Chemical Communications (The Journal of The Chemical Society, Section D)

NUMBER 18/1971

22 SEPTEMBER

Photochemical and Thermal Reactions of Carbonatobis(triphenylphosphine)platinum(11): a Convenient Precursor for Bis(triphenylphosphine)platinum(0)

By D. M. BLAKE* and R. MERSECCHI

(Chemistry Department, The University of Texas at Arlington, Arlington, Texas 76010)

Summary Carbonatobis(triphenylphosphine)platinum(II) and some analogues have been found to be precursors for dico-ordinate platinum(0) species.

THERE is continued interest in the chemistry of platinum(0) compounds, particularly those containing only two ligands per platinum atom, *e.g.*, $Pt^{0}(PPh_{3})_{2}$. This compound is very susceptible to reactions such as oxidative addition, addition of unsaturated molecules, and metal-metal bond formation. Unfortunately, the difficulty in preparing this species has hindered its study.^{1,2} We now report convenient new precursors which make available a wider range of co-ordinatively unsaturated, platinum(0) species.

Carbonatobis(triphenylphosphine)platinum(II)³ (1a) reacts either photochemically or thermally in alcoholic solvents to produce $Pt(PPh_3)_2$ in situ.[†] The reactions proceed without added reducing agents. This is demonstrated by the reactions shown in equation 1. Spectral and

$$PtL_{2}CO_{3} + X \xrightarrow{EtOH, 40^{\circ}} PtL_{2}X_{n}$$
(1)
(1) (2)

chemical properties of the new triphenylarsine complexes are similar to their known phosphine analogues. Isolation of the ethylene adduct, (2a), is convincing evidence for the formation of the dico-ordinate platinum(0) species as an intermediate.¹ In the case of (1c) (L = methyldiphenylphosphine) reduction occurs but no stable adducts have been obtained. With (1c) and carbon monoxide, instead of simple monomeric carbonyl complexes, one rapidly gets cluster compounds even at room temperature. This observation is in accord with the findings of others using different reducing systems.⁴ These reactions illustrate the utility of this method in the production of co-ordinatively unsaturated platinum(0) species, PtL_2 , *in situ* and indicate that the method can be extended to ligands other than triphenylphosphine.

In the absence of added ligands the reaction follows the course shown in equation 2. The yellow monomer, $Pt-(PPh_3)_2$,¹ was not obtained. Instead, an orange solid (3),

$$L_{2}PtCO_{3} \xrightarrow{\text{EtOH, dark}} (L_{2}Pt)_{2} + CO_{2}$$
(1a)
(3)
+ MeCHO + H_{2}O
(2)

is formed (50% yield, m.p. 248 °C). This compound was recrystallized from benzene-hexane. The molecular weight of (3) was found to be 1420 in benzene and remained constant in solutions for as long as 3 days.⁵ (3) was shown to be different from the yellow dimer having the same apparent composition but obtained by photolysis of oxalatobis(triphenylphosphine)platinum(II)² by comparison of their thin layer chromatograms. The yellow dimer can be obtained in 60% yield by photolysing (1a) in ethanol solution. The difference between the orange and yellow dimeric species remains to be elucidated. The reason for not obtaining the

† Reactions were carried out under nitrogen gas purified by passage through Alfa Inorganics De Ox catalyst and molecular sieves. Known compounds were identified by comparison of their physical properties with those of authentic samples. All new compounds gave satisfactory elemental analyses. monomer, $Pt(PPh_3)_2$, from the carbonato-complex probably lies in the relatively vigorous conditions necessary to bring about the reduction in the absence of added ligands.¹

During the reactions of (1a) shown in equations 1 and 2, with the exception of that with carbon monoxide, one mole of carbon dioxide per platinum is evolved. In the case of carbon monoxide 1.8 moles of CO₂ are produced. This, and the oxidation of ethanol and other alcohols to the corresponding aldehyde or ketone indicate that the carbonatoligand is the source of a usable oxygen atom.

We thank the donors of The Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

(Received, May 20th, 1971; Com. 808.)

¹ R. Ugo, G. LaMonica, F. Cariati, S. Cenini, and F. Conti, Inorg. Chim. Acta, 1970, 4, 390, and references therein.

^a D. M. Blake and C. J. Nyman, J. Amer. Chem. Soc., 1970, 92, 5359.
^a P. J. Hayward, D. M. Blake, G. Wilkinson, and C. J. Nyman, J. Amer. Chem. Soc., 1970, 92, 5873.
^a J. Chatt and P. Chini, J. Chem. Soc. (A), 1970, 1538.
^a An orange compound [Pt(PPh₃)₂]_n thought to be a trimer has been reported. R. D. Gillard, R. Ugo, F. Cariati, S. Cenini, and B. Bonati, Chem. Comp. 1966, 868. F. Bonati, Chem. Comm., 1966, 868.