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Synthesis and Physicochemical Studies of some Dicyclopentadiene Alkoxo Derivatives of Rhodium(I)

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Abstract

Reaction of $[C_{10}H_{12}RhCl]_2$ ($C_{10}H_{12}$ = dicyclopentadiene) with KOMe in MeOH–THF at low temperatures or with sodium hydroxide in presence of CF_3CH_2OH–THF medium gives the binuclear alkoxo bridged complexes, $[C_{10}H_{12}Rh(OR)]_2$ (R = CH_3 (**a**) and CH_2CF_3 (**b**)). The derivative **a** upon further treatment with β-diketones gives the mononuclear complexes, $[C_{10}H_{12}RhL]$ (L = anions of β-diketones). The IR, ^{1}H and ^{13}C NMR of these newly synthesized complexes throw light on their structural features.

Introduction

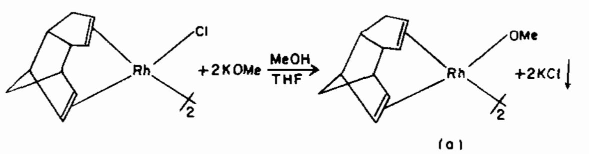
Compared to the alkoxide chemistry of earlier transition (including inner transition) metals [1], the chemistry of alkoxo derivatives of later transition elements does not appear to have received much attention except for a number of publications from our laboratories in recent years [2–12]. This may possibly be due to the insoluble and non-volatile nature of the alkoxides of later 3d metals [13] and the unstable nature of the alkoxides of platinum metals in general [14–17].

During recent years, intensive studies have been carried out on the applications of platinum metal complexes into homogeneous catalytic reactions including homogeneous hydrogenation of the C=C bonding.

In view of the above, it was thought worthwhile to synthesize alkoxy derivatives of rhodium containing dicyclopentadiene ($C_{10}H_{12}$) for the first time and to investigate their physicochemical characteristics.

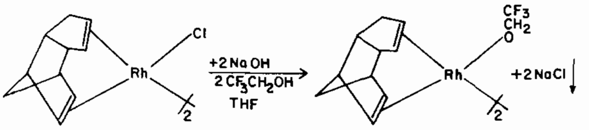
Results and Discussion

The reaction of rhodium(I) complex $[C_{10}H_{12}RhCl]_2$ with KOMe in 1:2 molar ratio in MeOH–THF medium, carried out at low temperatures (around −10 °C) can be represented by the following equation:

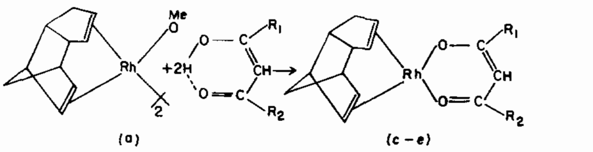


The complex **a** is a greenish yellow solid, soluble in dichloromethane and chloroform.

As compared to the methoxo bridged rhodium complex (**a**) the corresponding fluorinated alkoxo complex (**b**) appears to be quite stable; it can be synthesized at room temperature by the reaction of the chloride complex with two equivalents of sodium hydroxide in aqueous trifluoroethanol:



The reactions of complex **a** with β-diketones (LH) such as 2,4-pentanedione, benzoylacetone and dibenzoylmethane in a 1:2 molar ratio in CH_2Cl_2 medium have yielded the mononuclear β-diketonates of rhodium(I), $[C_{10}H_{12}RhL]$ complexes (L = anions of β-diketones) (**c**–**e**):



($R_1 = R_2$ = Me or Ph ; R_1 = Me and R_2 = Ph)

In these derivatives, the central metal rhodium is expected to attain a four coordination environment as reported earlier [16].

Infrared Spectra

In the IR spectra, the following points appear to be significant:

(1) In the spectra of the chloride complex, $[C_{10}H_{12}RhCl]_2$, two strong bands are observed at 247

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and 270 cm^{-1} due to the (Rh–Cl) vibrations. These bands disappear in the alkoxo derivatives of rhodium(I) [15].

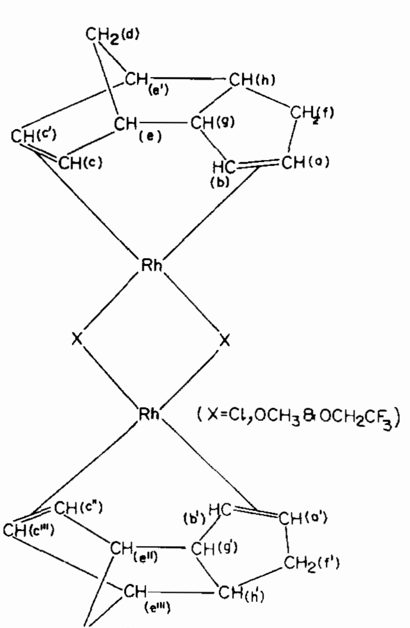
(2) In the alkoxo complexes, a strong broad band is observed at ≈ 1060 cm^{-1}, which is a characteristic absorption band for the ν(C–O) modes [14].

