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A New Synthesis of *cis*-(Alkene)dichloro(phosphine)platinum(II) Complexes

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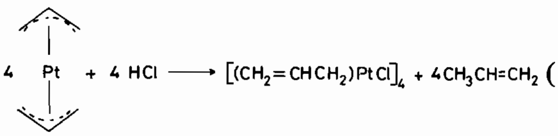
Abstract

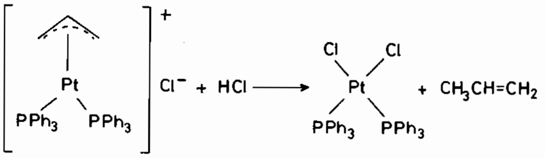
Propene complexes, *cis*-$[PtCl_2(PR_3)(\eta^2\text{-}C_3H_6)]$, are formed quickly and in good yield by the reaction of $[Pt(\eta^3\text{-}C_3H_5)Cl(PR_3)]$ with HCl. They are proposed as a preferred starting material in a general synthesis of alkene complexes, *cis*-$[PtCl_2(PR_3)(\eta^2\text{-}alkene)]$.

Introduction

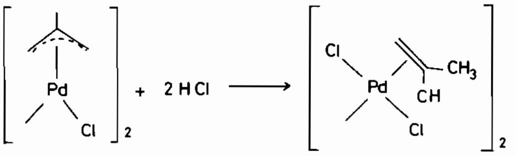
Allylplatinum(II) complexes usually react with HCl to form propene which is then released from the molecule. For example, *bis*(η^3-allyl)platinum(II) reacts to form tetrameric allylplatinum(II) chloride and liberate propene according to eqn. (1) [1]. The resulting tetramer, which is insoluble in most solvents, does not react further with HCl. The cationic complex, $[Pt(\eta^3\text{-}C_3H_5)(PPh_3)_2]^+Cl^-$, also reacts with HCl to liberate propene (eqn. 2) [2]. On the other hand, *bis*(η^3-2-methylallyl)-μ-dichlorodipalladium(II) has been reported to react with HCl in ether to form the very labile *bis*(η^2-2-methyl propene) complex [3] (eqn. 3), but an attempt to repeat the work failed [4].



(1)



(2)

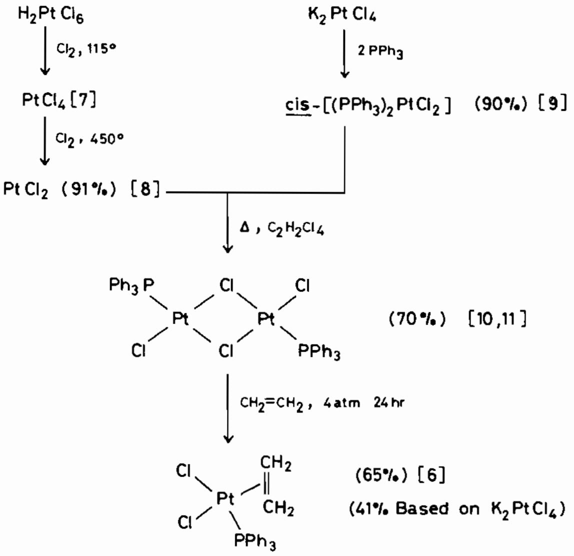


(3)

We wish to report at this time that $[Pt(\eta^3\text{-}C_3H_5)Cl(PR_3)]$ reacts readily with HCl to form *cis*-$[PtCl_2(PR_3)(\eta^2\text{-}C_3H_6)]$ in excellent yield and that this reaction can form the basis for an improved general synthesis of *cis*-dichloro(η^2-alkene)(phosphine)platinum(II) complexes.

Discussion

The standard literature procedure for the preparation of *cis*-dichloro(η^2-alkene)(phosphine)platinum(II) complexes involves the cleavage of chloro-bridged dimers by ethylene [5, 6]. These reactions are generally slow, and the preparations of the chloro-bridged dimers are tedious (Scheme 1 outlines the standard procedure).



Scheme 1.

