

Diolefin Rhodium(I) Complexes with Tropolone and Related Ligands

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Summary

Rhodium(I) tropolonate and salicylaldehyde complexes of the general formula $Rh(A)(diolefin)$ ($A =$ tropolonate, β -isopropyltropolonate, β -methyltropolonate and salicylaldehyde; diolefin = 1,5-cyclooctadiene, 2,5-norbornadiene and tetrafluorobenzobarrelene) have been prepared by several routes. The ability of $Rh(trop)(COD)$ to function as an intermediate for the synthesis of other neutral and cationic rhodium(I) complexes has been studied and its hydroformylation activity has been explored briefly.

Introduction

Whereas several types of complexes with β -ketoenolates have been reported for all the platinum metals group⁽¹⁾, the analogous complexes with tropolone and related ligands have been studied to a smaller extent^(2–5), and work has mainly concentrated on platinum derivatives⁽⁵⁾. In this paper we report some rhodium complexes of the general formulae $Rh(A)(diolefin)$ ($A =$ tropolonate, β -methyltropolonate, β -isopropyltropolonate and salicylaldehyde).

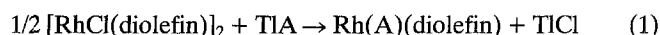
The tropolonate ligand and derivatives can be considered intermediate in character between salicylaldehyde and the well known β -diketonates. It has been reported that the salicylaldehyde derivatives form complexes which are less stable than the tropolonate complexes⁽²⁾.

Results and Discussion

Complexes of the $Rh(A)(diolefin)$ type

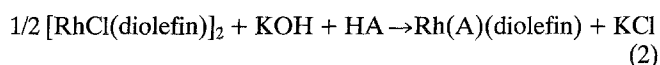
$Rh(A)(diolefin)$ complexes can be prepared by adding a stoichiometric amount of TIA [$A =$ tropolonate (trop),

β -isopropyltropolonate (i-Pr-trop) and salicylaldehyde (sal)] to dichloromethane or chloroform solutions of $[RhCl(diolefin)]_2$ ^(6–8) according to Equation (1):

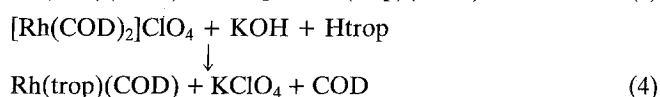
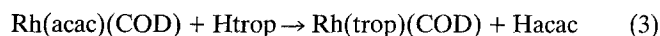


diolefin = 1,5-cyclooctadiene (COD), 2,5-norbornadiene (NBD) and tetrafluorobenzobarrelene (TFB).

An alternative route, specially used for the β -methyltropolonate (Me-trop) complexes, involves the reaction of $[RhCl(diolefin)]_2$ with HA and KOH, according to Equation (2):



Other preparative methods we have used for the synthesis of $Rh(trop)(COD)$ are exemplified by Equations (3) and (4):



All the complexes are stable in air at room temperature and are nonconducting in acetone or nitromethane solutions. Elemental analyses (carbon and hydrogen), melting points, colours and yields of the isolated $Rh(A)(diolefin)$ complexes are collected in Table 1.

The i.r. spectra of the complexes show absorptions characteristic of the coordinated diolefin⁽⁹⁾. Some representative absorptions in the 1300–1620 cm^{-1} region are listed in Table 2. For tropolonate complexes, the absorption in the 1320–1350 cm^{-1} range is assigned to $\nu(C-O)$; whereas the absorptions located at ca. 1500 and 1580 cm^{-1} are tentatively assigned to $\nu(C=O) + \nu(C=C)$ and $\nu(C=C)$ ⁽¹⁰⁾. The salicylaldehyde complexes show the expected $\nu(C-O)$ and $\nu(C=O)$

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Table 1. Analytical data, m.p.s, colour and yields for $Rh(A)(diolefin)$ complexes.

