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NEW REACTIONS OF 1,3- AND 1,4-CYCLOOCTADIENES

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Summary

The reactions of *cis,cis*-1,3-, *cis,trans*-1,3- and 1,4-cyclooctadienes with platinum(II) and palladium(II) in various solvent systems have been investigated. The occurrence of rearrangement of the coordinated dienes depends on the nature of the solvent. However, in Rh^I, Ir^I, Ru^{II} and Mo^0 systems, coordinated dienes always rearrange to the more stable 1,5-cyclooctadiene. New cyclooctadiene-metal complexes are reported along with new synthetic routes to some known cyclooctadienemetal complexes. Ligand exchange reactions of the diene-metal complexes and some reactions of coordinated cyclooctadienes are also described.

Introduction

Several reactions of *cis,cis*-1,3-cyclooctadiene(*c,c*-1,3-COD) [1-3], 1,4-cyclooctadiene (1,4-COD) [4, 5] and *cis,trans*-1,3-cyclooctadiene (*c,t*-1,3-COD) [6, 7] with transition metal ions have been previously investigated. It has been reported that *c,c*-1,3-COD and 1,4-COD generally yield 1,5-COD—metal complexes with the platinum group elements. *c,t*-1,3-COD, however, was found to undergo rearrangement to *c,c*-1,5-COD only in its reaction with Rh^{III}. The mechanisms of the rearrangements have been suggested to involve the formation of a metal hydride as an intermediate or in the transition state, the source of the hydride being the α-hydrogens of the alcoholic solvent, typically ethanol. To test this mechanism, we decided to investigate the reactions of these cyclooctadienes in various solvent systems including some containing no α-hydrogens. We expect-

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ed also that the results would throw some light on the mechanism of the rearrangement reactions and provide synthetic routes for new metal—olefin complexes or new routes for known complexes.

Experimental

1,4-COD and *c,t*-1,3-COD were prepared by the methods of Tayim and Kharboush [4], and Liu [8], respectively.

Reactions of c,c-1,3-COD

(i). *c,c*-1,3-COD (2 ml) was added to a solution of 0.5 g K_2PtCl_4 in 15 ml water. The mixture was stirred at room temperature for 24 h. The oily layer that formed was extracted with low boiling petroleum ether. Evaporation of the extract gave a yellow product; m.p. 137-165° (dec.). Analysis found: C, 25.71; H, 3.33; Cl, 18.63. $C_8H_{12}Cl_2Pt$ calcd.: C, 25.66; H, 3.23; Cl, 18.94. Molecular weight by vapour pressure in ethyleneglycol monoethylether found: 378; calcd.: 374. The compound is soluble in acetone and chloroform. Upon decomposition with aqueous KCN solution *c,c*-1,3-COD was recovered.

The same reaction was repeated with 20% ethanol and with 50% t-butanol as solvents. Identical compounds were obtained in all cases.

(ii). Two ml of *c,c*-1,3-COD was added to a solution of 0.3 g Na_2PtCl_6 in 15 ml absolute ethanol. The solution was stirred for six days. A white precipitate formed. It was filtered, washed successively with water, ethanol, and ether, and dried. The product, m.p. 250-270° (dec.) is identical to $PtCl_2$(1,5-COD) prepared by standard methods [4].

(iii). To 0.06 g of $Pd(C_6H_5CN)_2Cl_2$ in 30 ml t-butanol, *c,c*-1,3-COD (32 ml) was added. The solution was stirred for 15 min. A brown compound, m.p. 110-112°, separated. Upon concentrating the mother liquor a yellow compound was obtained; m.p. 200-209° (dec.). The brown compound gave *c,c*-1,3-COD upon decomposition with aqueous KCN while the yellow compound gave 1,5-COD.

The same reaction was repeated with CCl_4 as solvent. The yellow product obtained, m.p. 185-193° (dec.), gave a mixture of 1,4-COD (30%) and 1,5-COD (70%).

