Journal of Organometallic Chemistry, 152 (1978) C45—C47

Preliminary communication

A GENERAL AND CONVENIENT METHOD OF SYNTHESIZING DIHYDRIDOPLATINUM(II) COMPLEXES WITH BULKY PHOSPHINE LIGANDS

H.C. CLARK, A.B. GOEL and C.S. WONG
Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Chemistry Department, University of Guelph, Guelph, Ontario, N1G 2W1 (Canada)

(Received January 3rd, 1978)

Summary

Platinum(II) dihydrides containing bulky phosphine ligands, *trans*-PtH_2L_2 (L = PCy_3, P-i-Pr_3, P-n-Bu-t-Bu_2, PMe-t-Bu_2), have been prepared conveniently and in excellent yield from the reaction of the corresponding peroxycarbonato complexes with $NaBH_4$. A similar reduction of the dioxygen platinum(II) complexes also affords the dihydrides but less readily. All these dihydrides react with highly activated acetylenes to form the *trans*-hydridovinyl complexes.

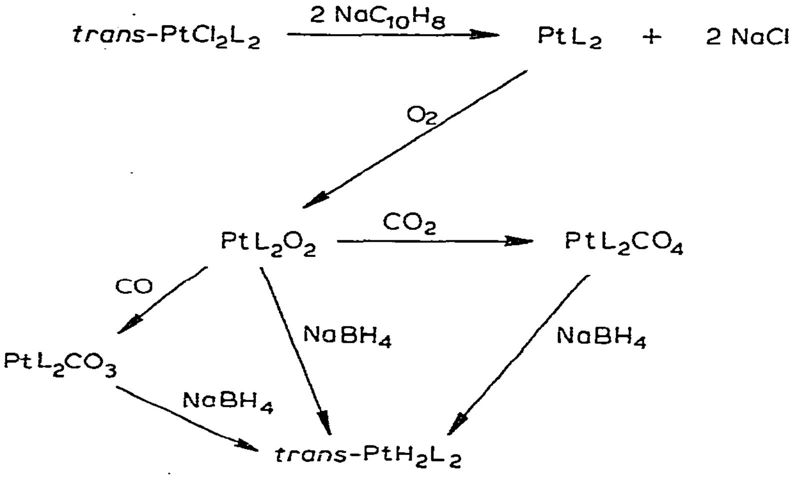
The chemistry of platinum(II) dihydrides is relatively unexplored compared with that of the monohydrides, probably due to the lack of a general synthetic route. Although Shaw et al. [1] have reported synthesis of these dihydrides by reducing *cis*-$PtCl_2L_2$ or *trans*-$PtHClL_2$ with excess $NaBH_4$ these starting materials are not readily available where L is a bulky phosphine. For example, hydrazine reduction of *trans*-$PtCl_2L_2$ [2] always produces a mixture of the unreacted starting material and the monohydride [2, 3]. Moreover, we find that the reaction of $Pt(PCy_3)_2$ with hydrogen [4], conducted in hexane, gives only very low yields of the dihydride.

We have been interested in the mechanistic studies of platinum(II) hydride reactions with unsaturated organic substrates. Since the reaction of *trans*-$PtHCl(PEt_3)_2$ with dimethylacetylene dicarboxylate (DMA) in benzene at elevated temperatures occurs [5] via a free radical mechanism, we expect the dihydrates, which have weaker Pt—H bonds (because of the high *trans* influence of the hydride ligand [6]), may behave similarly. Attempted syntheses of these platinum(II) dihydrides by the above methods [1] were unsatisfactory and gave poor yields. We wish to report here a more general and convenient method of preparation.

The reaction of platinum peroxycarbonato complexes, PtL_2CO_4 (L = PCy_3, P-i-Pr_3, P-n-Bu-t-Bu_2, PMe-t-Bu_2), with $NaBH_4$ in dry ethanol proceeds exceedingly rapidly at ambient temperatures to yield quantitatively the corresponding dihydrides. The reactions are usually complete within a few minutes of the addition of $NaBH_4$ to a suspension or solution of the peroxycarbonato complex in ethanol. The dihydrides can easily be isolated by removing the ethanol and then extracting the reaction mixture with benzene. Further recrystallization in ethanol/H_2O (or benzene/ethanol) gives white crystalline products. The peroxycarbonato complexes in turn can easily be prepared from *trans*-$PtCl_2L_2$ as follows. $PtCl_2L_2$ is reduced by sodium naphthalenide in THF under a nitrogen atmosphere to give the zerovalent PtL_2 complex; the passage of oxygen through a hexane extract of the reaction mixture precipitates the dioxygen complex ($\nu(PtO_2)$ at 817 to 826 cm^{-1}). Addition of CO_2 to a benzene solution of the dioxygen complex gives PtL_2CO_4 ($\nu(C{=}O)$ at $\sim$1680 cm^{-1}), the peroxycarbonate complex characterized by its infrared band at ca. 780 cm^{-1} [7].

