Inorganica Chimica Acta, 77 (1983) L5–L6

Chemistry of Metal Diene Complexes: a convenient Synthesis of Selected Bis(tertiary phosphine)platinum(0) Complexes and their Dioxygen Platinum(II) Adducts

ANIL B. GOEL* and SARLA GOEL

School of Chemistry, Georgia Institute of Technology, Atlanta, Ga. 30332, U.S.A.

Received February 25, 1983

Due to their unusual electronic structure, two coordinate tertiary phosphine complexes of zerovalent platinum triad have received considerable interest. Recent studies demonstrate that the stabilization of such complexes depends critically upon the steric bulk of the phosphine [1]. Several two-coordinate platinum(0) complexes, PtL_2, where L = a bulky tertiary phosphine such as Bu^t_3P, Bu^t_2RP, Cu_3P or Pr^i_3P have been reported recently [2]. The reported synthesis of these complexes either involves the reduction of the corresponding bis(tertiary phosphine)platinum(II) dichloride [2] or the reaction of phosphine with $(COD)_2Pt$ [3] (COD = 1,5-cyclooctadiene) which is not easily accessible. In the course of our investigations on the reactions of $(COD)PtCl_2$ we have recently reported a convenient synthesis of the stable methoxy bridged dinuclear platinum(II) complex, $[Pt_2(\mu\text{-}OCH_3)_2(C_8H_{12}\text{-}OCH_3)_2]$ [4] (*1*). Now we wish to report here the use of this complex in the convenient and one step synthesis of some selected bis(tertiary phosphine)-platinum(0) complexes and their dioxygen adducts.

The reaction of methoxy-bridged dinuclear platinum(II) complex, *1*, with two mol equivalents of tertiary phosphines (R_3P = Bu^t_3P, Bu^t_2MeP, $Bu^t_2Bu^nP$, Bu^tPh_2P), per platinum in alcoholic solvent such as methanol proceed exceedingly rapidly at ambient temperatures under inert atmosphere to yield the corresponding bis(tertiary phosphine)platinum(0) complex, $(R_3P)_2Pt(0)$, *2* (eqn. 1):

$$\tfrac{1}{2}[(C_8H_{12}OCH_3)Pt(OCH_3)]_2 + 2PR_3 \xrightarrow{CH_3OH} (R_3P)_2Pt(0) + C_8H_{11}OCH_3 \qquad (1)$$

Surprisingly, however, the reaction of Cy_3P or Pr_3P with *1* under the above conditions results in the for-

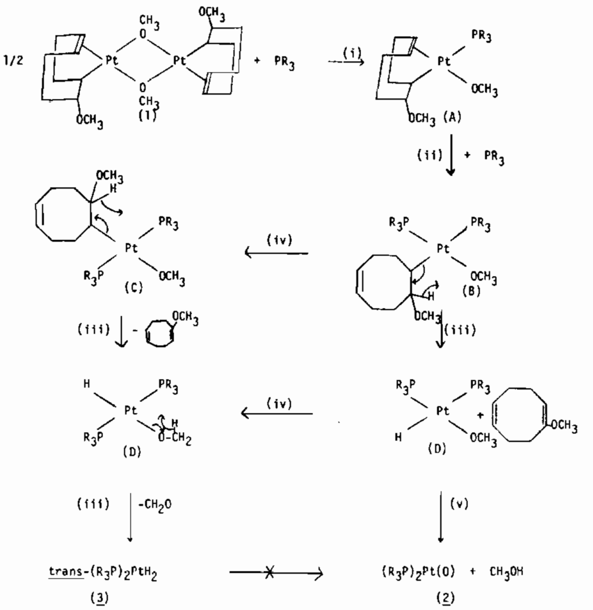
TABLE I. Spectroscopic Data for Pt(II) Dioxygen, Carbonato and Peroxy carbonato Complexes.

Complexes $(R_3P)_2Pt(Y)$ R_3P	I.R. Frequencies of the Functional Groups (cm^{-1})				^1H NMR of $(R_3P)_2PtO_2$		^{31}P NMR Data								
	$(R_3P)_2PtO_2$	$(R_3P)_2PtCO_3$	$(R_3P)_2PtCO_4$		δ (ppm)	J(P–H) (Hz)	$(R_3P)_2PtO_2$		$(R_3P)_2PtCO_3$		$(R_3P)_2PtCO_4$				
	νPtO_2	$\nu C{=}O$	$\nu C{=}O$	$\nu O{-}O$			δ (ppm)	J(Pt–P) (Hz)	δ (ppm)	J(Pt–P) (Hz)	δ (ppm) δ_1	δ_2	JPP^1 (Hz)	JPt–P (Hz)	$JPt{-}P^1$ (Hz)
Cy_3P	817	1682	1675	775	1.5(b)	–	21.01	3931	11.36	3567	7.14	10.40	17.14 14.7	3674	3125
Bu^tPh_2P	817	1681	1676	778	Bu^t = 1.11(d) Ph = 7.2(m)	15	35.08	4072							
Bu^t_2MeP	824	1682	1677	776	Bu^t = 1.20(d) Me = 1.13(d)	12.8 9; JPt–H = 35.5	34.98	4014	18.70	3684	10.05	14.22	17.14 14.7	3823	3218
$Bu^t_2Bu^nP$	826	1681	1677	777	Bu^t = 1.38(d) Bu^n = 0.8–1.9(b)	13	40.11	4053							