(iv). To a solution of 0.2 g $RhCl_3 \cdot 3H_2O$ in 15 ml t-butanol, 2 ml *c,c*-1,3-COD was added and the solution was refluxed for 2 h. The yellow precipitate formed was filtered and washed with ethanol, then ether, and dried; m.p. 220-235° (dec.). The product was identified as $[RhCl(1,5\text{-COD})]_2$ by comparison with an authentic sample prepared according to ref. 1.

(v). To 10 ml of the yellow ethanolic solution containing $Rh(CO)_2Cl_2^-$ [9] 1 ml of *c,c*-1,3-COD was added. The solution was refluxed for 2 h. The yellow precipitate obtained was filtered and washed with ethanol, then ether. It was identified as $[RhCl(1,5\text{-COD})]_2$.

(vi). Reaction *v* was repeated using $Rh(CO)_2Br_2^-$ [10] instead of $Rh(CO)_2Cl_2^-$. The product obtained, m.p. 222-228° (dec.), was identified as $[RhBr(1,5\text{-COD})]_2$.

Reactions of 1,4-COD

(i). Anhydrous $RuCl_3$ (0.15 g) in ethanol (15 ml) was treated with 1 ml 1,4-COD. The solution was refluxed for 2 h. The brown precipitate formed was filtered and washed with ethanol and then ether; m.p. 265° (dec.). The compound did not decompose in aqueous KCN. However, it was identified as $[RuCl_2(COD)]_n$ by comparison with an authentic sample.

Using the hydrated chloride $RuCl_3 \cdot 3H_2O$ identical results were obtained. Moreover, using t-butanol as a solvent afforded an identical compound.

(ii). To the red ethanolic solution containing $[Ru(CO)_2Cl_2]_n$ [11] was added 1 ml of 1,4-COD. The solution was refluxed for 1 h. The orange-brown crystals obtained were filtered and washed with ethanol, then ether, and dried. The compound obtained, m.p. 233-245° (dec.), was identified as $[Ru(CO)Cl_2(1,5\text{-}COD)]_2$.

(iii). To a solution of Na_2IrCl_6 (0.2 g) in 9 ml of 70% ethanol, 1 ml of 1,4-COD was added. The solution was refluxed for 9 h. The orange-red crystals which separated were filtered, washed with cold ethanol and dried. The product melting at 200° (dec.) was identified as $[IrCl(1,5\text{-}COD)]_2$.

(iv). To 10 ml of the yellow ethanolic solution containing $Rh(CO)_2Cl_2^-$ was added 1 ml of 1,4-COD and the solution was refluxed for 2 h. The yellow precipitate that formed was filtered and washed with ethanol then ether. It has a m.p. of 225-240° (dec.). It was identified as $[RhCl(1,5\text{-}COD)]_2$.

(v). A procedure similar to that of $Rh(CO)_2Cl_2^-$ was used for $Rh(CO)_2Br_2^-$ as a reactant. The product obtained, m.p. 228-228° (dec.), was identified as $[RhBr(1,5\text{-}COD)]_2$.

(vi). To $Mo(CO)_3(CH_3CN)_3$ obtained from 2.64 g $Mo(CO)_6$ [12] in 20 ml hexane, 3 ml of 1,4-COD was added. The mixture was refluxed for 16 h and then filtered while hot. Cooling the hexane filtrate overnight at —70° resulted in the precipitation of yellow crystals of the olefin complex; m.p. 114-117°. It was identified as $Mo(CO)_4(1,5\text{-}COD)$: ν(CO), 2010, 1910, 1853 and 1820 cm^{-1}.