Alternatively, the peroxycarbonato complex can be formed directly by passing oxygen and carbon dioxide into the hexane extract, provided that sufficient benzene is introduced to keep the dioxygen intermediate in solution.

Reaction of the dioxygen complex with carbon monoxide gives the carbonato complex which can be reduced smoothly to the dihydride under similar conditions.



($L = PCy_3$, $P\text{-}t\text{-}Bu_2\text{-}n\text{-}Bu$, $P\text{-}t\text{-}Bu_2Me$, $P\text{-}i\text{-}Pr_3$)

Similarly, the dioxygen complexes can also be reduced to the dihydrides by treatment with $NaBH_4$, but the reactions proceed much more slowly.

The dihydrides are white crystalline solids which are soluble in most organic solvents and which react with CCl_4 to give $PtHClL_2$. They have Pt—H stretching frequencies in the region 1710—1742 cm^{-1}, and resonances in the ^1H NMR spectra at τ 12.50 to 13.17 ppm. Each of the hydride signals appears as a triplet with ^{195}Pt satellites indicating a *trans* disposition of the two hydrogen ligands (J(P—H) 16.5 to 17.2 Hz, J(Pt—H) 778 to 788 Hz).

The reduction of $Pt(PPh_3)_2CO_4$ with $NaBH_4$ resulted only in some black decomposition products. Presumably the $PtH_2(PPh_3)_2$ is unstable under these conditions, leading to the formation of the unstable $Pt(PPh_3)_2$. It has been reported [8] that $Pt(PPh_3)_2(C_2H_4)$ is formed in high yield when the same reduction is carried out under an ethylene atmosphere.

We have also been able to prepare *trans*-$PtHRL_2$ (e.g. R = n-Bu, Me; L = PCy_3) by the reaction of RLi with *trans*-$PtHClL_2$: These complexes exhibit strong bands due to ν(PtH) in the region 1890—1924 cm^{-1}. A similar band has been observed by Kudo et al. [9] in the reaction of $Pt(acac)_2$, PCy_3 and Et_3Al and erroneously attributed to the dihydride; probably *trans*-$PtHEtL_2$ was obtained.

The platinum dihydrides react with dimethylacetylene dicarboxylate (DMA) or hexafluorobut-2-yne (C_4F_6) in benzene exothermically to yield *trans*-PtH(DMAH)L_2 and *trans*-PtH(C_4F_6H)L_2 respectively; ν(PtH) of these complexes appears at $\sim$2100 cm^{-1}. In the ^1H NMR spectra, the vinylic proton resonates at τ 3.0 ppm (J(PtH) $\stackrel{\sim}{\sim}$85Hz) (e.g. *trans*-PtH(DMAH)$(PCy_3)_2$, τ(DMAH) = 3.08, ^3J(PtH) 86.0 Hz, ^4J(HH) 4.4 Hz). The low field position of the vinylic proton signal and the large J(PtH) coupling constant are indicative of a *trans* Pt and H arrangement at the olefinic bond. This is consistent with those cases where insertion has been shown [5] to occur via a free radical process. The mechanism of these reactions is currently under investigation.

Acknowledgements

The continued financial support of the National Research Council of Canada is gratefully acknowledged.

References

1 B.L. Shaw and M.F. Uttley, J. Chem. Soc. Chem. Commun., (1974) 918 and ref. therein.
2 P.G. Leviston and M.G.H. Wallbridge, J. Organometal. Chem., 110 (1976) 271.
3 H.C. Clark, A.B. Goel and C.S. Wong, unpublished results.
4 J. Fornies, M. Green, J.L. Spencer and F.G.A. Stone, J. Chem. Soc. Dalton Trans., (1977) 1006.
5 H.C. Clark and C.S. Wong, J. Amer. Chem. Soc., 99 (1977) 7073.
6 T.G. Appleton, H.C. Clark and L.E. Manzer, Coord. Chem. Review, 10 (1973) 335.
7 P.J. Hayward, D.M. Blake, G. Wilkinson and C.J. Nyman, J. Amer. Chem. Soc., 92 (1970) 5873.
8 D.M. Blake, S. Shields and L. Wyman, Inorg. Chem. 13, (1974) 1595.
9 K. Kudo, M. Hidai and Y. Uchida, J. Organometal. Chem., 56 (1973) 417.