Complex	Colour	Yield (%)	Found (Calcd.)% C	H	M.p. (°)
$Rh(trop)(COD)$	orange-yellow	85	54.1(54.2)	5.3(5.2)	143–144
$Rh(trop)(NBD)$	orange-yellow	67	53.3(53.2)	4.0(4.1)	133–135 ^{a)}
$Rh(trop)(TFB)$	orange-yellow	63	50.2(49.5)	2.5(2.8)	172–174 ^{a)}
$Rh(i-Pr-trop)(COD)$	orange-yellow	78	55.7(56.8)	6.0(6.1)	122–124
$Rh(i-Pr-trop)(NBD)$	orange-yellow	86	55.0(56.1)	5.1(5.4)	121–123
$Rh(i-Pr-trop)(TFB)$	yellow	65	52.0(51.6)	3.4(3.4)	227–229 ^{a)}
$Rh(Me-trop)(COD)$	yellow	45	55.0(55.5)	5.6(5.5)	151–155 ^{b)}
$Rh(Me-trop)(NBD)$	orange-yellow	41	53.4(54.6)	4.9(4.6)	130–135 ^{b)}
$Rh(sal)(COD)$	yellow	45	53.5(54.2)	5.0(5.2)	138–140 ^{a)}
$Rh(sal)(NBD)$	orange-yellow	59	52.9(53.2)	4.0(4.1)	140–145 ^{b)}
$Rh(sal)(TFB)$	yellow	62	49.2(49.5)	2.6(2.8)	194–196 ^{a)}

^{a)} M.p. (dec.); ^{b)} Dec.

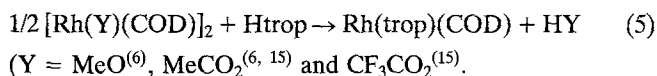
absorptions at 1330 and 1610 cm^{-1} respectively⁽¹¹⁾. The observed ^1H n.m.r. resonances of the Rh(A)(diolefin) complexes are collected in Table 2. In general, a complex multiplet is observed for the ring protons of the anionic ligands.

Reactivity

The Rh(A)(diolefin) complexes usually react readily with different ligands. We report below some representative examples starting from Rh(trop)(COD).

Thus, addition of the acidic bidentate ligands 8-hydroxyquinoline (Hoq), pyrazole (Hpz), and Schiff bases of salicylaldehyde (salanil, salen), lead to the displacement of the tropolonate group and formation of the previously described complexes: $\text{Rh}(\text{oq})(\text{COD})^{(12)}$, $[\text{Rh}(\text{pz})(\text{COD})]_2^{(13)}$, $\text{Rh}(\text{salanil})(\text{COD})$ and $\text{Rh}_2(\text{salen})(\text{COD})_2^{(14)}$.

Similarly, Rh(trop)(COD) reacts with CpTi to give the well known complex Rh(Cp)(COD)⁽⁶⁾. No reaction was observed when Rh(trop)(COD) was treated with MeCO_2Na , MeCO_2H and $\text{CF}_3\text{CO}_2\text{H}$ under reflux conditions. On the contrary, $[\text{Rh}(\text{Y})(\text{COD})]_2$ complexes react with tropolone at room temperature in dichloromethane or acetone solution according to Equation (5):



On the other hand, treatment of Rh(trop)(COD) with perchloric acid and several neutral ligands [pyridine (py), TMEDA (tmen), triphenylphosphine (PPh_3), bis(1,2-diphenylphosphino) ethane (diphos) and hexamethylbenzene (C_6Me_6)] permits the isolation of the following complexes: $[\text{Rh}(\text{COD})(\text{py})_2]\text{ClO}_4$, $[\text{Rh}(\text{COD})(\text{tmen})]\text{ClO}_4^{(16)}$, $[\text{Rh}(\text{COD})(\text{PPh}_3)_2]\text{ClO}_4$, $[\text{Rh}(\text{COD})(\text{diphos})]\text{ClO}_4^{(17)}$ and $[\text{Rh}(\text{COD})(\text{C}_6\text{Me}_6)]\text{ClO}_4^{(18)}$.