Reactions of c,t-1,3-COD

(i). To 10 ml of ethanolic solution of $Rh(CO)_2Cl_2^-$ was added 2 ml of *c,t*-1,3-COD. A yellow precipitate formed immediately. It was filtered and washed with ethanol and ether, respectively, and dried under vacuum. The compound, $Rh_2(CO)_4Cl_2(C_8H_{12})_5$, is hygroscopic, m.p. 93-95°. It is soluble in CH_2Cl_2 and $CHCl_3$, but only slightly soluble in acetone. Upon decomposition with aqueous KCN, *c,t*-1,3-COD was obtained. Analysis found: C, 56.58; H, 6.90; Cl, 7.61; $C_{44}H_{60}Cl_2O_4Rh_2$ calcd.: C, 56.89; H, 6.89; Cl, 7.65. ν(CO) 2020; ν(C=C) 1610, 1650; ν(RhCl) 356 cm^{-1}.

(ii). A reaction similar to *i* was carried out with $Rh(CO)_2Br_2^-$ as a reactant. A yellow product, $Rh_2(CO)_4Br_2(C_8H_{12})_5$, was obtained with m.p. 105-120° (dec.). It is soluble in CH_2Cl_2 and $CHCl_3$, and slightly soluble in acetone. Upon decomposition with aqueous KCN *c,t*-1,3-COD was obtained. Analysis found: C, 53.46; H, 6.63; Br, 14.81; $C_{44}H_{60}Br_2O_4Rh_2$ calcd.: C, 52.67; H, 6.31; Br, 15.77. ν(CO) 2020; ν(C=C) 1615, 1626 cm^{-1}; ν(RhBr) 245 cm^{-1}.

(iii). To 0.2 g K_2PtCl_4 in 10 ml water, excess LiBr was added, followed by 2 ml of *c,t*-1,3-COD. The solution was stirred overnight. The yellow compound obtained was filtered, washed with ethanol and ether, respectively, and dried under vacuum. The compound, $PtBr_2(C_8H_{12})_2 \cdot C_2H_5OH$, has a m.p. of 73-75°.

The olefin obtained upon decomposition of the compound with aqueous KCN was identified as *c,t*-1,3-COD. Analysis found: C, 36.10; H, 4.36; Cl, 26.07. $C_{18}H_{30}Br_2OPt$ calcd.: C, 35.05; H, 4.85; Cl, 25.94.

Reactions of the diene complexes

(i). Reaction of Pt(c,c-1,3-COD)Cl₂ with 1,4- and 1,5-COD. Three ml of 1,5-COD was added to a suspension of Pt(*c,c*-1,3-COD)Cl_2 (0.2 g) in 15 ml water. The mixture was stirred for 24 h. The white precipitate which formed was filtered, washed with ethanol and ether and finally dried. The diene obtained upon decomposition of the product was 1,5-COD.

A similar reaction was carried out with 1,4-COD instead of 1,5-COD. The product isolated gave upon decomposition with aqueous KCN a mixture of 1,4-COD and *c,c*-1,3-COD.

(ii). Reaction of Pd(c,t-1,3-COD)Cl₂ with various COD's A suspension of Pd(*c,t*-1,3-COD)Cl_2 (0.15 g) in 10 ml benzene was treated with 3 ml 1,5-COD. The mixture was stirred for two days. Analysis of the mother liquor during the reaction did not show the presence of *c,t*-1,3-COD. However, at the end of the reaction, free *c,t*-1,3-COD was detected in the reaction mixture.

A similar reaction was carried out with 1,4-COD. The reaction mixture contained free *c,t*-1,3-COD and 1,5-COD at the end of the reaction.

With *c,c*-1,3-COD, under similar reaction conditions except for a reaction time of 10 h rather than two days, Pd(*c,t*-1,3-COD)Cl_2 gave a brown solution which afforded a brown precipitate upon treatment with low-boiling petroleum ether. The brown product gave *c,c*-1,3-COD upon decomposition with aqueous KCN.

(iii). Reaction of Pd(1,4-COD)Cl₂ with pyridine, triphenylphosphine and dimethylsulfoxide. A solution of 0.1 g of Pd(1,4-COD)Cl_2 in 10 ml $CHCl_3$ was treated with 0.5 ml of pyridine. A yellowish white precipitate was formed after 5 min. The solution was filtered, washed with $CHCl_3$, then ether, and dried. The product, m.p. 260-293° (dec.) was identified as $Pd(py)_2Cl_2$.

