Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

METAL OLEFIN COMPLEXES

II. PALLADIUM(II) AND PLATINUM(II) COMPLEXES OF 1,2-DIVINYLCYCLOHEXANE BY THE METAL CATALYZED ISOMERIZATION OF 1,5-CYCLODECADIENE

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(Received November 5th, 1965; in revised form January 20th, 1966)

INTRODUCTION

Cyclic olefin complexes of palladium and platinum have been reported[1-5]. Preparation of the corresponding complexes of 1,5-cyclodecadiene and 1,6-cyclodecadiene could be predicted. The preparation of copper(I) and silver(I) metal olefin complexes of 1,5- and 1,6-cyclodecadiene were recently reported from these laboratories[6].

In the course of extending this work to the 1,5-cyclodecadiene complexes of palladium and platinum, we were able to synthesize the metal–olefin complexes of 1,2-divinylcyclohexane. These were obtained in alcoholic solvents at ambient temperature apparently by a metal-catalyzed isomerization of 1,5-cyclodecadiene to 1,2-divinylcyclohexane. The preparation of 1,2-divinylcyclohexane by the thermally initiated Cope rearrangement of 1,5-cyclodecadiene has been reported by Grob and co-workers[7,8], and by Heimbach[9].

The proposed mechanism by which an isomerization might occur is of interest in light of the recently reported catalytic formation of cyclododecatriene, cyclooctadiene and cyclodecadiene via π-allyl organometallic intermediates[10-12].

RESULTS AND DISCUSSION

The reaction of bisbenzonitrilepalladium dichloride in benzene with *cis,trans*-1,5-cyclodecadiene resulted in the formation of *cis*-1,2-divinylcyclohexane(DVCH)-palladium dichloride. This method of preparation, first used by Kharasch[14] for the preparation of several palladium metal–olefin complexes, has been recently applied by Chatt and co-workers[2] in the preparation of the very stable olefin–palladium complex 1,5-cyclooctadiene palladium dichloride. Chatt[1,15] has also prepared the 1,5-cyclooctadiene platinum dichloride complex by the addition of the diene to sodium chloroplatinite in n-propanol. By analogy an attempt to prepare a platinum

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complex of *cis,trans*-1,5-cyclodecadiene by this reaction yielded large pale yellow crystals of *cis*-DVCH-platinum dichloride after 6–7 days at room temperature. The complexes were recrystallized from hot chloroform.

No complex of *cis,cis*-1,6-cyclodecadiene could be prepared with the platinum salts under the same conditions. With bisbenzonitrilepalladium chloride in benzene a 1:1 palladium dichloride, 1,6-cyclodecadiene compound was prepared.

The identical DVCH complexes were obtained when DVCH, prepared by the thermally initiated rearrangement of 1,5-cyclodecadiene, was added to the palladium and platinum reagents. This reaction was much more rapid than that with the 1,5-cyclic diene.

Displacement of the olefin from the palladium(II) and platinum(II) complexes prepared from 1,5-cyclodecadiene yielded *cis*-DVCH. Displacement of the olefin from the palladium(II) 1,6-cyclodecadiene complex yielded *cis,cis*-1,6-cyclodecadiene. The displacement reaction was run at 0° to prevent the possibility of thermal isomerization of the 1,5-cyclic diene to the divinyl compound. VPC analysis of the displaced olefin indicated that no 1,5-cyclic diene was present and that the products were essentially pure DVCH (99%) and 1,6-cyclodecadiene (96%). The IR and NMR spectra were also identical to those of DVCH and 1,6-cyclodecadiene.

