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Reactions of Dodecacarbonyltriruthenium with Pentenes[1]

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Received July 21, 1975 AIC50520X

The isomerization of 1-pentene to *cis*-2-pentene and *trans*-2-pentene is catalyzed by $Ru_3(CO)_{12}$ in nonpolar solvents and the initial rate dependence from the $Ru_3(CO)_{12}$ and CO concentration is discussed. Addition of acids such as acetic acid increases the conversion rate; in both cases mechanisms involving π-allyl intermediates are suggested. Dehydrogenation by $Ru_3(CO)_{12}$ of the pentene equilibrium mixture yields the hydrides $H_4Ru_4(CO)_{12}$ and $H_2Ru_4(CO)_{13}$ and two isomers of molecular formula $HRu_3(CO)_9C_5H_7$, as main products. These two complexes were characterized by spectral methods and their behavior in reactions with hydrogen and $Ru_3(CO)_{12}$ is described.

Introduction

It has been shown that the reactions of trinuclear metal carbonyls of the group 8B with unsaturated hydrocarbons lead to isomerization of the hydrocarbons. Isomerization of alkenes with $Fe_3(CO)_{12}$ has been reported,[2] but no stable trinuclear complexes have been isolated. Reactions of $Ru_3(CO)_{12}$ with dienes showed isomerization of the unsaturated hydrocarbons and formation of trinuclear complexes in which a rearrangement of the ligands quite often occurs to satisfy the electronic requirements of the parent cluster.[3] Reactions of $Os_3(CO)_{12}$ with some olefinic ligands have also been reported.[4]

This paper reports details of the isomerization of pentenes with $Ru_3(CO)_{12}$ and the properties of the trinuclear complexes isolated.

Experimental Section

Elemental analyses were carried out with a F & M Model 185 CHN Analyzer. Infrared spectra were recorded on a double-beam Beckman IR-12 spectrophotometer with KBr optics and with carbon monoxide as calibrant. ^{1}H NMR spectra were determined on a Jeol JNM-PS-100 spectrometer and the mass spectra by a Hitachi Perkin-Elmer RMU-6H mass spectrometer using an ionizing energy of 50 eV. Gas chromatographic analyses were performed at 65°C by a C. Erba Fractovap Model B, using a 4-m column of 20% silicone oil 720 plus 2 m of 20% β,β'-oxydipropionitrile, both on Chromosorb P 60–80 mesh. Helium was used as carrier gas at 50 cm^3/min. Separations were performed by TLC, absorbent Kieselgel $PF_{254+368}$ Merck, eluent petroleum ether (bp 40–70°C) and 5% diethyl ether. All reactions were carried out in an atmosphere of nitrogen. Solvents were dried over molecular sieves. 1-Pentene and *cis*-2- and *trans*-2-pentene were Fluka pure grade. Dodecacarbonyltriruthenium was prepared according to the literature.[5]

Reactions of Dodecacarbonyltriruthenium and Pentenes. $Ru_3(CO)_{12}$ (0.400 g, 0.625 mmol) and 2.0 ml (17.7 mmol) of 1-pentene dissolved in *n*-hexane (700 ml) were refluxed for 24 hr. After cooling the solution was filtered and the solvent removed under reduced pressure. The residue was extracted by a mixture of *n*-heptane and 5% diethyl ether and separated by TLC, to give as main products three compounds **2**, **3**, **4**, and traces of **1** and **5**, recrystallized from *n*-heptane at 0°C. The same compounds were obtained when *cis*-2-pentene or *trans*-2-pentene were reacted with dodecacarbonyltriruthenium in analogous reaction conditions.

Anal. Calcd for $C_{14}H_8O_9Ru_3$: C, 26.97; H, 1.29; O, 23.09; Ru, 48.64. Found for **2**: C, 27.42; H, 1.0; O, 23.33; Ru, 48.6. Found for **3**: C, 26.64; H, 1.5; O, 22.61; Ru, 48.9.