---

*Author to whom correspondence should be directed at the present address: Ashland Chemical Company, P.O. Box 2219, Columbus, Ohio 43216, U.S.A.

0020-1693/83/$ 3.00



Scheme. (i) Bridge splitting reaction; (ii) Ligand substitution reaction; (iii) β-Hydrogen elimination; (iv) *cis* → *trans* isomeriazation; (v) Reductive elimination.

mation of bis(phosphine)platinum(II) dihydride, (R$_3$P)$_2$PtH$_2$, *3*, as the major product (>60%) and (R$_3$P)$_2$Pt(0) in minor amounts. Although we propose the following probable reaction pathways (shown in Scheme 1) for the formation of the complexes *2* and *3*, however, the reason (or reasons) for the different product selectivities associated with various phosphines is not clear at this time. It appears that the steric effect of the phosphine is not the only cause for this, since the phosphines such as Pr$^i_3$P (cone angle 160°) and Bu^{t}Ph$_2$P (cone angle 157°) [1] have similar steric parameters. However the former gives the dihydride complex *3* and the latter gives bis(phosphine)platinum(0) complex *2*.

The intermediate (*A*) proposed in the above scheme is supported by the fact that the reaction between complex *1* and tertiary phosphines in benzene indeed results in the formation of (*A*) [4]. A β-hydrogen elimination in the intermediate complexes (*B*) and (*C*) to afford the hydrido-platinum complex (*D*) is proposed on the basis of the formation of methoxycyclooctadiene as by-product. A similar β-hydrogen elimination process has also been reported earlier [5].

The reaction mixtures (eqn. 1) containing bis(tertiary phosphine)platinum(0) complexes reacts readily with O$_2$ or air to yield the corresponding dioxygen platinum(II) complexes, (R$_3$P)$_2$PtO$_2$ (*4*) (R$_3$P = Cy$_3$P, Bu^{t}Ph$_2$P, Bu$^t_2$MeP, Bu$^t_2$Bu^{n}P). When tri-t-butyl phosphine is used, no dioxygen– platinum(II) adduct is formed and the Bu$^t_3$P)$_2$Pt(0) was recovered in almost quantitative yield.

The IR spectra of these complexes *4* show a band in the region 817–826 cm^{-1} characteristic of νPtO$_2$. ^{31}P NMR spectra show a singlet in the region 21.01–40.11 ppm (w.r. to H$_3$PO$_4$) associated with large platinum satellites (J^{195}Pt–^{31}P $\sim$ 3931–4072 Hz). These dioxygen complexes *4* undergo known reactions such as addition of CO$_2$ to a benzene solution of these to give (R$_3$P)$_2$-PtCO$_4$ (*5*), (νC=O at ~1677 cm^{-1} and νO–O ~776 cm^{-1}) and reaction with CO which results in the formation of (R$_3$P)$_2$PtCO$_3$ (*6*) (νC=O ~1681 cm^{-1}). The spectral data of dioxygen (*4*), peroxycarbonate (*5*) and carbonate (*6*) complexes are given in Table I.

A detailed mechanistic study on the formation of complexes *2* and *3* in the reaction of methoxy-bridged dinuclear complex *1* with tertiary phosphine and also on the various types of reactions of complex *2* is in progress.

References

1 C. A. Tolman, *Chem. Rev., 77,* 313 (1977) and references cited therein.
2 S. Oksuka, T. Yoshida, M. Matsumoto and K. Nakatsu, *J. Am. Chem. Soc., 98,* 5850 (1976).
3 M. Green, J.A. K. Howard, J. L. Spencer and F. G. A. Stone, *J. Chem. Soc. Dalton,* 271 (1977).
4 A. B. Goel, S. Goel and D. G. Van Der Veer, *Inorg. Chim. Acta, 54,* L169 (1981).
5 A. B. Goel and S. Goel, *Inorg. Chim. Acta, 45,* L85 (1980);
H. C. Clark, A. B. Goel and S. Goel, *J. Organometal. Chem., 216,* C25 (1981).