*Journal of Organometallic Chemistry*, 105 (1976) C32—C34
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**Preliminary communication**

# THERMALLY INDUCED *ortho*-METALATION OF DICARBOMETHOXYACETYLENEBIS(TRIPHENYLPHOSPHINE)PLATINUM

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(Received August 21st, 1975; by publisher December 10th, 1975)

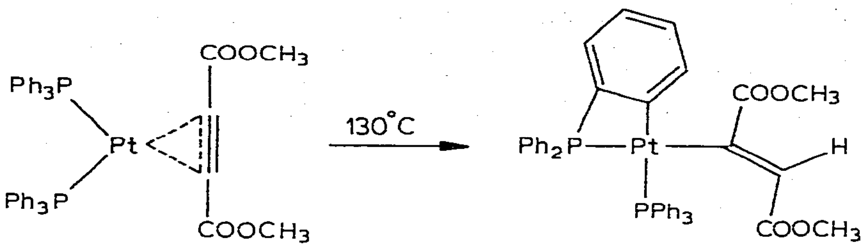
## Summary

Heating a toluene solution of dicarbomethoxyacetylenebis(triphenylphosphine)platinum(0) at 130°C gives the *ortho*-metalated complex $(Ph_3P)(Ph_2\overline{PC_6H_4)Pt}$-*trans*-$(COOMe)C{=}CHCOOMe$.

As part of a study of the photochemical behaviour of the title compound and other related acetylene complexes, we found it necessary to examine the thermal stability of at least one member of the series. Dicarbomethoxyacetylenebis(triphenylphosphine)platinum(0) (I) was chosen as a model, and it has been found to give, under thermal conditions, a product resulting from internal metalation. In view of the recent interest in this type of reactivity [1,2] we report out results separately from those obtained in the photochemical study.

A solution of I (135 mg) in toluene-$d_8$ was filtered through florisil into an NMR tube, and degassed by five freeze-pump-thaw cycles. The PMR tube was then sealed under vacuum. Heating the solution of the complex for several hours at 130°C resulted in substantial changes in the PMR spectrum, and after 24 hours at this temperature all starting material had reacted. Heating for an additional 2 hours caused no further reaction. The orange solid obtained upon evaporation of the solvent was recrystallized three times from dichloromethane/methanol to give a white crystalline material (57 mg) whose carbon and hydrogen analyses were almost identical to those of the starting material. (Found: C, 58.54; H, 4.21, $C_{42}H_{36}O_4P_2Pt$ calcd.: C, 58.53; H, 4.18%). On this basis and from the following evidence, we have assigned structure II to this product.

The IR spectrum (Nujol mull) showed no bands in the region between 2800 and 1720 $cm^{-1}$ indicating the absence of any $\pi$-bonded acetylene or $\sigma$-bonded acetylide. The remainder of the spectrum was quite different from that of I. Two strong bands at 1715 and 1702 $cm^{-1}$ are assigned to $\nu(C{=}O)$ of the two vinylic ester functions, and a somewhat less intense band at 1582 $cm^{-1}$



(II)

to $\nu$(C=C) of the vinyl group. A series of five closely spaced bands between 755 and 695 $cm^{-1}$ are attributed to aromatic C—H bond out-of-plane deformations, the one at 725 $cm^{-1}$ quite possibly being due to those of an *ortho*-disubstituted phenyl group [3,4]. In the spectrum of a $CH_2Cl_2$ solution of II, the band due to $\nu$(C=C) was broadened and shifted to 1575 $cm^{-1}$. In contrast, the IR of I in the same solvent showed two extremely weak bands at 1586 and 1572 $cm^{-1}$. The region between 1500 and 1400 $cm^{-1}$ in $CH_2Cl_2$ showed, for I, two sharp bands at 1478 and 1428 $cm^{-1}$ but, for II, displayed three at 1478, 1458 and 1430 $cm^{-1}$. In the case of an *ortho*-metalated manganese complex the third band has been assigned to $\nu$(C=C) modes of the metalated ring [1].

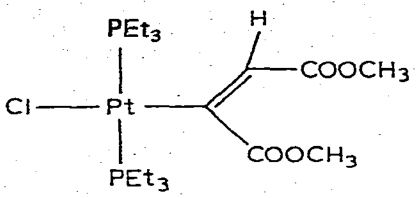
The PMR spectrum of II displayed two sharp three-proton singlets at $\delta$ 3.28 and 3.56 ppm which are assigned to the methyl protons of the ester functions [5]. The vinyl proton appears as a 1:4:1 triplet centred at $\delta$ 5.70 ppm. Each peak is further split into a doublet of doublets, $J$(PH) 10.4 and 2.5 Hz, $J$(Pt—H) 95.4 Hz. The stereochemistry of the complex II has been assigned as follows. Independent studies [6] in this laboratory have yielded a series of isomeric vinylplatinum(II) complexes having *cis* and *trans* configurations at platinum and *cis* and *trans*-alkenyl stereochemistries, a total of four isomers in all. A comparison of the above coupling constants for II with those for these four isomers, shows that II must have a *trans* vinyl group and two *cis* phosphines.

It has been reported that a noticeable downfield shift in the NMR spectrum occurs for phenyl protons *ortho* to palladium or platinum in internal metalated aryl phosphite derivatives [7]. The aromatic region of the PMR spectrum of II shows, in addition to the broad complex band at ~$\delta$ 7.1 ppm, a 6 or 7 line multiplet centred at $\delta$ 7.9 ppm which integrates for one proton. This peak can quite reasonably be assigned to the "aromatic" protons *ortho* to the platinum atom in II. The PMR spectrum of I in the same solvent shows only a single broad band for the phenyl protons.

The mass spectrum of II shows a parent ion at 861.18 (calcd. 861.17) and, significantly, a peak centred at 718 corresponding to loss of the alkenyl group: $C(COOCH_3)=CHCOOCH_3$.

The mechanism of this reaction can be viewed as a two-step sequence in which there is first oxidative-addition of an aryl C—H bond to the metal atom. While such internal metalation reactions have been observed for a number of platinum [4,8] and other transition metal complexes [1,2,9], the hydride is usually eliminated subsequently in the form of $H_2$ [4,9], as part of an alkane [9c] or as some other more complex species [9a]. The formation of II is thus unique in that it must occur by a subsequent insertion of the acetylene into the Pt—H bond formed by internal metalation. Perhaps the closest analogy is the case of olefin hydrogenation occuring during metalation described by James et al. [10].

Insertions of acetylenes into Pt—H bonds have been studied in some detail with *cis*-alkenyl complexes being the usually observed products [5,11]. On the other hand, examples of alkenyl *cis—trans* isomerization in rhodium(III) complexes have been reported recently [12], so a similar isomerization was considered for the present case. Complex III* was heated in toluene-$d_8$ for prolonged periods at 150°C. Since no isomerization of the vinyl group could be detected by PMR, the formation of the *trans*-vinylic product II apparently results from an insertion mechanism which differs substantially from those previously proposed. Interestingly, this *trans*-vinylic geometry has also been observed [13] in acetylene insertion reactions with platinum(II) hydrides under conditions where a radical process appears to be operative.



(III)

The continued financial support of the National Research Council of Canada and the award of an N.R.C.C. Post-doctorate Fellowship to K.E.H. are gratefully acknowledged.

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* Obtained via isomerization of the *cis* phosphine complex.