The IR spectra of the DVCH compounds (Table 1) are rather complex and no detailed analysis has yet been attempted. Some noteworthy observations however, can be made from the bands observed in the 1510–1500 cm^{-1} region. These bands have been assigned to the carbon–carbon stretching frequencies, modified by the coordina-

TABLE 1

INFRARED ABSORPTION SPECTRA OF PALLADIUM (II) AND PLATINUM (II) COMPLEXES OF 1,2-DIVINYLCYCLOHEXANE (DVCH)

DVCH	*DVCH-PdCl*$_2$	*DVCH-PtCl*$_2$
3077 (s)cm^{-1}	3096 (s)cm^{-1}	3096 (s)cm^{-1}
3000–2817 (vs)	3086 (s)	3021 (s)
1825 (m)	3021 (s)	2924 (vs)
1645 (vs)	2995 (s)	2857 (vs)
1450 (vs)	2924 (vs)	1500 (m)
1420 (vs)	2857 (vs)	1460 (m)
1355 (m)	1505 (m)	1443 (s)
1337 (m)	1460 (m)	1414 (m)
1299 (m)	1440 (m)	1332 (m)
1285 (m)	1415 (m)	1312 (m)
1139 (m)	1330 (m)	1297 (m)
1095 (m)	1309 (m)	1033 (s)
1040 (m)	1295 (m)	1018 (s)
998 br. (vs)	1266 (m)	1008 (s)
980 (s)	1015 (s)	991 (m)
910 br. (vs)	1007 (s)	979 (s)
875 (s)	993 (m)	870 (m)
845 (m)	980 (s)	849 (w)
809 (m)	866 (w)	823 (w)
789 (m)	844 (w)	808 (w)
779 (m)	809 (w)	798 (m)
761 (s)	796 (w)	758 (w)
704 br. (s)	760 (w)	643 (s)

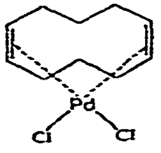
tion of the olefin to the metal ion. The carbon double bond stretching frequency has been lowered by approximately 140–150 cm^{-1} from the band at 1645 cm^{-1} due to the terminal vinyl group absorption in DVCH. This is in agreement with observations made of several other metal–olefin complexes of platinum(II) and palladium(II)[15,16]. The relatively strong carbon–hydrogen frequency of the alkene group is also apparent in the 3100–3050 cm^{-1} region. The terminal vinyl group δ(CH out of plane) vibration at 910 cm^{-1} is absent in the complexed olefin. This may be due to obstruction in the vibration of the nonterminal hydrogen of the vinyl group as a result of interaction with the metal ion coordinated to the double bond.

TABLE 2

INFRARED ABSORPTION SPECTRA OF PALLADIUM(II) 1,6-CYCLODECADIENE ($C_{10}H_{16}$)

$C_{10}H_{16}$	$C_{10}H_{16}PdCl_2$
3077 (m)	3003 (m)
3030–2833 (s)	2959 (s)
2793 (m)	2915 (s)
2660 (m)	2857 (s)
1675 (m)	1497 (s)
1655 (m)	1445 (s)
1471–1418 br. (s)	1422 (m)
1397 (m)	1351 (s)
1374 (m)	1255 (s)
1342 (m)	1241 (m)
1319 (m)	1163 (m)
1259 (s)	1020 (m)
1161 (s)	970 (s)
1026 (s)	887 (m)
1002 (s)	806 (m)
975 (m)	759 (m)
963 (m)	709 (m)
846 (s)	625 (m)
777 (s)	
714–694 br. (vs)	

The IR spectrum of the palladium 1,6-cyclic diene compound (Table 2) shows a strong band at 1497 cm^{-1} that is assigned to the coordinated olefin. The alkene band in the 3100–3050 cm^{-1} region is also present. From 1400–700 cm^{-1} the spectrum is somewhat similar to the uncomplexed olefin. Both the characteristic double bond absorptions for the olefin at 1675 and 1655 cm^{-1} have been shifted to a lower frequency indicating that the palladium is coordinating with both double bonds. Whether the metal is centrally located above the cyclic diene (I) or bridging between successive diene molecules in a polymeric structure (II) has not been determined. The insolubility



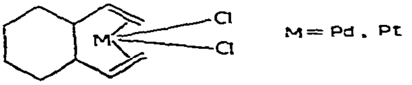
(I)

