ALKYL DERIVATIVES OF PLATINUM AND RHODIUM AS INTERMEDIATES IN HOMOGENEOUS REACTIONS OF OLEFIN HYDROGENATION AND ISOMERISATION *

V.S. PETROSYAN, A.B. PERMIN, V.I. BOGDASHKINA and D.P. KRUT'KO

Chemistry Department, M.V. Lomonosov Moscow State University, Moscow 119899 (U.S.S.R.)

(Received January 31st, 1985)

Summary

Literature data and results obtained on the mechanisms of olefin hydrogenation and isomerisation using platinum and rhodium complexes, in particular, with Pt–Sn and Rh–Sn bonds were analysed. The role of alkyl derivatives of platinum and rhodium in these reactions is discussed.

Intensive studies of transition metal alkyl derivatives began from the end of the fifties, when Chatt and Shaw [1,2] observed the stabilizing influence of ligands with strong σ-donating and/or π-accepting properties on the transition metal–carbon σ-bond with alkyl derivatives of platinum(II). The mono- and di-alkyl derivatives of platinum were obtained by the reaction of organolithium and organomagnesium compounds with [PtHal$_2$(PR$_3$)$_2$] complexes. σ-Aryl complexes of rhodium were obtained [3] in an analogous manner.

The interest in alkyl derivatives of platinum and rhodium increased highly after it was realized that these compounds might be intermediates in various homogeneous catalytic reactions.

It is now generally accepted [4,5] that catalytic cycles of olefin hydrogenation, hydroformylation and isomerisation of platinum and rhodium complexes include the formation of alkyl and hydridoalkyl intermediates formed via insertion of alkene into metal–hydrogen bonds. Thus this reaction, as well as the structures and properties of the alkyl derivatives formed, were widely researched.
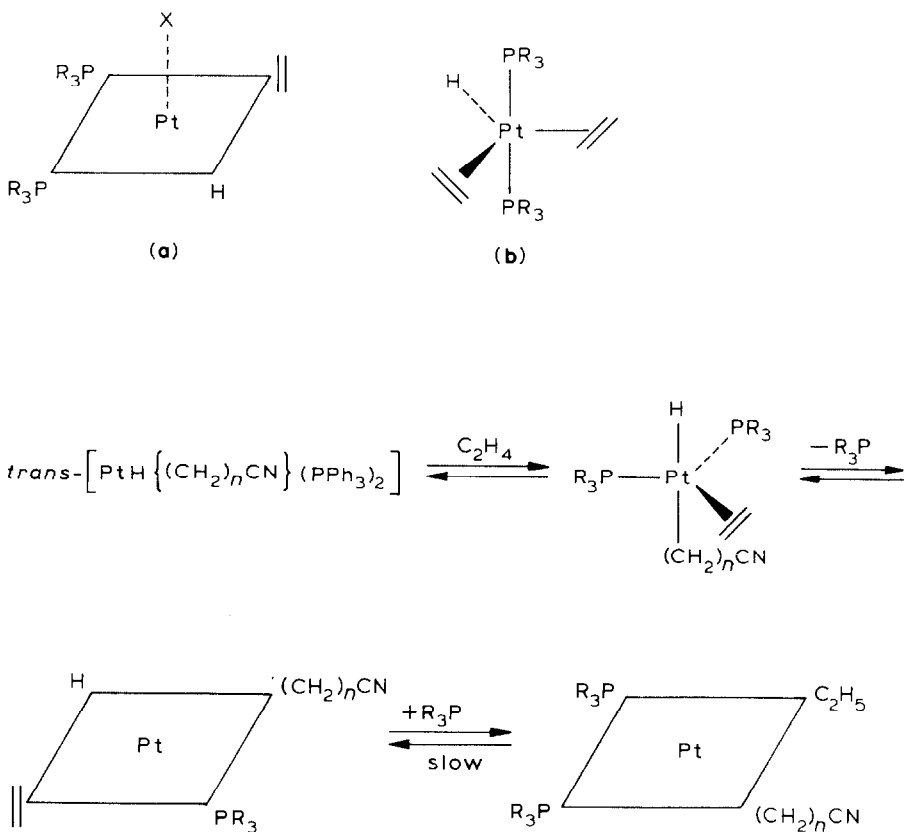
The ethylene insertion reaction into the Pt–H bond in *trans*-[PtHCl(PEt$_3$)$_2$] was described for the first time more than twenty years ago [6]. It takes place under forced conditions (95°C, 40 atm of C$_2$H$_4$), resulting in [Pt(Et)Cl(PEt$_3$)$_2$] in 25% yield. The insertion of propylene into *trans*-[PtHCl(PEt$_3$)$_2$] occurs at 220 atm but octene-1 does not react with this complex [7]. Insertion reactions of alkenes and