Scheme 2 outlines an improved synthetic procedure starting with K_2PtCl_4. This procedure yields the *cis*-propene complex rather than the ethylene complex; however, the propene is readily displaced by other alkenes. For example, the known complex [12], *cis*-$[PtCl_2(PMe_2Ph)(\eta^2\text{-}CH_2{=}CHCH_2OH)]$, is obtained in 88% yield from *cis*-$[PtCl_2(PMe_2Ph)(\eta^2\text{-}$

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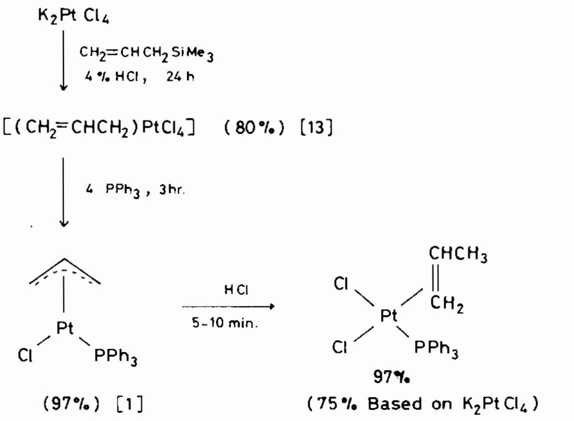
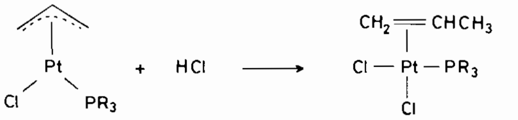


Scheme 2.

$CH_2{=}CHCH_3)]$. The propene complex thus serves as a convenient starting material for the preparation of other complexes [6].

Table I contains yield and analytical data for several complexes prepared by the new procedure. Yields are 87 percent or better for all of the complexes except for that of $P(n\text{-}Bu)_3$. The low yield with $P(n\text{-}Bu)_3$ may be significant and could indicate either steric or electronic problems in this complex. Since $[(CH_2{=}CHCH_2)PtCl]_4$ reacts readily with $P(n\text{-}Bu)_3$, the problem with the synthesis appears to be the final step (eqn. 5). We have observed that when



(5)

R = t-Butyl, reaction (5) fails completely. We, therefore, suggest that the steric requirements of the phosphine ligand may play a significant role in determining the yields in reaction (5) [the cone angle of $P(t\text{-}Bu)_3$ is 182 ± 2] [14]. This conclusion is tentative at this time and is based on the assumption that the reaction is initiated by protonation at platinum.

The stereochemistry of the square planar complexes was assigned using IR spectroscopy, and the results are included in Table I. The 200 MHz ^{1}H-nmr spectra of the complexes prepared are as required for the proposed structures. The spectra of the PMe_2Ph and PPh_3 complexes are known [15] and our results for these complexes are in good agreement with the earlier work. Table II summarizes the nmr results.

Experimental

Reactions were conducted in an atmosphere of pre-purified nitrogen. Carbon and hydrogen analyses were performed locally on a Perkin-Elmer Model 240C Elemental Analyzer. ^{1}H nmr spectra were obtained on a Nicolet Model NT-200 in $CDCl_3$. IR spectra were obtaind on a Perkin-Elmer Model 683 Spectrometer as Nujol mulls on CsI plates. The complexes, $[Pt(\eta^3\text{-}C_3H_5)Cl(PR_3)]$, were prepared according to the literature [1] in essentially quantitative yield.

Preparation of cis-[$PtCl_2(PR_3)(CH_2{=}CHCH_3)$] ($PR_3$= PPh_3, PPh_2Me, $PPhMe_2$, PBu_3)

In a typical reaction, $[Pt(\eta^3\text{-}C_3H_5)Cl(PR_3)]$ [1] (0.5 g) was dissolved in acetone (3 ml). Conc. HCl (1 ml) was added; the solution was stirred for 5–10 minutes, and water (15 ml) was added to precipitate the propene complex which was filtered, washed with water and dried *in vacuo*. In the case of PBu_3 the product was washed with ether after the initial drying.

Preparation of cis-[$PtCl_2P(OPh)_3(CH_2{=}CHCH_3)$]

In a typical reaction, $[Pt(\eta^3\text{-}C_3H_5)P(OPh)_3Cl]$ (1.0 g, 1.7 mmol) was allowed to react with dry HCl saturated CH_2Cl_2 (10 ml). After 5 min. the volume of the reaction mixture was reduced to 4 ml *in vacuo*. The white propene complex was obtained upon addition of hexane (10 ml) and was isolated, washed with additional hexane and dried *in vacuo*.