The Rh(trop)(COD) complex, in the presence of an excess of triphenylphosphine, is an active catalyst precursor for the homogeneous hydroformylation of 1-heptene. The experimental results suggest that the tropolonate and cyclooctadiene ligands are cleaved from the rhodium ion under hydroformylation conditions (100°; total pressure 50 atm) and therefore species of the type $\text{RhH}(\text{CO})_x(\text{PPh}_3)_2^{(19)}$ ($x = 1$ or 2) could be responsible for the catalysis. In fact, the cleavage of coordinated β -ketoenolates on dicarbonyl-rhodium(I)- β -ketoenolates complexes under hydroformylation conditions has been recently reported by Schurig⁽²⁰⁾. Nevertheless, this type of compound can be used as stable catalyst precursors.

Table 2. I.r. and ^1H n.m.r. data for Rh(A)(diolefin) complexes.

Complex	Representative i.r. data 1300–1620 cm^{-1}	^1H n.m.r. ^{a)} Diolefin protons (τ)	A protons (τ)
Rh(trop)(COD)	1350, 1495, 1585	5.65(CH=CH) 7.5(CH ₂) 8.19(CH ₂)	2.5–3.0(H-ring)
Rh(trop)(NBD)	1350, 1500, 1585	5.94(CH=CH) 6.14(CH) 8.76(CH ₂)	2.5–3.0(H-ring)
Rh(trop)(TFB)	1350, 1500, 1590	6.13(CH=CH) 4.44(CH)	2.5–3.0(H-ring)
Rh(i-Pr-trop)(COD)	1350, 1495, 1570, 1585	5.72(CH=CH) 7.55(CH ₂) 8.18(CH ₂)	2.6–3.2(H-ring) 7.16(CH) 8.75(CH ₃) ^{b)}
Rh(i-Pr-trop)(NBD)	1350, 1495, 1570, 1585	5.96(CH=CH) 6.2(CH) 8.7(CH ₂) ^{c)}	2.6–3.1(H-ring) 7.16(CH) 8.75(CH ₃) ^{b)}
Rh(i-Pr-trop)(TFB)	1350, 1495, 1570, 1585	6.14(CH=CH) 4.44(CH)	2.6–3.0(H-ring) 7.10(CH) 8.75(CH ₃) ^{b)}
Rh(Me-trop)(COD)	1350, 1500, 1570, 1585	5.74(CH=CH) 7.50(CH ₂) 8.18(CH ₂)	2.6–3.1(H-ring) 7.60(CH ₃)
Rh(Me-trop)(NBD)	1350, 1500, 1570, 1585	5.98(CH=CH) 6.14(CH) 8.76(CH ₂)	2.6–3.1(H-ring) 7.58(CH ₃)
Rh(sal)(COD)	1330, 1610	5.78(CH=CH) 7.54(CH ₂) 8.20(CH ₂)	2.6–2.8; 3.0–3.4(H-ring) 1.03(H-ald)
Rh(sal)(NBD)	1320, 1610	6.04(CH=CH) 6.18(CH) 8.80(CH ₂)	2.5–2.8; 3.0–3.4(H-ring) 1.05(H-ald)
Rh(sal)(TFB)	1330, 1610	6.10(CH=CH) 4.44(CH)	2.5–2.8; 3.1–3.4(H-ring) 1.02(H-ald)

^{a)} Data obtained using CDCl_3 solutions; ^{b)} J(CH–CH₃) = 6 Hz; ^{c)} Partially masked by CH₃ groups.

Experimental

$\text{RhCl}_3 \cdot 3 \text{H}_2\text{O}$, diolefins (COD, NBD), salicylaldehyde and solvents (reagent grade) were obtained from E. Merck, tropolone from Aldrich Chemical Co and β -isopropyl-tropolone from Koch-Light Labs. Ltd. Tetrafluorobenzobarrelene, β -methyltropolone and the thallium derivatives were prepared by published procedures^(5, 21, 22).

The C and H analyses were made with a Perkin-Elmer 240 microanalyser; the i.r. spectra were recorded on a Perkin-Elmer 567 spectrophotometer (over the range 4000–200 cm^{-1}) using Nujol mulls between KBr discs or polyethylene sheets. The ^1H n.m.r. spectra were obtained on a Varian XL-100 instrument. Melting points were determined with a Bristoline apparatus provided with microscope and heating device.