When 0.5 g of triphenylphosphine was used as a reactant in refluxing chloroform, yellow $Pd((C_6H_5)_3P)_2Cl_2$ was obtained after 10 min; m.p. 305°.

Using 0.5 ml of dimethyl sulfoxide (DMSO) afforded the orange-yellow $Pd(DMSO)_2Cl_2$ upon refrigeration overnight; m.p. 190-205° (dec.); ν(SO) 1029 cm^{-1}.

(iv). Reaction of 1,4-COD with methoxide ion. A mixture of 0.1 g of Pd(1,4-COD)Cl_2 and 0.2 g anhydrous Na_2CO_3 in methanol (20 ml) was boiled for few minutes. The hot solution was filtered. Upon cooling the filtrate to —70° a creamy yellow compound formed. It was filtered, washed with methanol and dried; m.p. 140-145° (dec.).

The reaction was also carried out in cold methanol where the mixture was stirred at room temperature for 3 h, after which the suspension was filtered, washed with water and dried, affording a quantitative yield of the product.

(v). Reaction of 1,4-COD with sodium acetate. To a suspension of 0.1 g of Pd(1,4-COD)Cl_2 in 10 ml methanol, 0.048 g sodium acetate was added. The suspension was stirred for 3 h. It was then filtered, washed several times with methanol, then with ether, and dried. The product has a yellow color, m.p. 160° (dec.). It is soluble in $CHCl_3$ but insoluble in ethanol and acetone.

(vi). Reaction of 1,4-COD with benzylamine. To a suspension of 0.1 g Pd(1,4-COD)Cl_2 in 10 ml methanol 0.05 ml benzylamine was added. After stirring for 10 min the solution became clear. It was left standing for 3 h. The solution was evaporated to dryness. The yellow residue was washed several times with ether. The yellow compound obtained has a m.p. of 110-115° (dec.); it is soluble in acetone and $CHCl_3$.

(vii). Reactions of Pd(c,t-1,3-COD)Cl_2. Dichloro(*c,t*-1,3-COD)palladium(II) was treated with pyridine, DMSO, triphenylphosphine, methoxide anion and benzylamine in a procedure similar to that used for Pd(1,4-COD)Cl_2. Products identical to those obtained with Pd(1,4-COD)Cl_2 were also obtained from the reaction of Pd(*c,t*-1,3-COD)Cl_2 with pyridine, triphenylphosphine and DMSO. However, the methoxide anion gave with Pd(*c,t*-1,3-COD)Cl_2 a yellow-green compound, m.p. 125-130° (dec.).

(viii). Reaction of $Rh_2(CO)_4Cl_2$(c,t-1,3-COD)$_5$ with pyridine and triphenylphosphine. To a solution of 0.1 g of $Rh_2(CO)_4Cl_2$(COD)$_5$ in 10 ml of $CHCl_3$, pyridine (0.2 ml) was added, followed by an excess of n-heptane. The orange-brown precipitate obtained was washed several times with n-heptane and then with ether. The product has a m.p. of 85°. It is soluble in acetone and $CHCl_3$.

A similar procedure was followed using triphenylphosphine instead of pyridine. The yellow product has a m.p. of 205-210° (dec.); ν(CO) 1955 cm^{-1}.

(ix). Reaction of $Rh_2(CO)_4Br_2$(c,t-1,3-COD)$_5$ with pyridine and triphenylphosphine. A procedure similar to that of the reaction of $Rh_2(CO)_4Cl_2$(*c,t*-1,3-COD)$_5$ was followed. Pyridine afforded an orange-brown compound; m.p. 110-120° (dec.); triphenylphosphine afforded a yellow compound; m.p. 170-185° (dec.); ν(CO) 1926 cm^{-1}.