– (diene)–$PdCl_2$–(diene) – $PdCl_2$

(II)

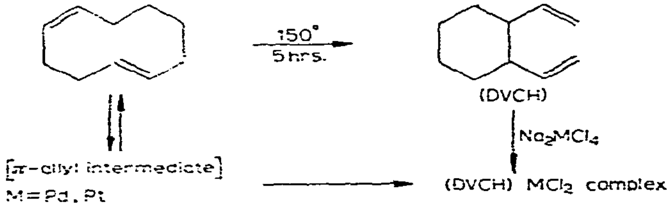
of the compound made molecular weight determinations impossible. This insolubility also suggests the possibility that the polymeric structure may be more likely.

Molecular weight determination in chloroform indicated that the DVCH complexes are both monomeric in solution. The structure of the complex (III) is probably such that the ligand contains the metal ion in a square planar configuration. This arrangement allows coordination of the π-electrons from the double bond to the metal atom and bond reinforcement due to "back-coordination" by non-bonding electrons of the metal ion *dp*-hybrid orbitals to the antibonding orbitals of the olefin. Such a structure would be similar to the bidentate 1,5-cyclooctadiene Pt(II) and Pd(II) complexes[15].



(III)

The mechanism by which the metal catalyzed isomerization of 1,5-cyclodecadiene to *cis*-DVCH has occurred is still under investigation. A possible mechanistic scheme however can be proposed on the basis of these and other preliminary results. The proposed mechanism is outlined in eqn. (1).



(1)

This mechanism assumes that a π-allyl type of intermediate may form which can readily be converted to both positional and geometric isomers of cyclodecadiene.

The *trans,trans* isomer of 1,5-cyclodecadiene was shown to be unstable and capable of easily rearranging at 70° to *trans*-DVCH by a Cope rearrangement. Grob[7,8] postulated that the transannular rearrangement is attributed to the relief of strain and to the proximity of carbon atoms 1 and 6 in the *trans,trans*-1,5-isomer.

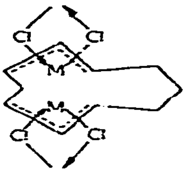
Heimbach[9] has investigated the valence isomerization of *cis-trans*-1,5-cyclodecadiene. He reported that thermal isomerization at 150° yielded stereospecific (> 99.7 %) *cis*-1,2-divinylcyclohexane. The mechanism that is proposed again involves transannular interaction between the carbon atoms in the 1 and 6 positions of the *cis,trans*-1,5-isomer.

Symmetrical isomers such as *cis,cis*-1,6 and -1,4 do *not* possess strong interaction between carbon atoms 1 and 6. They therefore would be more stable towards rearrangement to DVCH at moderate temperatures. This was shown in part by the stability of the 1,6 isomer in the presence of the alcoholic solutions of the metal salts at ambient temperature.

Furthermore, the isomerization of *cis,trans*-1,5-cyclodecadiene to *cis,cis*-1,6-cyclodecadiene and its metal olefin complex has been accomplished with transition metal catalysts without the formation of DVCH[17]. Details of this reaction will be published shortly. The absence of DVCH is again in agreement with the predicted stability of the 1,6-isomer towards rearrangement to DVCH. The 1,4-isomer has also been prepared in small quantities from 1,5-cyclodecadiene[18].

The postulation that the catalytically activated Cope reaarrangement occurs through a π-allyl type intermediate is still open to question since the allylic intermediate itself has not been isolated. However, the preparation of such complexes as palladium π-cyclohexenyl[19] and the di(π-allyl) complexes and intermediates prepared by Wilke and co-workers[13] lends support to the postulated π-allyl intermediate.

Several types of π-allyl intermediates are possible. The intermediate could be a metal halide π-allyl complex (IV) containing two separate complexing groups, one at each double bond.