(3) A strong band at ≈ 540 cm^{-1} may be assigned to the Rh–O stretching vibrations.

(4) The $C\overset{\cdots}{=}C$ and $C\overset{\cdots}{=}O$ vibrations appear at 1525–1555 and 1560–1590 cm^{-1} respectively in the β-diketonate complexes (**c**–**e**). It may, therefore, be inferred that chelate formation takes place through the O,O′-coordination of β-diketone anions [18].

^1H NMR Spectra

The ^1H NMR spectra of rhodium(I) complexes were recorded in $CDCl_3$. The frequencies of these derivatives are listed below:



$[C_{10}H_{12}RhCl]_2$

δ 6.13, $H_aH_{a'}$; δ 4.67, $H_cH_{c'}H_{c''}H_{c'''}$; δ 4.24, $H_bH_{b'}$; δ 3.37, $H_gH_{g'}$; δ 2.90, $H_hH_{h'}$; δ 2.36, $H_eH_{e'}$-$H_{e''}H_{e'''}$; δ 2.0, $H_fH_{f'}$; δ 1.63, $H_dH_{d'}$.

$[C_{10}H_{12}Rh(OCH_3)]_2$

δ 5.34, $H_aH_{a'}$; δ 3.95, $H_cH_{c'}H_{c''}H_{c'''}$; δ 3.42, $H_bH_{b'}$; δ 3.18, $H_gH_{g'}$; δ 2.70, $H_hH_{h'}$; δ 2.50, $H_eH_{e'}$-$H_{e''}H_{e'''}$; δ 2.0, $H_fH_{f'}$; δ 1.62, $H_dH_{d'}$; δ 2.62, alkoxy protons.

$[C_{10}H_{12}Rh(OCH_2CF_3)]_2$

δ 5.49, $H_aH_{a'}$; δ 4.15, $H_cH_{c'}H_{c''}H_{c'''}$; δ 3.83, $H_bH_{b'}$; δ 3.52, $H_gH_{g'}$; δ 3.28, $H_hH_{h'}$; δ 2.86, $H_eH_{e'}$-$H_{e''}H_{e'''}$; δ 2.0, $H_fH_{f'}$; δ 1.64, $H_dH_{d'}$; δ 2.25, alkoxy protons.

It may be inferred from the above data that most of the signals due to saturated protons appear in almost the same region in the PMR spectra of the chloro bridged as well as their corresponding alkoxy bridged rhodium(I) complexes. The signals due to the olefinic protons appear to shift slightly towards a higher region on replacing the chloro by the alkoxo group, which shows that the π-type interactions are retained in the alkoxo derivatives, unlike the platinum analogues which behave differently [14].

^{13}C NMR Spectra

Important signals observed in the ^{13}C NMR spectra of rhodium(I) complexes in $CHCl_3$ are listed below:

$[C_{10}H_{12}RhCl]_2$

δ 93.45, $C_aC_{a'}$ ($J = 16$ Hz); δ 79.6, 77.0, $C_cC_{c'}C_{c''}$-$C_{c'''}$; ($J = 15$ Hz); δ 65.0, $C_bC_{b'}$ ($J = 18$ Hz); δ 55.8, $C_eC_{e'}C_{e''}C_{e'''}$; δ 53.0, $C_hC_{h'}$; δ 41.3, $C_fC_{f'}$; δ 31.3, $C_dC_{d'}$.

$[C_{10}H_{12}Rh(OCH_3)]_2$

δ 92.85, $C_aC_{a'}$ ($J = 18$ Hz); δ 76.0, $C_cC_{c'}C_{c''}C_{c'''}$ ($J = 18$ Hz); 63.4, alkoxy carbons; 61.3, $C_bC_{b'}$ ($J = 18$ Hz); 57.9, $C_eC_{e'}C_{e''}C_{e'''}$; 44.0, $C_hC_{h'}$; 33.8, $C_fC_{f'}$; 25.2, $C_dC_{d'}$.

It has been reported that $^1J(Rh_C)$ for olefinic carbon atom is not large (10–14 Hz) and for cyclopentadienyl group it is zero [14]. $^1J(Rh_C)$ values for olefinic C atom from the above data are found to be in the range of 15–18 Hz. These observations are in conformity with those of the PMR spectra and indicate the presence of π-type interactions in the metal ring bonding system of the alkoxo derivatives also [19].