Catalytic hydrogenation of c,t-1,3-COD. A solution of 20 ml *c,t*-1,3-COD in 85 ml CH_2Cl_2 containing 0.75 g $PtCl_2[(C_6H_5)_3P]_2$ and 1.50 g $SnCl_2 \cdot 2H_2O$ was placed in an autoclave bomb. The reaction vessel was flushed three times with hydrogen at 650 psi. It was then charged with H_2 at 650 psi. The solution was heated to 70° and stirred at that temperature for 4 h. The solution was then cooled to room temperature, filtered and distilled under aspirator pressure at room temperature to drive off the solvent. The olefin was then distilled under aspirator pressure at 50°. Analysis of the olefin mixture by gas chromatography showed that it contained *c,c*-1,3-COD and little *cis*-cyclooctene.

Gas chromatographic analyses were carried out with a Varian Aerograph GC-1520B Gas Chromatograph. A thermal conductivity detector was used. The carrier gas was helium. A 10' × 1/4" Cu column with 20% diethylglycol adipate on 60-80 Chromosorb W was used. At a filament current of 100 mA, column temperature of 125°, a gas flow-rate of 45 ml per min and a pressure of 50 psi, the retention times were: *c,c*-1,3-COD, 11.5 min; *c,t*-1,3-COD, 10 min; 1,4-COD, 12.5 min; and 1,5-COD, 16 min.

Results and discussion

Reactions of c,c-1,3-COD

The results of the reactions of *c,c*-1,3-COD with Pt^{II} in various solvent systems are shown in Table 1.

TABLE 1

REACTIONS OF *c,c*-1,3-COD

Reactant	Solvent	Product
K_2PtCl_4	Water	$PtCl_2$(*c,c*-1,3-COD)
K_2PtCl_4	20% Ethanol	$PtCl_2$(*c,c*-1,3-COD)
K_2PtCl_4	50% Ethanol	$PtCl_2$(1,5-COD)
K_2PtCl_4	50% t-Butanol	$PtCl_2$(*c,c*-1,3-COD)
Na_2PtCl_6	Absolute ethanol	$PtCl_2$(1,5-COD)
$RhCl_3 \cdot 3H_2O$	t-Butanol	[RhCl(1,5-COD)]$_2$
$Rh(CO)_2Cl_2^-$	Ethanol	[RhCl(1,5-COD)]$_2$
$Rh(CO)_2Br_2^-$	Ethanol	[RhBr(1,5-COD)]$_2$
$Pd(C_6H_5CN)_2Cl_2$	t-Butanol	Pd(*c,c*-1,3-COD)Cl_2 + Pd(1,5-COD)Cl_2
$Pd(C_6H_5CN)_2Cl_2$	CCl_4	Pd(1,4-COD)Cl_2 + Pd(1,5-COD)Cl_2

Coordinated *c,c*-1,3-COD rearranges readily to 1,5-COD in ethanol and 50% ethanol solutions. However, a *c,c*-1,3-COD—platinum complex is obtained in water or in 50% t-butanol; this complex has not hitherto been reported. The result supports the suggestion that the absence of hydrogen atoms in α-position with respect to the OH group in the alcohol makes the formation of the platinum hydride intermediate unlikely. Thus, rearrangement does not take place in such solvent systems. Coordinated *c,c*-1,3-COD rearranges readily, however, in Rh^{III} system even in t-butanol. In the case of Pd^{II} rearrangement takes place even in CCl_4. In this case one may think of the olefin itself as being the source of hydrogen for the hydride formation. The difference in the rearrangement in Pt^{II}, Pd^{II} and Rh^I systems is therefore related to the ease of the formation of the metal—olefin bond in the first place, palladium(II) being the most reactive, followed by Rh^I then Pt^{II}.

The reaction of Rh^I afforded the same product as obtained from the reaction of Rh^{III} with *c,c*-1,3-COD.