Mass spectra: **1**, *m/e* 628 (^{102}Ru) $[M]^+$, followed by loss of nine carbonyl groups, corresponding to the molecular formula $Ru_3(CO)_9C_5H_{10}$; **2**, *m/e* 626 $[M]^+$, followed by loss of nine carbonyl groups, corresponding to the molecular formula $Ru_3(CO)_9C_5H_8$; **3**, *m/e* 626 $[M]^+$, followed by loss of nine carbonyl groups, corresponding to the molecular formula $Ru_3(CO)_9C_5H_8$; **4**, *m/e* 774 $[M]^+$, followed by loss of thirteen carbonyl groups; **5**, *m/e* 748 $[M]^+$, followed by loss of twelve carbonyl groups.

Action of Hydrogen on 2. A slow stream of hydrogen was bubbled through a cyclohexane solution of **2** (0.100 g dissolved in 250 ml) for 2 hr under reflux. After cooling the solution was filtered and the solvent removed under vacuum. The residue was extracted with a mixture of *n*-heptane and 10% diethyl ether and separated by TLC to yield **6** and **3** with traces of **5**.

Mass spectrum of **6**: *m/e* 628 $[M]^+$ followed by loss of nine carbonyl groups and corresponding to the molecular formula $Ru_3(CO)_9C_5H_{10}$.

Action of Hydrogen on 3. The reaction was carried on similar to that of hydrogen and **2**. After 2 hr **3** was unchanged and formation of **5** and metallic ruthenium occurred when the reaction was extended to 15 hr.

Isomerization of 1-Pentene Catalyzed by $Ru_3(CO)_{12}$. Ten milliliters of a 3.7×10^{-4} *M* toluene solution of dodecacarbonyltriruthenium was sealed under nitrogen in a 70-ml tube equipped with a GC septum to add and remove known amounts of 1-pentene and other substances by a liquid or gas syringe. The ampoules were placed in a thermostatic tank at 70.4°C. The extent of the isomerization reaction was checked by GC analyses of solution samples until 10% conversion and the area of the peaks was integrated to determine the initial rate. Experimental values of the equilibrium isomer composition were measured on ampoules kept in the thermostatic tank for suitably long times.

Isomerization of 1-Pentene Catalyzed by 1, 2, 3, 4, and 5. Ten milliliters of a 3.7×10^{-4} *M* toluene solution[6] of the complexes **1**, **2**, **3** and of the hydrides **4** and **5** were sealed under nitrogen in a tube and known volumes of 1-pentene were added to each solution as described above. The reaction temperature was 70.4°C. Aliquots of the solutions were analyzed by GC and the initial isomerization rate was measured by the decrease of the 1-pentene concentration.

Isomerization of 1-Pentene with CH_3COOD as Cocatalyst. $Ru_3(CO)_{12}$ (0.050 g, 0.08 mmol), 2.0 ml of 1-pentene (17.7 mmol), and 1.1 ml of CH_3COOD (17.7 mmol) were sealed under nitrogen in a 70-ml tube and reacted in a thermostatic tank at 50.0° for 3 days. Mass and ^{1}H NMR spectra showed that deuterium was present in the equilibrium mixture just as CH_3COOD.

Results and Discussion

1-Pentene is converted to *cis*-2-pentene and *trans*-2-pentene when refluxed in *n*-hexane with dodecacarbonyltriruthenium. GC analysis of the reactant solution shows that the equilibrium composition, 3% 1-pentene, 23% *cis*-2-pentene, 74% *trans*-2-pentene, is reached in a few hours. *cis*-2-Pentene and *trans*-2-pentene are isomerized to the same equilibrium mixture in about the same time.

A number of reactions of $Ru_3(CO)_{12}$ and 1-pentene were carried out under analogous conditions and stopped at different times to observe the appearance of complexes. Analyses by TLC and infrared spectroscopy of the concentrated solution indicate that trace amounts of **1**, **2**, and **4** are detectable after about 50% conversion of 1-pentene. Identical complexes are obtained from both 1-pentene and 2-pentene isomers and this fact further supports the conclusion that the bulk of each complex is formed after the achievement of the equilibrium.