Experimental

Methanol, tetrahydrofuran dichloromethane were dried by the literature methods [9]. Acetylacetone (BDH) was used after careful fractionation (boiling point 135–137 ℃). 2,2,2-Trifluoroethanol (Aldrich) was used after distillation.

Infrared spectra were recorded as CsI pellets in the region 4000–200 cm^{-1} on a Perkin-Elmer 557 spectrophotometer. Far infrared spectra were recorded on a CSMCRI FT-IR model in the region 500–24 cm^{-1}. The NMR spectra were recorded on a Perkin-Elmer Model R 32B at 90 MHz using $SiMe_4$ as internal standard. Carbon and hydrogen were determined by AMDEL (Australian Microanalytical Service), Victorial, Australia.

Methods of Preparation

Reaction of $[C_{10}H_{12}RhCl]_2$ with KOMe in methanol

KOMe in methanol was added slowly to a solution of $[C_{10}H_{12}RhCl]_2$ in tetrahydrofuran at low

TABLE I. Reactions of $[C_{10}H_{12}RhCl]_2$ with NaOH/KOR in Tetrahydrofuran–Parent Alcohol

Reactants	Molar ratio (medium)	Products	Analysis (%) found (calc.)	
			Carbon	Hydrogen
$[C_{10}H_{12}RhCl]_2$ + NaOH (0.41 g) (0.06 g)	1:2 (methanol + THF)	$[C_{10}H_{12}Rh(OMe)]_2$ greenish solid, soluble in $CHCl_3$, CH_2Cl_2	49.07 (49.61)	5.45 (5.62)
$[C_{10}H_{12}RhCl]_2$ + NaOH (0.45 g) (0.07 g)	1:2 (2,2,2-trifluoroethanol + THF)	$[C_{10}H_{12}Rh(OCH_2CF_3)]_2$ yellow solid, soluble in $CHCl_3$, CH_2Cl_2	42.91 (43.11)	3.95 (4.19)
$[C_{10}H_{12}RhCl]_2$ + K (0.46 g) (0.07 g)	1:2 (methanol + THF)	$[C_{10}H_{12}Rh(OMe)]_2$ greenish solid, soluble in $CHCl_3$, CH_2Cl_2	49.16 (49.61)	5.72 (5.62)

TABLE II. Reactions of $[C_{10}H_{12}RhCl]_2$ with β-Diketones in Dichloromethane

Reactants	Molar ratio (medium)	Products	Analyses (%) found (calc.)	
			Carbon	Hydrogen
$[C_{10}H_{12}Rh(OMe)]_2$ + acacH (0.38 g) (0.14 g)	1:2 (CH_2Cl_2)	$[C_{10}H_{12}Rh\ acac]$ dark yellow solid, soluble in $CHCl_3$, CH_2Cl_2	53.12 (53.89)	5.98 (5.68)
$[C_{10}H_{12}Rh(OMe)]_2$ + bzacH (0.31 g) (0.19 g)	1:2 (CH_2Cl_2)	$[C_{10}H_{12}Rh\ bzac]$ dark yellow solid, soluble in $CHCl_3$, CH_2Cl_2	60.02 (60.61)	5.45 (5.30)
$[C_{10}H_{12}Rh(OMe)]_2$ + dbmH (0.41 g) (0.34 g)	1:2 (CH_2Cl_2)	$[C_{10}H_{12}Rh\ dbm]$ dark yellow solid, soluble in $CHCl_3$, CH_2Cl_2	65.31 (65.50)	5.21 (5.02)

temperatures, around −10 °C. The colour of the solution is changed from orange to greenish dark yellow. The solvent was removed under reduced pressure, followed by addition of dichloromethane, to separate the soluble product from the insoluble KCl. The greenish dark yellow filtrate was concentrated and the product was crystallized (in 70% yield) in CH_2Cl_2– MeOH mixture (Table I).

Reaction of $[C_{10}H_{12}RhCl]_2$ with NaOH in 2,2,2-trifluoroethanol

$[C_{10}H_{12}RhCl]_2$ was dissolved in 2,2,2-trifluoroethanol and tetrahydrofuran and a calculated amount of sodium hydroxide was added with stirring at room temperature. A clear dark yellow solution is obtained. After removal of the solvent under reduced pressure, the complex was extracted with the minimum amount of dichloromethane. The product was crystallized (in 60% yield) in CH_2Cl_2–CF_3CH_2OH mixture (Table I).

Reactions of $[C_{10}H_{12}RhCl]_2$ with β-diketones in dichloromethane

2,4-Pentanedione, benzoylacetone or dibenzoylmethane (LH) was added to a clear greenish dark yellow solution of $[C_{10}H_{12}RhCl]_2$ in dichloromethane. The mixture was stirred for about 24 h. The solvent was then removed under reduced pressure and the products were crystallized at low temperatures in n-hexane and dichloromethane mixture (Table II).

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