Reactions of 1,4-COD

Although no mention of the geometric isomerism of the olefin is made here, all the reactions of 1,4-COD reported so far are those of *cis,cis*-1,4-COD. The results of the reactions of 1,4-COD with Ru^{III}, Ru^{II}, Ir^{IV}, Rh^I and Mo^0 are listed in Table 2.

TABLE 2

REACTIONS OF 1,4-COD

Reactant	Solvent	Product
$RuCl_3 \cdot 3H_2O$	Ethanol	[$RhCl_2$(1,5-COD)]$_n$
$RuCl_3 \cdot 3H_2O$	t-Butanol	[$RuCl_2$(1,5-COD)]$_n$
Na_2IrCl_6	70% Ethanol	[IrCl(1,5-COD)]$_2$
$[Ru(CO)_2Cl_2]_n$	Ethanol	[Ru(CO)Cl_2(1,5-COD)]$_2$
$Rh(CO)_2Cl_2^-$	Ethanol	[RhCl(1,5-COD)]$_2$
$Rh(CO)_2Br_2^-$	Ethanol	[RhBr(1,5-COD)]$_2$
$Mo(CO)_3(CH_3CN)_3$	Hexane	$Mo(CO)_3$(1,5-COD)

The new reactions with $\mathrm{Ru^{II}}$, $\mathrm{Ru^{III}}$, $\mathrm{Rh^{I}}$ and $\mathrm{Mo^{0}}$ gave the known products $[\mathrm{RhCl_2}(1,5\text{-COD})]_n$, $[\mathrm{Ru(CO)Cl_2}(1,5\text{-COD})]_2$, $[\mathrm{RhCl}(1,5\text{-COD})]_2$, $[\mathrm{RhBr}(1,5\text{-COD})]_2$, and $\mathrm{Mo(CO)_4}(1,5\text{-COD})$. In all these reactions 1,4-COD has rearranged to 1,5-COD. Unlike $\mathrm{IrCl_3 \cdot 3H_2O}$ [5], $\mathrm{Ir^{IV}}$ gave the dimeric complex $[\mathrm{IrCl}(1,5\text{-COD})]_2$.

Reactions of c,t-1,3-COD

The reaction of *c,t*-1,3-COD with $\mathrm{Rh(CO)_2Cl_2^-}$ and $\mathrm{Rh(CO)_2Br_2^-}$ afforded the complexes $\mathrm{Rh_2(CO)_4Cl_2}(c,t\text{-}1,3\text{-COD})_5$ and $\mathrm{Rh_2(CO)_4Br_2}(c,t\text{-}1,3\text{-COD})_5$ in which two hexacooordinate $\mathrm{Rh^{I}}$ atoms are bridged by a *c,t*-1,3-COD molecule. The carbonyls are in the *trans* configuration as suggested by the fact that only one carbonyl stretching is observed in the IR spectrum around 2025 $\mathrm{cm^{-1}}$. The IR spectra also show absorption due to a free C=C bond at 1610 and 1650 $\mathrm{cm^{-1}}$ for the chloro complex and at 1615 and 1625 $\mathrm{cm^{-1}}$ for the bromo complex.

In the platinum complex $\mathrm{Pt}(c,t\text{-}1,3\text{-COD})_2\mathrm{Br_2}$, *c,t*-1,3-COD also behaves as a monodentate ligand; ν(C=C) 1625 $\mathrm{cm^{-1}}$.

Reactions of cyclooctadiene complexes

The results of the reactions of cyclooctadiene complexes with various reactants are shown in Table 3. They can be classified into: *(a)* Ligand exchange reactions and *(b)* Reactions of coordinated olefins.