Characterization of the Complexes. Compound **1**, $Ru_3(CO)_9C_5H_{10}$, always present in small quantity, could not be obtained as a pure sample; it was characterized only by its mass spectrum. The main reaction products are the two isomers **2** and **3** of molecular formula $Ru_3(CO)_9C_5H_8$. **3** is obtained from **2** by thermal rearrangement.

The high-field absorptions in the ^{1}H NMR spectra of **2** and **3** (Table I) clearly indicate that they bear hydrogen directly bonded to ruthenium. The other resonances show that they are lower homologues of the pair of isomers isolated in the

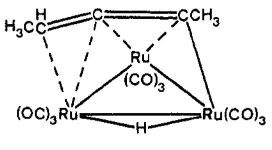
Table I. Ir and ^{1}H NMR Data for **2**, **3**, **4**, **5**, and **6**

Complex	Color	ν(CO),[a] cm^{-1}	Chemical shift[b]
2	Yellow	2094 ms, 2067 s, 2043 vs, 2026 s, 2021 shm, 2008 ms, 2000 m, 1986 w	6.49 q (1), 7.36 s (3), 8.33 d (3), 30.7 s (1)
3	Bright yellow	2095 ms, 2069 s, 2043 vs, 2026 s, 2014 ms, 2007 s, 1997 w	3.32 d (1), 7.17 s (6), 30.1 d (1)
4	Red	2078 vs, 2067 vs, 2054 vs, 2035 m, 2024 s, 2010 w, 1880 w	28.5
5	Yellow	2081 s, 2068 vs, 2031 m, 2025 s, 2010 w	27.6
6	Yellow	2105 ms, 2076 vs, 2055 vs, 2042 vs, 2028 s, 2015 vs, 2008 s, 1992 m	7.17 q (3), 7.24 s (2), 8.72 t (3), 28.0 sb (2)

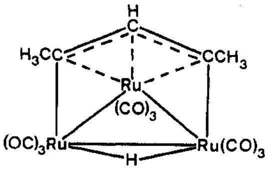
[a] Solvent *n*-heptane. [b] Solvent CCl_4 for **2** and **3**, $CDCl_3$ for **4**, **5**, and **6**.

reaction of $Ru_3(CO)_{12}$ with hexadienes.[3] CH_3–CH and CH_3 are the only proton-bearing carbons and at the ends of the hydrocarbon chain in **2**, whereas a CH, whose proton is coupled with the hydrido proton ($J \simeq 2$ Hz), and two CH_3's, at the ends of the hydrocarbon chain, are present in **3**.

^{1}H NMR evidence, however, is not enough to allow a clear picture of the bonding of the ligand to the metal atoms in the two complexes. Nevertheless, on the basis of x-ray analyses carried out for the two isomers of molecular formula $HRu_3(CO)_9C_6H_9$, obtained in the reaction of $Ru_3(CO)_{12}$ and hexadienes,[3,7,8] the proposed structures of **2** and **3** are the following:



2



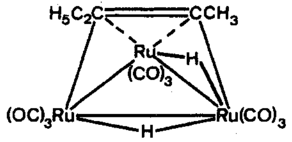
3

The experimental data indicate that **4** and **5** are the well known hydrides $H_2Ru_4(CO)_{13}$ and $H_4Ru_4(CO)_{12}$.[9]

Hydrogenation of Complexes. Loss of hydrogen from the ligand takes place during the formation of **2** and leads to the hydrido complexes $H_2Ru_4(CO)_{13}$ and $H_4Ru_4(CO)_{12}$. To verify whether **2** comes from $Ru_3(CO)_{12}$ directly or through **1**, we tried to dehydrogenate **1** with $Ru_3(CO)_{12}$, but all attempts were unsuccessful. On the other hand, reaction of $HRu_3(CO)_9C_5H_7$ (**2**) with gaseous hydrogen yields complex **6**, an isomer of **1**.

The room-temperature ^{1}H NMR spectrum of **6** suggests that CH_3 and CH_2–CH_3 are the ends of the hydrocarbon chain. The broad high-field absorption is well resolved into two doublets at τ 25.6 and 30.2 ($J \simeq 2$ Hz) at −60°C. Upon raising the temperature these peaks broaden, coalesce (−10°C), and eventually sharpen (+58°C). Upon lowering the temperature the quartet at τ 7.17 becomes a complex multiplet, but the superposition with the signal at τ 7.24 makes definitive analysis difficult.