Synthesis of Rh(trop)(diolefin) complexes

A mixture of $[\text{RhCl}(\text{diolefin})]_2$ and the stoichiometric amount of Tl(trop) were boiled under reflux in CH_2Cl_2 or CHCl_3 , with stirring, for 2 h. The TlCl formed was filtered off through kieselguhr and the orange filtrate was evaporated to 2–3 cm^3 . The complexes were precipitated by addition of petroleum ether and recrystallized from CH_2Cl_2 :petroleum ether.

Alternative methods for the synthesis of Rh(trop)(COD) were as follows:

(i) A slight excess of Htrop was added to a MeOH solution of Rh(acac)(COD)⁽⁶⁾. After addition of H_2O the precipitate was filtered off, washed with MeOH, and air dried.

(ii) $[\text{Rh}(\text{COD})_2]\text{ClO}_4^{(15)}$ was treated with a slight excess of Htrop and an aqueous solution of KOH. The suspension was stirred for 15 min and then filtered and washed with MeOH.

Rh(i-Pr-trop)(diolefin) complexes

A stoichiometric amount of Tl(i-Pr-trop) was added to a CH_2Cl_2 solution of the $[\text{RhCl}(\text{diolefin})]_2$ complex. After stirring for 4 h at room temperature, the TlCl formed was removed by filtration through kieselguhr. The resulting yellow solution was evaporated to 3–4 cm^3 and crystallization was induced by the addition of petroleum ether. The resulting solid was filtered off, washed with petroleum ether and air-dried.

Rh(Me-trop)(diolefin) complexes

To a suspension of the dimeric $[\text{RhCl}(\text{diolefin})]_2$ complex and the stoichiometric amount of HMe-trop in Et_2O , was

added dropwise, with vigorous stirring, an aqueous solution of KOH. After stirring at room temperature for 2 h the Et₂O layer was separated, dried with anhydrous MgSO₄ and evaporated. The crystals thus obtained were recrystallized from CH₂Cl₂-petroleum ether.

Rh(sal)(diolefin) complexes

A slurry of [RhCl(diolefin)]₂ and the stoichiometric amount of Tl(sal) in CHCl₃ was boiled under reflux for 2 h followed by filtration through kieselguhr. The resulting solution was evaporated to dryness and the residue was extracted with the minimal amount of CH₂Cl₂.

Addition of petroleum ether caused precipitation of the complex which was recrystallized from CH₂Cl₂:petroleum ether.

Reactions of Rh(trop)(COD)

i) A MeOH solution of Rh(trop)(COD) was treated with a slight excess of the corresponding acidic ligand (Hoq, Hpz, room temperature; Hsalanil, H₂salen, reflux conditions) and the mixture was stirred for 15 min. The products were filtered off, washed with MeOH or Et₂O and air dried.

ii) A Me₂CO solution of Rh(trop)(COD) was treated with 1 mol of HClO₄, followed by addition of a stoichiometric amount of py, TMEDA, Ph₃P, (Ph₂PCH₂)₂ or Me₆C₆. The resulting solution was concentrated to ca. 3 cm³ and the desired product was precipitated by addition of Et₂O.

The products of the above reactions were characterized mainly by comparison of their i.r. and n.m.r. spectra with pure samples obtained by reported methods^(6, 12–14, 16–18).

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Dioxouranium(VI) Complexes with Potentially Dibasic Tridentate Schiff Base Ligands. Characterization of the Uranyl Complexes of Salicylaldehyde-2-hydroxyanil and its Substituted Derivatives

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Summary

Some 1:1, 2:3, and 1:2 uranyl complexes of salicylaldehyde-2-hydroxyanil (H₂SAP) and its substituted (3-methoxy-, 5-nitro-, 5-chloro- and 3,5-dichloro-) derivatives have been synthesized and characterized. The conductivity, i.r., ¹H n.m.r. and visible spectroscopic data allow discussion

of the varying ligating behaviour of the potentially dibasic tridentate Schiff base ligands toward dioxouranium(VI).

Introduction

The Schiff base complexes of dioxouranium(VI), particularly those using mono- and dibasic tridentate ligands, have attracted considerable interest in recent years^(1–4). Many of the ligands are N-substituted salicylaldimines which can potentially form five- and six-membered chelate rings with their

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