---

* Dedicated to Prof. O.A. Reutov on the occasion of his 65th birthday on September 5th, 1985.

perfluoroalkenes into various monohydride complexes of rhodium have also been described for $[HRh(CN)_5]^{3-}$ [8,9], $[HRh(NH_3)_5]^{2+}$ [10], $[HRhCl_2(PPh_3)_2]$ [11], and $[HRhCl_2(AsMePh_2)_3]$ [12]; these reactions proceed under mild conditions. Alkyl complexes of rhodium are readily formed by protonation of alkene complexes, for example, $[(\eta^5-C_5H_5)RhL_2]$, where L = alkene [13].

Platinum hydrides with tin trihalide ligands are much more active in olefin insertion reactions compared to the corresponding halogeno complexes [14]. Clark, Halpern and coworkers [15] studied the reaction of ethylene with $trans$-$[PtHCl(PEt_3)_2]$ in the presence of $SnCl_2$, occurring at 20°C and 1 atm. They proposed that the insertion of ethylene into the Pt–H bond is the rate-determining step for the reaction. The cationic complexes of platinum, e.g. $trans$-$[PtH(PR_3)_2L]^+$, where L is a weakly bonded ligand, e.g. acetone or methanol [16] and $trans$-$[PtH(NO_3)(PR_3)_2]$ [17,18] are very active in the insertion reaction. For $trans$-$[PtHCl(PR_3)_2]$ the insertion of ethylene, propene and butene-1 proceeds readily in the presence of catalytic amounts of $AgPF_6$ [19]. Here the reaction also proceeds via the cationic complexes, which exist in solution in an equilibrium with the starting hydride. Depending on the temperature the reaction proceeds either with formation of an hydridoolefinic intermediate, $trans$-$[PtH(C_2H_4)(PR_3)_2]$ (at $-50°C$) or $trans$-$[PtEt(C_2H_4)(PR_3)_2]$ (at $+20°C$). It was proposed [15] that the ethylene insertion reaction proceeds via pentacoordinated transition states "**a**" or "**b**".
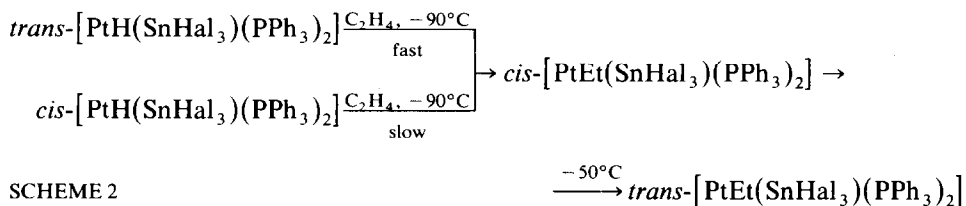

(a)   (b)

SCHEME 1

A number of papers [15,18,20] describe the kinetics for the olefin insertion reactions into cationic platinum complexes. The insertion of ethylene into (hydrido)-ω-cyanoalkyl complexes $[PtH\{((CH_2)_nCN\}(PPh_3)_2]$ ($n = 2$, 3) occurs with relative ease. It was concluded [21], that the mechanism shown in Scheme 1 takes place.

The insertion reaction of alkene into a metal–hydrogen bond was also considered theoretically [22,23]. It was shown that a cis-arrangement of alkene and hydrido ligands and coplanarity of metal–hydrogen and carbon–carbon bonds are necessary. Thorn and Hoffmann [22] performed calculations for ethylene insertion into trans-$[PtHCl(PH_3)_2]$ and concluded that insertion in the pentacoordinated intermediate proceeds with a higher energy barrier than in the cis-hydridoalkene complex, although preliminary isomerisation of the initially formed trans-isomer is necessary in the latter case. They pointed out also that the role of a $SnHal_3$ ligand substantially accelerating the insertion of alkene is not clear.