^{1}H NMR results suggest for **6** the structure shown below similar to that reported for $H_2Ru_3(CO)_9C_8H_8$[10] and $H_2Ru_3(CO)_9C_8H_{12}$;[11] the asymmetric hydride assignment has been ascertained by ^{13}C NMR spectra of $H_2M_3(CO)_9C_8H_{12}$ (M = Ru, Os).[13] The temperature dependence of the signal at τ 7.17 is similar to that reported for $HRu_3(CO)_9C_4H_3(C_6H_5)_2$.[3]



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Treatment of **3** with gaseous hydrogen under mild conditions does not give a bonding rearrangement similar to that of **6**, presumably as it should require the breakdown of a stable Ru–C bond.

Table II. 1-Pentene Isomerization[a]

$Ru_3(CO)_{12}$ concn, m*M*	Polar substances v/v solution	Initial rate, % hr^{-1}
0.37		7
0.16		3
0.11		2
0.05		1
0.37	Acetic acid 5.0 × 10^{-3}	75
0.37	Acetic acid 2.5 × 10^{-3}	75
0.37	Acetic acid 0.5 × 10^{-3}	75
0.37	Ethyl acetate 10.0 × 10^{-3}	7
0.37	Acetone 10.0 × 10^{-3}	7

[a] Variation of initial rate upon $Ru_3(CO)_{12}$ and polar substances concentrations. Volume of toluene solution = 10 ml. Temperature = 70.4°C. Initial [1-pentene] = 46 m*M*.

Isomerization Processes. Qualitative results about 1-pentene isomerization, catalyzed by the reaction products, exhibit a conversion initial rate lower (**1**, **3**, and **4**), similar (**2**), or higher (**5**) with respect to $Ru_3(CO)_{12}$. Moreover the initial rate of the isomerization catalyzed by **2** and **5** increases about proportionally with the complex concentration. Very different values of the initial cis/trans ratio were observed with $Ru_3(CO)_{12}$ (0.3–0.4) and $H_4Ru_4(CO)_{12}$ (**5**) (0.9–1.0). These results and the very low concentrations of all the products, before the equilibrium achievement, demonstrate that their contributions to the whole catalytic process are not substantial.

Examination of the factors affecting the catalytic activity of $Ru_3(CO)_{12}$ shows that the conversion initial rate is proportional to the carbonyl concentration and decreases with increasing CO partial pressure. In particular the equilibrium isomer composition is reached in several days when the reaction is carried on in sealed vials, whereas a few hours are enough when under reflux. The above results suggest that the dissociation of Ru–CO bonds of dodecacarbonyltriruthenium, to give an active unsaturated species, is the rate-determining step.

More insight about the isomerization mechanism was obtained by addition of polar substances, such as acetic acid, acetone, or ethyl acetate (Table II). Presence of small amounts of acetic acid induces a tenfold increase on the initial rate, but leaves the initial cis/trans ratio substantially unchanged (Figure 1). This fact can be explained by assuming the coordination of protons on the metal cluster to give a cationic metal hydride species, containing weaker Ru–CO bonds.[12] During the isomerization, however, no scrambling of hydrogen between acid and pentenes takes place, as observed by using CH_3COOD. This finding excludes the operation of a metal hydride addition–elimination mechanism. Addition of Lewis bases, such as acetone or ethyl acetate, has no effect on both the initial rate and the cis/trans ratio.