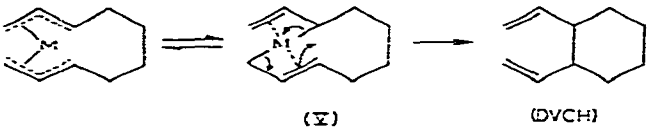


(IV)

This is very unlikely, however, since if such a complex were formed it should also be formed with 1,6-cyclodecadiene. Then this, too, would rearrange to the DVCH complex and thus contradict the experimental evidence.

Finally, such a π-allyl complex could be expected to result in chloride addition to the olefin. No chloro-addition products have been obtained from any of these reactions.

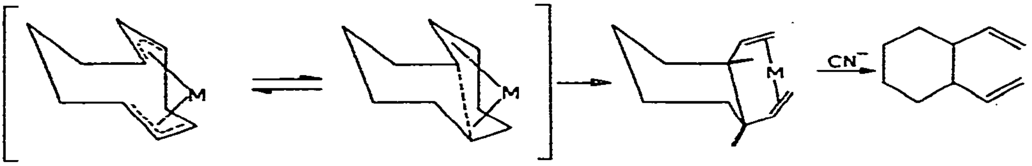
Another possibility would be an open ring complex (V) similar to the intermediate proposed by Wilke[10] in the preparation of 1,5-cyclodecadiene from butadiene and ethylene by a nickel catalyzed cyclooligomerization.



Such an intermediate could readily go to DVCH by an intramolecular rearrangement. Wilke[13] has proposed such a mechanism for the rearrangement of di(π-allyl)nickel to biallyl with the metal alternating between the bi- and zero-valent states. Schrauzer[20] has recently commented that the reaction can be more easily explained with the metal in the zero-valent state. An open ring π-allyl however, does not seem to correspond to our experimental evidence. Such an intermediate would not explain the isomerization of 1,5- to 1,6-cyclodecadiene. Furthermore, this type of complex should yield large amounts of acyclic dienes and trienes which VPC analysis did not show. As was pointed out by the referee, it is conceivable that the metal-catalyzed isomerization process proceeds through a π-allylic hydrido[21] or a hydrido alkyl[22] intermediate. Nicholson and Shaw[23] have proposed the π-allylic hydrido mechanism for the isomerization of cyclooctadiene catalyzed by noble metal salts. Frye, Kuljian, and Viebrock[24] favor the π-allylic hydrido mechanism for the ligand rearrangement of 1,3- to 1,5-cyclooctadiene by palladium(II) and platinum(II) complexes.

We feel that the π-allylic hydrido mechanism can be used to explain isomerization of 1,5-cyclodecadiene to 1,4- and 1,6-cyclodecadiene but it may not explain the formation of DVCH as easily. Our work has shown that under the reaction conditions described the DVCH complexes were the only products obtained from 1,5-cyclodecadiene. The formation of the DVCH complex may be explained however on the basis of a π-allylic hydrido type mechanism if the formation of a closed ring di-π-allyl intermediate is considered.

It is therefore proposed that the reaction intermediate is a closed ring di-π-allyl type complex (VI) with the metal in either the bi- or zero-valent state. Such a proposed intermediate could then convert easily with a corresponding hydride shift to *cis*-DVCH. It could also readily yield either 1,4-, 1,5- or 1,6-cyclodecadiene isomers depending on the reaction conditions and the stability of the isomer. The intermediate complex would be similar to the cyclododecatrienenickel complex isolated by Wilke[13].



(VI)

The stereochemistry of the product and of such a Cope rearrangement mechanism has already been well defined[9,25–28].

The energy required for the "catalytic" Cope rearrangement of *cis,trans*-1,5-cyclodecadiene to *cis*-1,2-divinylcyclohexane should be small considering the ring size and location of the double bond. Another consideration which may favor such a "catalytic" Cope rearrangement is the lower entropy factor involved when the material is bunched up in the complex and not randomly spread out. In addition the driving force for the molecular rearrangement via the catalytic process could be the tendency of the cyclic diene system to achieve the greater molecular stabilization of divinylcyclohexane.

The effect of heat and the electron donor properties of the solvent on the isomerization reaction have been found to be very important in determining what the reaction product shall be.