We have studied the mechanistic details for alkene insertion reaction into a Pt–H bond in a series of phosphine complexes: trans-$[PtH(SnHal_3)(PR_3)_2]$, where Hal = Cl, Br; PR_3 = PPh_3, $PMePh_2$, $PBuPh_2$, PBu_3, PEt_3, by means of ^{119}Sn, ^{31}P, ^{13}C and ^1H NMR spectroscopy. It was first shown [24], that insertion of ethylene into trans- and cis-$[PtH(SnHal_3)(PPh_3)_2]$ occurs at $-90°C$ according to Scheme 2.

$$trans\text{-}\left[PtH(SnHal_3)(PPh_3)_2\right] \xrightarrow[\text{fast}]{C_2H_4, \ -90°C}$$

$$cis\text{-}\left[PtH(SnHal_3)(PPh_3)_2\right] \xrightarrow[\text{slow}]{C_2H_4, \ -90°C} \Bigg\} \rightarrow cis\text{-}\left[PtEt(SnHal_3)(PPh_3)_2\right] \rightarrow$$

SCHEME 2 $\xrightarrow{-50°C} trans\text{-}\left[PtEt(SnHal_3)(PPh_3)_2\right]$

Insertion of the alkenes, ethylene, propene, butene-1, isobutene, hexene-1 into trans-$[PtH(SnHal_3)(PR_3)_2]$, where PR_3 were various phosphines, formed at $-90°C$ also cis-$[PtR(SnHal_3)(PR_3)_2]$, compounds, which are at equilibrium with the initial reagents. The rate of the reaction and the stability of the cis-complexes formed depend on the nature of phosphine, halogen and alkene as follows:

PR_3: $PMePh_2 \approx PBuPh_2 \gg PPh_3 > PBu_3 > PEt_3$; Hal: Br > Cl; Alkene: ethylene $\gg$ propene > butene-1 $\approx$ hexene-1 $\gg$ isobutene. Either formation of more stable trans-alkyl complex or decomposition to the initial reagents takes place at $-50°C$, depending on the alkene insertion rate and/or the equilibrium position.

The formation of alkylrhodium derivatives has been observed in our laboratory as a result of ethylene and hexene-1 insertion into the Rh–H bond in monohydride complexes of rhodium, which we obtained as follows:

$$\left[Rh(PPh_3)_3X\right] + HCl \rightarrow \left[RhH(PPh_3)_3XCl\right] + \left[Rh_2H_2(PPh_3)_4Cl_4\right]$$

$$(X = Cl, SnCl_3)$$
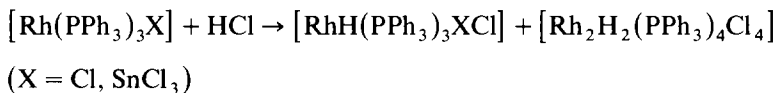
As a result of the insertion reaction we obtained $[RhRCl_2(PPh_3)_2]$, which seems to have a trigonal bipyramidal structure. The reaction proceeds readily both for X = Cl and X = $SnCl_3$, however, unlike the platinum complexes, alkyl derivatives of rhodium with $SnCl_3$ ligands are unstable.

Thus, the literature data and the results we obtained show that alkyl derivatives of platinum and rhodium are readily formed from metal hydrides under conditions

used for carrying out homogeneous catalytical reactions of hydrogenation and isomerisation of alkenes. In some cases (when higher and substituted alkenes are inserted) these complexes have low thermodynamic stability and exist only in solution at low temperatures and in minor quantities.

To elucidate the mechanisms of olefin hydrogenation and isomerisation reactions that proceed via alkylmetal intermediates it is very important to know that primary or secondary alkyls are formed by the interaction of metal hydride with alkene-1. As the insertion of alkene proceeds via a concerted four-centered mechanism [22,23] without intermediate formation of carbonium ions the addition of the metal hydride is possible both according to and against the Markovnikov rule. Apparently, the direction of the addition depends on the relative polarisation of the metal–hydrogen bond as well as on the sterical hindrances in the transition state [25,26]. There is little information on secondary alkyl complexes of platinum and rhodium, however, the activity of metal hydrides in alkene isomerisation reactions supports their formation, although in minor quantities.