(a). Ligand exchange reactions. Palladium(II) complexes were investigated more intensively for this purpose since they are more readily prepared and more reactive than other platinum-group metal complexes. The following results were obtained: (1) 1,5-COD and 1,4-COD displace *c,c*-1,3-COD from its platinum(II) complexes. (2) 1,5-COD and 1,4-COD displace *c,t*-1,3-COD from its palladium(II) complexes. In the case of 1,4-COD, this is accompanied by its

TABLE 3

REACTIONS OF DIENE COMPLEXES

Reactants	Product
$\mathrm{Pd}(c,t\text{-}1,3\text{-COD})\mathrm{Cl_2}$ + pyridine	$\mathrm{Pd(py)_2Cl_2}$
$\mathrm{Pd}(c,t\text{-}1,3\text{-COD})\mathrm{Cl_2}$ + triphenylphosphine	$\mathrm{Pd[(C_6H_5)_3P]_2Cl_2}$
$\mathrm{Pd}(c,t\text{-}1,3\text{-COD})\mathrm{Cl_2}$ + DMSO	$\mathrm{Pd(DMSO)_2Cl_2}$
$\mathrm{Pd}(c,t\text{-}1,3\text{-COD})\mathrm{Cl_2}$ + $\mathrm{CH_3O^-}$	$\mathrm{Pd_2(C_8H_{12} \cdot OMe)_2Cl_2}$ [a]
$\mathrm{Pd}(c,t\text{-}1,3\text{-COD})\mathrm{Cl_2}$ + $\mathrm{CH_3COO^-}$	$\mathrm{Pd_2(C_8H_{12} \cdot OOCCH_3)_2Cl_2}$ [a]
$\mathrm{Pd}(c,t\text{-}1,3\text{-COD})\mathrm{Cl_2}$ + $\mathrm{C_6H_5CH_2NH^-}$	$\mathrm{Pd_2(C_8H_{12} \cdot HNCH_2C_6H_5)_2Cl_2}$
$\mathrm{Pd}(1,4\text{-COD})\mathrm{Cl_2}$ + pyridine	$\mathrm{Pd(py)_2Cl_2}$
$\mathrm{Pd}(1,4\text{-COD})\mathrm{Cl_2}$ + triphenylphosphine	$\mathrm{Pd[(C_6H_5)_3P]_2Cl_2}$
$\mathrm{Pd}(1,4\text{-COD})\mathrm{Cl_2}$ + DMSO	$\mathrm{Pd(DMSO)_2Cl_2}$
$\mathrm{Pd}(1,4\text{-COD})\mathrm{Cl_2}$ + $\mathrm{CH_3O^-}$	$\mathrm{Pd_2(C_8H_{12} \cdot OMe)_2Cl_2}$ [b]
$\mathrm{Pd}(1,4\text{-COD})\mathrm{Cl_2}$ + $\mathrm{CH_3COO^-}$	$\mathrm{Pd_2(C_8H_{12} \cdot OOCCH_3)_2Cl_2}$ [b]
$\mathrm{Pd}(1,4\text{-COD})\mathrm{Cl_2}$ + $\mathrm{C_6H_5CH_2NH^-}$	$\mathrm{Pd_2(C_8H_{12} \cdot HNCH_2C_6H_5)_2Cl_2}$ [b]
$\mathrm{Rh_2(CO)_4Cl_2}(c,t\text{-}1,3\text{-COD})_5$ + pyridine	$\mathrm{Rh(py)_3Cl_3}$
$\mathrm{Rh_2(CO)_4Cl_2}(c,t\text{-}1,3\text{-COD})_5$ + triphenylphosphine	$\mathrm{Rh(CO)Cl[(C_6H_5)_3P]_2}$
$\mathrm{Rh_2(CO)_4Br_2}(c,t\text{-}1,3\text{-COD})_5$ + pyridine	$\mathrm{Rh(py)_3Br_3}$
$\mathrm{Rh_2(CO)_4Br_2}(c,t\text{-}1,3\text{-COD})_5$ + triphenylphosphine	$\mathrm{Rh(CO)Br[(C_6H_5)_3P]_2}$

[a] The relative positions of the substituent on the ring and the double bond are 2 and 6, respectively.

