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Preliminary communication

A FACILE FORMATION OF π-ALLYLPLATINUM(II) COMPLEXES BY DECARBOXYLATION OF ALLYLOXYCARBONYLPLATINUM(II) COMPLEXES

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Summary

Allyloxycarbonyl complexes of Pt^{II} undergo ready decarboxylation to give the corresponding π-allylplatinum(II) complexes. The importance of olefin coordination to a platinum atom in the transition state is suggested.

Acylmetallic complexes are well known to undergo decarbonylation to give alkylmetal complexes, a process which is of practical importance in many transition metal-catalyzed organic reactions [1]. On the other hand, very few studies have been reported of an analogous decarboxylation reaction of alkoxycarbonyl complexes of metals. For example, it was recently reported [2] that thermolyses of several alkoxycarbonyl complexes of Ni^{II} and Pd^{II} fail to give any evidence to support the formation of a metal—alkyl bond. We describe here a new decarboxylation reaction, namely the ready conversion of allyloxycarbonylplatinum(II) complexes to the platinum π-allylplatinum(II) complexes** in which, olefin coordination is thought to play an important role in the transition state.

The reaction of $CH_2{=}CR^1CH_2OH$ with $[PtCl(PR^2{}_3)_2(CO)]ClO_4$ in the presence of Na_2CO_3 at room temperature readily afforded $Pt(COOCH_2CR^1{=}CH_2)Cl(PR^2{}_3)_2$ (I)*** (Ia, $R^1 = H, PR^2{}_3 = PPh_3$; Ib, $R^1 = Me$, $PR^2{}_3 = PPh_3$; Ic, $R^1 = H$, $PR^2{}_3 = PPh_2Me$; Id, $R^1 = Me$, $PR^2{}_3 = PPh_2Me$). Ic and Id could also be prepared from $Pt(COOMe)Cl(PPh_2Me)_2$ and the corresponding allylic alcohols in CH_2Cl_2. The infrared spectra of I showed two intense absorption bands at around 1640 and 1050 cm^{-1} (nujol mulls) characteristic of the PtCOOR moiety, although a ν(C=C) band may also be involved in the former absorption. We believe complexes I have *trans* square

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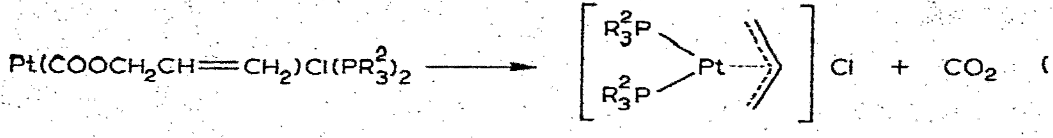
[**] The formation of a Pt—H bond from $[PtCl(PR_3)_2(CO)]BF_4$ and H_2O was previously suggested [3] to involve $Pt(COOH)Cl(PR_3)_2$ as an intermediate.
[***] Satisfactory elemental analyses were obtained for all the new complexes.

planar configuration without any interaction between the C=C bond and the platinum atom since (i) the olefinic proton signals in the NMR spectra of I in $CDCl_3$ showed no couplings with ^{195}Pt and ^{31}P nuclei, (ii) the phosphine methyl proton signals in Ic and Id appeared as clear 1/2/1 triplets accompanied by ^{195}Pt satellites, (iii) the $\nu(Pt-Cl)$ value for Ic ($280\ cm^{-1}$) is much the same as that for *trans*-$PtMeCl(PPh_2Me)_2$ ($269\ cm^{-1}$) [4].

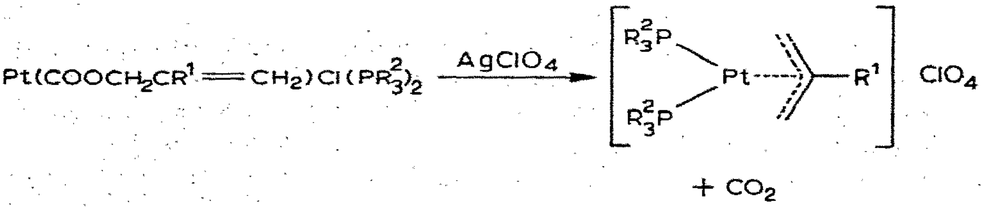
A decarboxylation of I could be performed in several ways. Thus, Ia and Ic were easily converted to $Pt(\pi\text{-}C_3H_5)(PR^2{}_3)_2Cl$ in refluxing benzene solution.



(1)

$PR^2_3 = PPh_3$ and PPh_2Me

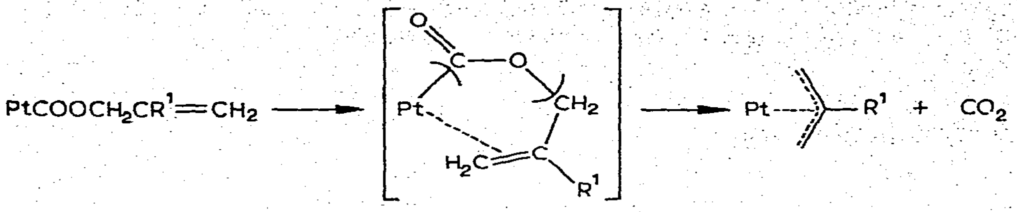
Ic also was found to decompose slowly to yield the π-allyl complex in $CDCl_3$ even at room temperature, but Ib and Id were much more reluctant to undergo similar decarboxylation. Particularly interesting is the fact that treatment of Ia, Ic and Id with an equimolar amount of $AgClO_4$ in CH_2Cl_2/acetone gave the corresponding π-allylplatinum(II) complexes much more readily than the thermal process.



(2)

$R^1 = H$, $PR^2_3 = PPh_3$ and PPh_2Me; $R^1 = Me$, $PR^2_3 = PPh_2Me$

Furthermore, addition of a catalytic amount of $SnCl_2$ to a CH_2Cl_2 solution of Ia resulted in marked acceleration of reaction (1) ($PR^2{}_3 = PPh_3$). Such enhanced reactivities of I by treatment with either $AgClO_4$ or $SnCl_2$ may be compared with the ready addition of the Pt—H bond of *trans*-$PtHCl(PR_3)_2$ to a C=C bond of olefins when silver salts [5] or $SnCl_2$ [6] used as catalysts. The role of these catalysts in the olefin insertion was ascribed to the stabilization of an intermediate π-olefin—platinum complex through removal of the chloride ligand by the former catalyst or formation of the $SnCl_3^-$ ligand with highly *trans* activating ability in the latter case. Consequently, all of our findings described above seem to be compatible with a transition state involving intramolecular coordination of the C=C bond to the platinum atom in reactions (1) and (2).



A similar cyclic intermediate was proposed previously [7] in the formation of π-allylplatinum(II) complexes and aldehydes from platinum(II) hydrido complexes and diallyl ethers.

References

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