Secondary alkyl complexes of platinum, obtained by the following reaction [27]:

$$trans\text{-}\left[PtRCl(PPh_3)_2\right] + R'M \rightarrow cis\text{-}\left[PtRR'(PPh_3)_2\right]$$

$$(M = Li, MgBr; R' = i\text{-}C_3H_7, s\text{-}C_4H_9)$$

are unstable and isomerise readily into normal alkyl complexes either at room temperature (i-C_3H_7) or lower (s-C_4H_9). As this isomerisation proceeds under conditions where an equilibrium between the platinum hydride and alkyl complexes seems not to be achieved, the mechanism of this process is apparently concerted. Migration of hydrogen in an ethyl complex of palladium resulting in averaging of CH_3 and CH_2 signals in the ^1H NMR spectrum at room temperature proceeds also via a concerted mechanism [28]. Propyl and butyl derivatives of platinum, formed as a result of a reaction between the cationic hydride $trans$-[PtH(PR$_3$)$_2$(acetone)]$^+$ and propene or butene-1, have normal structures according to their ^1H NMR spectra [16,19]. Alkyl complexes obtained by protonation of alkene compounds of rhodium [13] have predominantly normal structures. A study of pentene-1 isomerisation using a deuterated catalyst [RhD(CO)(PPh$_3$)$_3$] shows that deuterium exchange with pentene proceeds much faster than isomerisation indicating predominant formation of primary alkyl complexes [29]. However, complexes with secondary alkyl groups were described in several papers. Reaction of [RhH(AsMePh$_2$)$_3$Cl$_2$] with acrylonitrile leads to formation of [Rh{CH(CN)CH$_3$}Cl$_2$(AsMePh$_2$)$_3$] [12]. Insertion of
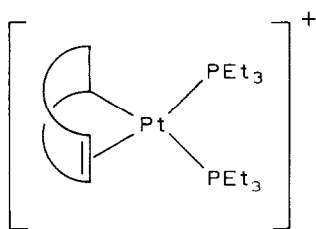
(c)

cyclooctadiene-1,5 or norbornadiene double bonds into the Pt–H bond in *trans*-[PtH(NO)$_3$(PEt$_3$)$_2$] leads to the cationic complex c, stabilized apparently due to a chelate effect of the organic ligand coordinated to the platinum atom by its double bond [30].

Thus, kinetic and thermodynamic factors favor the formation of primary alkyl complexes as a result of insertion of terminal olefins into metal–hydrogen bonds in platinum and rhodium hydrides. The formation of secondary alkyl complexes takes place in substantial lower quantities, however, the ease of metal hydride β-elimination from position 3 of an alkyl group adds to the situation that alkene isomerisation usually competes with hydrogenation and dominates in some cases.

Another problem in the chemistry of alkyl-platinum and -rhodium complexes, which is important in understanding the hydrogenation and isomerisation mechanisms of alkenes, is the pathway of their conversion into the final products: alkanes and alkenes. The alkene β-elimination under catalytical conditions forms an equilibrium mixture of terminal and internal alkenes. This reaction is the opposite of alkene insertion into metal–hydrogen bonds and proceeds according to the principle of microscopic reversibility via the same mechanism. There are several papers devoted to the mechanism of this reaction. Thermal decomposition of *cis*-dialkyl platinum derivatives has been studied and it was concluded that the first step of this decomposition is β-elimination of alkene as follows [27]:

$$cis\text{-}\left[\mathrm{PtRR'(PPh_3)_2}\right] \xrightarrow{\Delta} \mathrm{RH} + \mathrm{R'(-H)} + \mathrm{Pt^0}$$
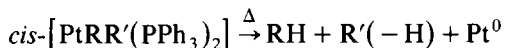
The data obtained showed that the ease of β-elimination depends on the number of β-hydrogen atoms. The concentration of tertiary phosphine influences the thermal decomposition rate of *cis*-[PtR$_2$(PR$_3'$)$_2$] (R = C$_2$H$_5$, n-C$_3$H$_7$; R' = C$_2$H$_5$, C$_6$H$_5$) and shows that the rate-determining step of the reaction is dissociation of phosphine from the complex [31]. In the study of alkenes β-elimination [32] from *cis*-[PtRX(PEt$_3$)$_2$] (R = n-C$_3$H$_7$, n-C$_4$H$_9$) it was shown especially that decomposition of n-butyl derivative gives 49% *cis*- and 2% *trans*-butene-2 as well as 49% butene-1. The formation of butenes-2 is explained by the authors [32] as being due to intramolecular migration of the double bond in the hydridoolefinic intermediate. The activation parameter values ($\Delta H^{\neq} \approx 22$ kcal. mol^{-1}, $\Delta S^{\neq} \approx 0$ e.u.) pointed to the dissociative character of the process.

It is generally accepted [4,5,25] that hydrogenolysis of the alkyl complex formed in monohydride metal/alkene/hydrogen catalytic systems takes place with regeneration of the monohydride. This hydrogenation catalytical cycle step is insufficiently studied. Among related reactions the hydrogenolysis of Pt–Si bonds in trimethylsilyl derivatives of platinum under formation of hydride complexes has been studied by Glockling and co-workers [33,34]. The reaction of dialkyl compounds, *cis*-[PtR$_2$(PR$_3'$)$_2$], with hydrogen was the subject of a very recent study [35]. It has been shown that the reaction proceeds readily with formation of alkane at a hydrogen pressure about 2–4 atm and +25°C and when platinum has bulky substituents (for example R = neopentyl, L = PEt$_3$, PPh$_3$ or R = CH$_3$, L = P-i-Pr$_3$). Compounds with less bulky substituents react less readily or are completely unaffected by hydrogen at all under the conditions studied. On the basis of kinetical data it has been concluded [35] that dissociation of phosphine with formation of an active monophosphine intermediate [PtR$_2$(PR$_3'$)] is the rate-determining step. The hydrogenolysis of the

Pt–C bond proceeds with formation of a platinum(IV) dihydride with subsequent reductive elimination of alkane.

There is an alternative way for conversion of alkyl derivatives of platinum metals to alkanes which is the protodemetallation reaction with participation of a protic solvent or a hydrogen halide formed when dihalide complexes of platinum interact with molecular hydrogen. The process of the protodemetallation reaction was proved by Shilov and coworkers [36,37] in studies of ethylene hydrogenation in methanol with $H_2PtCl_6/SnCl_2$ (1/5) as the catalyst. Hydrogenation of ethylene with deuterium in CH_3OH or hydrogen in CH_3OD gives monodeuterated ethane; this implies that one hydrogen atom in ethane originates from the solvent molecule and another from molecular hydrogen. Such a mechanism apparently does not take place in the case of hydrogenation in the presence of phosphineplatinum complexes, $[PtCl_2(PR_3)_2]$, activated by $SnCl_2$ in aprotic solvents. This is because the quantity of hydrogen chloride formed by reduction of the platinum dichloride complex is small and as we know from the literature [38], and our data, the protodemetallation reaction proceeds slowly and hardly can compete with hydrogenolysis of alkyl derivatives of platinum metals under real catalytical conditions.

In summary, it should be emphasized that participation of platinum and rhodium alkyl complexes in homogeneous reactions of olefin hydrogenation and isomerisation is well established. These complexes are formed by insertion of olefin into metal–hydrogen bonds and this reaction proceeds quickly in many cases and almost quantitatively. The insertion reaction is studied in some detail kinetically and theoretically, although some details require refinements. As a result of the insertion reaction of terminal olefins the primary alkyl complexes form preferentially, but the secondary alkyl derivatives are formed in substantially lower quantities. Alkyl complexes of platinum and rhodium undergo hydrogenolysis or protodemetallation with formation of alkane, or β-elimination takes place giving a mixture of isomeric alkenes. These important reactions are still insufficiently studied.