Further investigations are underway to determine how changes in temperature, solvent, or transition metal affect these reactions.

EXPERIMENTAL

The *cis,trans*-1,5-cyclodecadiene and *cis,cis*-1,6-cyclodecadiene were obtained from the Columbian Carbon Company, Lake Charles Chemical Research Center. The olefins were purified by vacuum distillation to yield (VPC) 93% 1,5- and 96% 1,6-diene.

Elemental microanalysis were performed by Alfred Bernhardt, Microanalytisches Laboratorium, Mulheim, Germany.

The infrared absorption spectra were obtained on a Beckman IR8 Spectrophotometer equipped with a linear wave length scale and sodium chloride optics. The spectra of the complexes were observed by using potassium bromide pellets.

The molecular weights were obtained on a Mechrolab Vapor Pressure Osmometer, Model 301A. Measurements were made on solutions containing the solute dissolved in chloroform. The concentrations used in the determination ranged from 0.05 to 0.15 weight %. The solvent was calibrated within the concentration range of 0.02 to 0.40 molal by using benzil as a standard.

1,2-Divinylcyclohexanepalladium dichloride, $C_{10}H_{16}PdCl_2$

(*A*) A 1.2 g (3.1 mmole) sample of bisbenzonitrilepalladium(II) dichloride prepared by the method described by Kharasch[14] was dissolved in 50 ml of boiling benzene. The solution was filtered and to the filtrate was added 2 ml (0.01 mole) of *cis,trans*-1,5-cyclodecadiene. After standing at room temperature for 3 h, bright gold flakes separated from the solution. The solid was removed by filtering, washed in cold ethanol and dried over calcium chloride (yield 0.8 g). The product was recrystallized from hot chloroform. (Found: C, 38.24; H, 5.02; Cl, 22.08; Pd, 33.85; mol. wt., 330. $C_{10}H_{16}Cl_2Pd$ calcd.: C, 38.31; H, 5.14; Cl, 22.61; Pd, 33.93%; mol wt., 314.) The complex decomposes above 123°.

(*B*) A 1.2 g (3.1 mmole) sample of bisbenzonitrilepalladium(II) dichloride was dissolved in 50 ml of boiling benzene and the solution filtered. To the filtrate was added 2 ml (0.01 mole) of 1,2-divinylcyclohexane that had been prepared by refluxing a solution of *cis,trans*-1,5-cyclodecadiene for 5 h at 150°. Immediately upon addition a bright gold precipitate was formed. The solid was removed by filtration, washed in cold ethanol and dried over calcium chloride (yield 0.9 g). This compound is identical in infrared spectra to that prepared from 1,5-cyclodecadiene.

1,2-Divinylcyclohexaneplatinum dichloride, $C_{10}H_{16}PtCl_2$

(*A*) A 2.5 g (5.5 mmole) sample of sodium chloroplatinite tetrahydrate (or 2.9 g of sodium chloroplatinate tetrahydrate) was dissolved in 30 ml of n-propanol. To the propanol solution was added 2 ml (0.01 moles) of *cis,trans*-1,5-cyclodecadiene. The solution was kept at room temperature for two weeks. The pale yellow crystals which formed were filtered off, washed in cold ethanol and dried over calcium chloride. The solid was only sparingly soluble in organic solvents but could be recrystallized from hot chloroform, or acetone (yield 0.5 g). (Found: C, 29.75; H, 4.17; Cl, 17.63; Pt, 48.56; mol. wt., 408. $C_{10}H_{16}PtCl_2$ calcd.: C, 29.86; H, 4.01; Cl, 17.72; Pt, 48.50% mol. wt., 402.) The complex melts at 205°, decomposes at 210°.