[b] The relative positions of the substituent on the ring and the double bond are 2 and 7, respectively.

rearrangement to 1,5-COD. (3) *c,c*-1,3-COD displaces *c,t*-1,3-COD from its palladium(II) complex. (4) *c,t*-1,3-COD does not displace 1,4- or 1,5-COD from their complexes. (5) No COD displaces 1,5-COD from its Pt^{II} or Pd^{II} complexes.

The order of reactivity of these complexes with respect to olefin displacement is M(*c,t*-1,3-COD) > M(*c,c*-1,3-COD) > M(1,4-COD) > M(1,5-COD). This is not unexpected since *c,t*-1,3-COD generally behaves as a monodentate. The other dienes behave as bidentate ligands with increasing favourable steric features on going from 1,3- to 1,4- to 1,5-COD.

Reactions of Pd(1,4-COD)Cl_2 and Pd(*c,t*-1,3-COD)Cl_2 with pyridine, triphenylphosphine and DMSO result in the displacement of the dienes by these ligands. The facile formation of Pd$(DMSO)_2Cl_2$ suggests that the NMR spectra of Pd—olefin complexes in DMSO are actually those of the free olefin. Conclusions to the effect that the NMR spectra of some coordinated olefins are almost identical to those of the free olefins have to be considered carefully.

The reactions of $Rh_2(CO)_4X_2$(*c,t*-1,3-COD)$_5$ (X = Cl, Br) with pyridine and triphenylphosphine also result in the displacement of the COD. Thus, $Rh(py)_3X_3$ and $Rh(CO)X[(C_6H_5)_3P]_2$ have been obtained. These products were identified by comparison with the compounds formed by the reaction of $Rh(CO)_2Cl_2^-$ with triphenylphosphine [8] and pyridine [13].

(b). Reactions of coordinated ligands. In these reactions the addition of strong nucleophiles to the coordinated olefin results in the formation of complexes containing a metal—π-olefin bond and a simple σ-bond. The products of the reaction of Pd(1,4-COD) and Pd(*c,t*-1,3-COD) complexes with CH_3O^-, CH_3COO^- and $C_6H_5CH_2NH^-$ have been assigned structures by comparison with the corresponding complexes [14, 15] of 1,5-COD, norbornadiene and bicyclo[2.2.1]heptatriene derivatives. In all these complexes the nucleophile was found to have an *exo* configuration, indicating that nucleophilic attack on the double bond occurs from the side opposite to the metal [16]. Thus, the products of the reactions of the methoxide anion with Pd(1,4-COD)Cl_2 and Pd(*c,t*-1,3-COD)Cl_2 are di-μ-dichlorobis(2-methoxycyclooctyl-6-enyl)dipalladium(II) and di-μ-dichlorobis(2-methoxycyclooctyl-7-enyl)dipalladium(II), respectively.

The compounds obtained from addition to Pd(*c,t*-1,3-COD)Cl_2 are identical to those obtained from addition to Pd(*c,c*-1,3-COD)Cl_2. This implies that addition to the *c,t*-1,3-COD complex occurs at the *trans* double bond.

(c). Catalytic hydrogenation of c,t-1,3-COD. Homogeneous catalytic hydrogenation of *c,t*-1,3-COD was attempted with the hope that the *cis* double bond may be hydrogenated to yield *trans*-cyclooctene. This would provide a facile route for the preparation of *trans*-cyclooctene. However, the formation of *c,c*-1,3-COD and only a small amount of *cis*-cyclooctene suggests that *c,t*-1,3-COD is catalytically isomerised to *c,c*-1,3-COD which, then, is hydrogenated to *cis*-cyclooctene. This isomerisation is different from thermal isomerisation whereby *c,t*-1,3-COD, in refluxing benzene, isomerises to bicyclo[4.2.0]oct-7-ene [8]. *c,t*-1,5-COD has been reported to yield *cis*-cyclooctene upon hydrogenation in a different system [17] which suggests that hydrogen may add more readily to the *trans* double bond than to the *cis* double bond.

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