References

1 Chatt J. and Shaw B.L. J. Chem. Soc., (1959) 705.
2 Chatt J. and Shaw B.L. J. Chem. Soc., (1959) 4020.
3 Chatt J. and Underhill A.E. J. Chem. Soc., (1963) 2088.
4 James B.R. Homogeneous Hydrogenation, Wiley-Interscience, N.Y., 1973.
5 James B.R. Adv. Organometal. Chem., 17 (1979) 319.
6 Chatt J. and Shaw B.L. J. Chem. Soc., (1962) 5075.
7 Chatt J., Coffey R.S., Gough A. and Thompson D.T. J. Chem. Soc., A, (1968) 190.
8 Lawson D.N., Mays M.J. and Wilkinson G. J. Chem. Soc., A, (1966) 52.
9 Jewsbury R.A. and Maher J.P. J. Chem. Soc., A, (1971) 2847.
10 Thomas K., Osborn J.A., Powell A.R. and Wilkinson G. J. Chem. Soc., A, (1968) 1801.
11 Baird M.C., Mague J.T., Osborn J.A. and Wilkinson G. J. Chem. Soc., A, (1967) 1347.
12 Dewhirst K.C. Inorg. Chem., 5 (1966) 319.
13 Seiwell L.P. Inorg. Chem., 15 (1976) 2560.
14 Cramer R. and Lindsey R.V., Jr. J. Amer. Chem. Soc., 88 (1966) 3534.
15 Clark H.C., Jablonski C.R., Halpern J., Mantovani A. and Weil T.A. Inorg. Chem., 13 (1974) 1541.
16 Clark H.C. and Kurosawa H. J. Chem. Soc., Chem. Communs., (1971) 957.
17 Clark H.C., Jablonski C.R. and Wong C.S. Inorg. Chem., 14 (1975) 1332.
18 Clark H.C. and Wong C.S. J. Amer. Chem. Soc., 96 (1974) 7213.
19 Clark H.C. and Kurosawa H. Inorg. Chem., 11 (1972) 1275.
20 Clark H.C. and Jablonski C.R. Inorg. Chem., 13 (1974) 2213.

21 Ros R., Michelin R.A., Bataillard R. and Roulet R. J. Organomet. Chem., 165 (1979) 107.
22 Thorn D.L. and Hoffmann R. J. Amer. Chem. Soc., 100 (1978) 2079.
23 Dedieu A. Inorg. Chem., 20 (1981) 2803.
24 Bogdashkina V.I., Permin A.B., Petrosyan V.S. and Reutov O.A. Dokl. Akad. Nauk SSSR, 266 (1982) 631.
25 Masters C. Homogeneous Transition-Metal Catalysis, London, N.Y., Chapman and Hall, 1981.
26 Clark H.C., Fiess P.L. and Wong C.S. Canad. J. Chem., 55 (1977) 177.
27 Komiya S., Yamamoto A. and Yamamoto T. Chem. Lett., (1978) 1273.
28 Chinakov V.D., Zudin Y.N., Nekipelov V.M. and Likholobov V.A. IIIrd All-Union Conference on Spectroscopy of Coordination Compounds, Krasnodar, Abstracts of papers, 1984, p. 95.
29 Evans D., Osborn J.A. and Wilkinson G. J. Chem. Soc., A, (1968) 3133.
30 Deeming A.J., Johnson B.F.G. and Lewis J. J. Chem. Soc., Chem. Commun., (1970) 598.
31 McCarthy T.J., Nuzzo R.G. and Whitesides G.M. J. Amer. Chem. Soc., 103 (1981) 3396.
32 Alibrandi G., Minniti D., Romeo R. and Vitarelli P. Inorg. Chim. Acta, 81 (1984) L23.
33 Glockling F. and Hooton K.A. J. Chem. Soc., A, (1968) 827.
34 Clemmit A.F. and Glockling F. J. Chem. Soc., A, (1969) 2163.
35 Reamey R.H. and Whitesides G.M. J. Amer. Chem. Soc., 106 (1984) 81.
36 Khrusch A.P., Tokina L.A. and Shilov A.E. Kinet i Katal, 7 (1966) 901.
37 Khrusch A.P., Shvetsova N.F. and Shilov A.E. Kinet i Katal, 10 (1969) 1226.
38 Belluco U., Michelin R.A., Uguagliati P. and Crociani B. J. Organomet. Chem., 250 (1983) 565.