Thus a mechanism involving a π-allyl metal hydride intermediate is suggested for the isomerization of 1-pentene catalyzed by $Ru_3(CO)_{12}$ without or with these substances. The

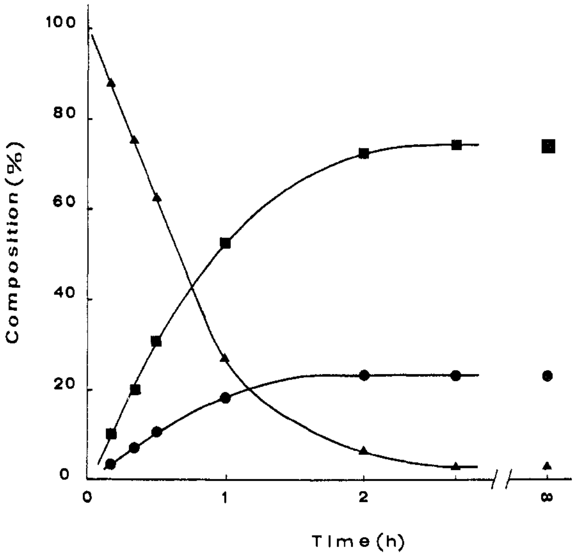

Figure 1. Isomerization of 1-pentene catalyzed by a toluene solution of $Ru_3(CO)_{12}$ in the presence of acetic acid. Variation of composition with time: ▲, 1-pentene; ●, *cis*-2-pentene; ■, *trans*-2-pentene. [Olefin] = 46 m*M*; [complex] = 0.37 m*M*; acetic acid 2.5×10^{-3} v/v solution; temperature = 70.4°C.

almost constant value of the cis/trans ratio, in the range 0.3–0.4, is in agreement with the proposed mechanism. The same mechanism was proved to be operating in the isomerization of 1-pentene with $Fe_3(CO)_{12}$.[2c]

Acknowledgment. We thank the C.N.R. (National Research Council) for financial support.

Registry No. **2**, 56943-14-7; **3**, 56943-13-6; **4**, 21077-76-9; **5**, 34438-91-0; **6**, 56943-12-5; $Ru_3(CO)_{12}$, 15243-33-1; 1-pentene, 109-67-1; CH_3COOD, 758-12-3.

References and Notes

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Synthesis and Characterization of Some Cobalt(III) Catechol Complexes

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Received June 3, 1975 AIC503778

A number of new cobalt(III) complexes containing one bidentate *o*-dihydroxy aromatic ligand and amine counterligands have been prepared and characterized. The complexes can be prepared by procedures similar to those employed for synthesis of cobalt(III)–amino acid complexes. In addition to normal spectral characterization, a preliminary electrochemical investigation by cyclic voltammetry revealed substantial changes in the properties of the dihydroxyaromatic ligands by virtue of their coordination to the metal.

Introduction

Although the coordination chemistry of catechol and its derivatives has not been studied extensively, these molecules constitute an interesting class of bidentate ligands. The fact that catechol and its substituted derivatives[1] can undergo one- or two-electron oxidations to the *o*-semiquinone or *o*-quinone, respectively, offers the possibility of preparing complexes with unusual oxidation states. A fundamental knowledge of the coordination chemistry of catechol is important for understanding certain biochemical processes. Aromatic dioxygenases normally use some type of catechol derivative as a substrate.[2–7] Since most of the aromatic dioxygenases have a metal ion at the active site (usually iron),[2–11] it is probable that the catechol chelates to the metal during catalysis. Most schematic mechanisms for the action of this class of enzymes include just such a step. Besides developing basic information on the coordination properties of catechol it will be useful to those working in the area of dioxygenase chemistry to know in what ways the chemical properties of the catechol system change upon coordination. Another area of biochemical interest to which catechol coordination chemistry is pertinent is that of certain ferric chelators called siderochromes, in particular, those siderochromes using phenolate ligands. Enterochelin, for example, is a cyclic triester of 2,3-dihydroxy-*N*-benzoyl-L-serine in which the metal binding site is three catechol groups.[12]

There are many reports in the literature of catechol–metal complexes. Most of these are solution studies in which no compounds are isolated. There are also a number of reports in the old literature of catechol complexes with unusual formulations.[13] Röhrscheid et al. have reported preparation and characterization of complexes containing two catecholate or two tetrachlorocatecholate anions.[14] In some cases catechol complexes have been prepared by oxidative addition to low oxidation state metals.[15]

In this paper we report a variety of catechol and substituted catechol complexes of cobalt(III). Our objective was to prepare complexes containing one catechol bound to the metal with counterligands sufficient to complete the coordination sphere. The complexes which have been prepared were