(*B*) A 2.5 g (5.5 mmole) sample of sodium chloroplatinite tetrahydrate (or 2.9 g of sodium chloroplatinate tetrahydrate) was dissolved in 30 ml of n-propanol. To this solution was added 2 ml (0.01 moles) of 1,2-divinylcyclohexane. The solution was allowed to remain at room temperature for 24 h. The yellow crystalline solid was removed by filtering, washed in cold ethanol, and dried over calcium chloride (yield 0.7 g). The infrared spectra is identical to that of the complex prepared in Method (*A*).

cis,cis-1,6-Cyclodecadienepalladium dichloride, $C_{10}H_{16}PdCl_2$

A 1.2 g (3.1 mmole) sample of bisbenzonitrilepalladium(II) dichloride was dissolved in 50 ml of boiling benzene. The solution was filtered and to the filtrate was added 2 ml (0.01 moles) of *cis,cis*-1,6-cyclodecadiene. The orange precipitate which formed immediately was filtered and washed in cold ethanol. The solid was insoluble in chlorinated hydrocarbon solvents, ethanol, ether, acetone, DMF, nitromethane, and benzene (yield 1.0 g). Found: C, 38.49; H, 4.91; Cl, 21.83; Pd, 33.76. $C_{10}H_{16}Cl_2Pd$ calcd.: C, 38.31; H, 5.14; Cl, 22.61; Pd 33.93 %. The complex decomposes above 145°.

Displacement reaction

To a 1.0 g sample of complex in 10 ml of carbon tetrachloride was added a solution of 1.0 g potassium cyanide in 25 ml of water. This mixture was stirred at 0° for 3–4 h. The olefin contained within carbon tetrachloride phase was separated from the mixture and dried with calcium chloride. The carbon tetrachloride was then removed by a rotating evaporator at 0° leaving a condensed olefin solution. The displaced olefin was examined by NMR and IR. The spectra were compared with those of 1,2-divinylcyclohexane, 1,5-cyclodecadiene and 1,6-cyclodecadiene.

ACKNOWLEDGEMENT

This research was carried out with the encouragement of the Columbian Carbon Company to whom we are grateful for their gift of the olefins. J.C.T. wishes to acknowledge the financial support received from the Esso Research Laboratories, Humble Oil and Refining Company, Baton Rouge, Louisiana.

SUMMARY

The *cis*-1,2-divinylcyclohexane complexes of palladium(II) and platinum(II) were prepared at ambient temperature from bisbenzonitrilepalladium(II) dichloride and sodium chloroplatinite by the metal-catalyzed rearrangement of *cis,trans*-1,5-cyclodecadiene. The mechanism by which the rearrangement could have occurred is discussed and a closed ring π-allylic intermediate proposed.

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SHORT COMMUNICATIONS

A revised structure for the butatriene iron carbonyl complexes

We have reported the formation of butatriene di-iron pentacarbonyl, $C_4H_4Fe_2(CO)_5$ (I), and related complexes[1]. The mass spectrum of I now showed the correct composition of I to be $C_4H_4Fe_2(CO)_6$[*]. The parent peak (M^+) appeared at m/e 332 (calcd. for $C_4H_4Fe_2(CO)_6$, 332). The presence of six CO groups was indicated by the appearance of six similarly-shaped groups of peaks at the interval of m/e 28, *i.e.* at $M^+ - 28 \cdot n$ ($n = 1, 2, \ldots 6$). The previous elemental analysis[1] also conformed to the hexacarbonyl structure. (Found: C, 35.85; H, 1.27. $C_{10}H_4Fe_2O_6$ calcd.: C, 36.19; H, 1.21 %.) The infrared pattern of the metal carbonyl stretching region is similar to that of the other di-iron hexacarbonyl compounds, *e.g.* $(RC{\equiv}CR)_2Fe_2(CO)_6$[2], in which the disposition of $Fe_2(CO)_6$ moiety will presumably be similar to I. Therefore, the composition of the substituted butatriene iron carbonyl complexes[3] previously reported probably have the similar di-iron hexacarbonyl structure.

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Received June 10th, 1966

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[*] The same mass spectral result was also reported by R. B. King, *J. Am. Chem. Soc.*, 88 (1966) 2075.