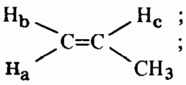
TABLE I. Yield, Analytical and IR Results.

cis-$[PtCl_2(PR_3)(\eta^2\text{-}C_3H_6)]$	% Yield	Color	M.P. (°C)	Analysis (Calcd./Found)		ν(Pt–Cl)^b (cm^{-1})
				%C	%H	
PPh_3	97	white	175–80 d.	44.22/43.98	3.71/3.62	296s, 328s
PPh_2Me	98	white	150–5 d.	37.81/37.97	3.77/3.84	299s, 323s
$PPhMe_2$	87	white	133–38 d.	29.61/29.3	3.84/3.82	291s, 329s
$P(n\text{-}Bu)_3$	43^a	white	87–90 d.	35.3/35.12	6.52/6.69	287s, 326s
$P(OC_6H_5)_3$	90	white	84–87	40.79/40.53	3.42/3.31	300s, 338s

[a] $[Pt(\eta^3\text{-}C_3H_5)Cl(PBu_3)]$ intermediate not isolated; therefore yield is based on $[(CH_2CHCH_2)PtCl]_4$. Other yields calculated for reaction (5). [b] Spectra observed as Nujol mulls on CsI plates.

TABLE II. 200 MHz ^{1}H-nmr Results for *cis*-[$PtCl_2(PR_3)(\eta^2$-$C_3H_6)$].

PR_3	Chemical Shifts (δ *vs.* TMS)[a]				J(Pt-H)/Hz			J(H–H)/Hz		
	a	b	c[b]	CH_3	a	b	CH_3	a–c	b–c	c–CH_3
PPh_3	4.38	3.58	4.4	1.93	63[b]	66[b]	44	c	c	c
PPh_2Me	4.35	3.40	4.4	1.93	60[b]	66[b]	46	c	c	c
$PPhMe_2$	4.32	3.71	4.5	1.86	62[b]	66[b]	48	c	c	c
P(n-Bu)$_3$	4.44	3.96	4.8	1.98	65	75	46	13.7	7.1	6.0
$P(OPh)_3$	4.57	4.44	5.4	1.70	60	71	48	14.1	7.7	6.2

[a]Protons labeled  ; spectra observed in $CDCl_3$. ;

[b]Values estimated from broad signals.

[c]Not observed.

Preparation of cis-[$PtCl_2(CH_2$=$CHCH_2OH)(PPhMe_2)$] from cis-[$PtCl_2(CH_2$=$CHCH_3)(PPhMe_2)$]

In a typical reaction, *cis*-[$PtCl_2(CH_2$=$CHCH_3$)-($PPhMe_2$)] (0.45 g, 1.0 mmol) was refluxed with allyl alcohol (2 ml, 29 mmol) in methylene chloride (2 ml) for 20 minutes. The reaction mixture was then cooled to room temperature and the solvent was removed *in vacuo*. Ethyl ether (3 ml) was then added, and the mixture was cooled to –78° to crystallize *cis*-[$PtCl_2(CH_2$=$CHCH_2OH)(PPhMe_2)$] which was isolated by filtration, washed with ether and dried *in vacuo* (0.41 g, 88%). *Anal.* calcd. for $C_{11}H_{17}Cl_2OPPt$: C = 28.58; H = 3.71%. Found: C = 28.73; H = 3.82%.

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References

1 B. E. Mann, B. L. Shaw and G. Shaw, *J. Chem. Soc. A:*, 3536 (1971).
2 H. C. Volger and K. Vrieze, *J. Organomet. Chem., 13,* 495 (1968).
3 R. Huttel, J. Kratzer and M. Bechter, *Chem. Ber., 94,* 766 (1961).
4 A. D. Ketley and J. Braatz, *Chem. Commun.,* 169 (1968).
5 J. Chatt, N. P. Johnson and B. L. Shaw, *J. Chem. Soc.,* 1662 (1964).
6 A. Panunzi, A. DeRenzi, R. Palumbo and G. Paiaro, *J. Am. Chem. Soc., 91,* 3879 (1969).
7 R. N. Keller, *Inorg. Syn., 2,* 253 (1946).
8 A. J. Cohen, *Inorg. Syn., 6,* 209 (1960).
9 L. Malatesta and C. Cariello, *J. Chem. Soc.,* 2323 (1958).
10 R. J. Goodfellow and L. M. Venanzi, *J. Chem. Soc.,* 7533 (1965).
11 A. C. Smithies, P. Schmidt and M. Orchin, *Inorg. Syn., 12,* 240 (1970).
12 J. R. Briggs, C. Crocker, W. S. McDonald and B. L. Shaw, *J. Chem. Soc., Dalton Trans.,* 64 (1980).
13 J. W. Fitch, E. M. Haschke and M. H. Quick, *Syn. React. Inorg. Metal-Org. Chem., 5,* 7 (1975).
14 C. A. Tolman, *J. Am. Chem. Soc., 92,* 2956 (1970).
15 J. Ashley-Smith, Z. Douek, B. F. G. Johnson and J. Lewis, *J. Chem. Soc., Dalton Trans.,* 128 (1974).