reaction. Thus we observed that cyclic saturated Pt^{II} aminoalkyl complexes do not react with carbon monoxide at low pressure *, whereas the analogous complexes **3** are easily carbonylated under mild conditions, giving the five-membered chelate aminoacyl complexes (**4**) as yellow crystalline solids (Scheme 2). Complexes **3** seem to be even more reactive than analogous saturated Pd^{II} complexes [9]. The reaction of CO with 1.0 mmol of **3** in 10 ml of benzene is complete under ambient conditions after few minutes and gives nearly quantitative yields. The products gave satisfactory elemental analyses and MW determinations and were characterized by IR (Nujol mull) and ^{1}H NMR spectroscopy (in $CDCl_3$) **4a**: IR (cm^{-1}); 1640 (ν(CO)), 265 (ν(Pt—Cl)); NMR (δ, ppm): 1.58 s (*Me*), 1.65 s (*Me*), 3.53 bs (CH_2, ^3J(H—Pt) 24 Hz), 3.09 d (N*Me*$_2$, ^4J(H—P) 2.5 Hz, ^3J(H—Pt) 31 Hz). **4b**: IR (cm^{-1}): 1630 (ν(CO)), 255 (ν(Pt—Cl)); NMR (δ, ppm): 1.57 s (*Me*), 1.66 s (*Me*) 1.52 d (CH*Me*), 3.33 dq (CH ^4J(H—P) 8.5 Hz, ^3J(H—Pt) 25 Hz), 3.04 d (N*Me*, ^4J(H—P) 2 Hz, ^3J(H—Pt) 29 Hz), 3.10 d (N*Me*, ^4J(H—P) 3 Hz, ^3J(H—Pt) 29 Hz).

SCHEME 2



The formation of a five-membered chelate product (**4**) appears to be a necessary condition for the insertion reaction, and attempts to obtain the CO insertion

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* Prolonged reaction times result only in extensive decomposition to unidentified products.

under mild conditions with various open-chain ammonioalkenyl complexes were unsuccessful, the chelation being precluded by the protonation of the nitrogen atom. For instance, treatment of the chloride-bridged complex $[\text{PtCl}(\text{Me}_2\text{C}{=}\text{CCH}_2\text{NHMe}_2)(\text{PPh}_3)]_2^+$ (obtained by reaction of **3a** with aqueous fluoboric acid) with carbon monoxide results only in bridge-splitting with CO coordination. The reaction of the carbonyl complex thus formed with PPh_3 results in the displacement of coordinated CO, whereas treatment with base causes deprotonation of the nitrogen atom and the immediate "chelation assisted" insertion of coordinated carbonyl group into the C—Pt σ-bond with formation of **4a**. It is interesting to note that an analogous insertion reaction promoted by the cyclization was observed for aminoalkyl complexes of Mo, W, and Fe [10].

The aminoacyl complexes **4** undergo a ready oxidative cleavage of the C—Pt σ-bond with formation of aminoacidato complexes (**5**). Thus by heating complex **4a** at reflux in methanol with an excess (5 : 1) of hydrogen peroxide for 3 min, good yields (up to 80%) of pale yellow crystals (**5a**) are obtained. IR (cm^{-1}): 1650 (ν(CO), 345 (ν(Pt—Cl)); NMR (δ, ppm): 1.83 s (*Me*), 2.06 s (*Me*), 3.33 d (CH_2, ^4J(H—P) 4 Hz, ^3J(H—Pt) 16 Hz), 2.90 d (N*Me*$_2$, ^4J(H—P) 2.5 Hz, ^3J(H—Pt) 23 Hz). Analogous oxidations were recently described for platinum alkyl [11] and palladium aminoaryl [12] complexes, while an efficient conversion of palladium aminoacyl complexes into β-aminoacid derivatives was achieved by oxidation with bromine [13]. The formation of **5** is a rare example of an easily performed, high yield oxidative cleavage of an acyl—metal bond, occurring through the insertion of an oxygen atom in the carbon—metal bond with formation of a stable complex. Moreover the coordinated new aminoacids so obtained can be quantitatively recovered as the hydrochlorides $[\text{Me}_2\text{C}{=}\text{C(COOH)CHRNHMe}_2]\text{Cl}$ (**6**) by treating **5** with HCl in CHCl_3 and precipitating the inorganic moiety as $[\text{PtCl}_2(\text{PPh}_3)_2]$. **6a**: NMR ($\delta$, ppm): 2.06 s(*Me*), 2.22 s (*Me*), 4.10 s (CH_2), 2.90 s (N*Me*$_2$). **6b**: NMR (δ, ppm): 2.00 s (*Me*), 2.09 s (*Me*), 1.51 d (CH*Me*), 4.42 q (CH), 2.89 s (N*Me*), 3.02 s (N*Me*). 2,2-dimethyl-2-sila-5-pentanesodium sulphonate as internal reference in D_2O solution).

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