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ISOLATION, CHARACTERIZATION AND RESOLUTION OF 1,3,5,7-TETRAMETHYL-2,6,9-TRIOXO-BICYCLO[3.3.1]NONA-3,7-DIENE *

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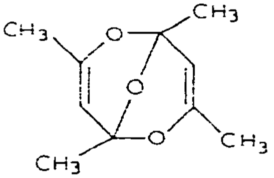
Summary

1,3,5,7-Tetramethyl-2,6,9-trioxo-bicyclo[3.3.1]nona-3,7-diene, a dimer of acetylacetone which is formed as a coordinated species through a Pt(II) promoted condensation, can be displaced from the complex by sodium cyanide treatment. This new compound forms stable chelate π-complexes with Pd(II) and Rh(I) and has been resolved into optical isomers by fractional crystallization of a diastereoisomeric Rh(I) complex.



Introduction

The title compound (henceforth denoted TOND) was identified in 1967 by D. Gibson et al. as a ligand in a Pt(II) complex [2], and its structure was later confirmed by X-ray crystallographic analysis [3]. However, in spite of its unusual structure, no attempt to isolate uncoordinated TOND has been previously reported.

We wish to report below the isolation and characterization of TOND, the preparation of its complexes with Pd(II) and Rh(I), and the resolution of its enantiomers. The results provide an additional example of syntheses of organic substrates made possible by transition metal chemistry [2,4].

Experimental

All solvents and reagents were of reagent grade. Melting points are uncorrected. IR spectra were recorded with a Perkin—Elmer spectrophotometer

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* Some account of this work has been presented in a preliminary note [1].

Model 457 in nujol mulls or in CCl_4 solution. ^1H NMR spectra were recorded on a Varian T-60-A spectrometer at 29°C. Mass spectra were determined on a AEI MS 902 spectrometer. Optical measurements were made with a Perkin—Elmer Model 141 polarimeter using 1.00-dm cells. Microanalyses were carried out by the Mikroanalitisches Laboratorium A. Bernhardt, Elbach, West Germany. (*S*)-α-methylbenzenemethanamine had $[\alpha]_D^{20}$ —40.3 (neat).

Potassium bis(1-acetylacetonyl)(2,4-pentanedionato)platinate(II), K[Pt(acac)$_3$]

This complex was prepared by published procedure [5] with some modifications. To a solution of $K_2[PtBr_4] \cdot H_2O$ (61.1 g, 0.10 mol) in 250 ml of water, 40.0 g (0.40 mol) of acetylacetone, dissolved in 160 ml of 2.5 *M* KOH, was added. The mixture was stirred at room temperature for 48 h. The solution colour faded and a green-yellow precipitate was formed. The precipitate was filtered off, washed with ethanol, benzene, ether and dried (46.7 g, 88% yield). This compound had IR and ^1H NMR spectra identical with those reported [5] for the $K[Pt(acac)_3]$complex.

Dichloro(3,4,7,8-η)-1,3,5,7-tetramethyl-2,6,9-trioxo-bicyclo[3.3.1]nona-3,7-dieneplatinum(II), [PtCl$_2$(TOND)]

To a solution of $K[Pt(acac)_3]$ (45.1 g, 0.085 mol) in 1.5 l of water, 6 *N* HCl was added dropwise at room temperature with stirring, until precipitation of a green-yellow solid was complete. The solid was filtered off, washed with water and dried. Recrystallization from chloroform/ether gave 28.6 g (75% yield) of pale green crystals, m.p. 200—210°C (dec). The IR and ^1H NMR spectra of the complex were identical with those previously reported [2].

1,3,5,7-Tetramethyl-2,6,9-trioxo-bicyclo[3.3.1]nona-3,7-diene, TOND

$[PtCl_2(TOND)]$ (26.9 g, 0.060 mol) was added in portions with stirring to a solution of 14.7 g (0.30 mol) of NaCN in 150 ml of water at 0°C. n-Pentane (50 ml) was then added, and when the dissolution of the platinum complex was complete, the organic layer was removed. The aqueous solution was extracted three times with 50 ml of n-pentane. The combined organic layers were washed twice with 10 ml of water and dried over Na_2SO_4. Evaporation of the n-pentane extract under vacuum gave a white solid, which was sublimed at room temperature (0.05 mmHg) to give 10.5 g (ca. 100%) of TOND, m.p. 48—49°C (Found: C, 65.99; H, 7.68. $C_{10}H_{14}O_3$ calcd: C, 65.92; H, 7.74). Mass spectrum (70 eV) showed the parent peak at *m/e* 182 (5% $C_{10}H_{14}O_3^{+\cdot}$) and the base peak at *m/e* 43 (CH_3CO^+). IR spectrum (in CCl_4 solution) showed the following absorption bands (cm^{-1}): 3075vw, 3000m, 2960m, 2940sh, 2925m, 1720vw, 1680vs, 1440m, 1385vs, 1345s, 1240vs, 1200s, 1150m, 1130w, 1095m, 1070s, 1040w, 1025w, 995m, 945s, 880s, 860vs, 690m, 585w, 555w, 510w, 460w, 410w. In the region 700—850 cm^{-1} the IR spectrum (in nujol mull) showed bands at 825m and 790s cm^{-1}.

The UV spectrum of freshly sublimed TOND in ethanol showed no absorption bands above 220 nm. A solution of TOND in ethanol/water 50% v/v containing 5% of H_2SO_4 showed intense absorption maxima in the 220—250 nm region and a band near 1700 cm^{-1} in the IR spectrum indicating the presence of a ketonic group.

Dichloro(3,4,7,8-η)-1,3,5,7-tetramethyl-2,6,9-trioxo-bicyclo[3.3.1]nona-3,7-dienepalladium(II), [PdCl$_2$(TOND)]

Freshly prepared [6] $[\{PdCl_2(C_2H_4)\}_2]$ (0.822 g, 0.002 mol) was suspended in 10 ml of benzene and a solution of TOND (0.911 g, 0.005 mol) in 5 ml of benzene was added with stirring. Gas evolution was observed. After 1 h stirring at 5°C, the solvent was removed in vacuo and the resulting solid was washed with n-pentane, then dissolved in the minimum amount of chloroform. Dilution of the chloroform solution with ether gave 1.18 g (82% yield) of an orange crystalline complex, m.p. 105—110°C (dec.) (Found: C, 33.28; H, 3.85; Cl, 19.60; mol.-wt. 345, osmometric in $CHCl_3$. $C_{10}H_{14}Cl_2O_3Pd$ calcd: C, 33.41; H, 3.92; Cl, 19,52; mol.-wt. 359.5). The IR spectrum showed characteristic absorption bands at 1505 cm^{-1} (coordinated olefinic grouping) and 1240 cm^{-1} (unsaturated ether grouping).

Di-μ-chlorobis(3,4,7,8-η)-1,3,5,7-tetramethyl-2,6,9-trioxo-bicyclo[3.3.1]nona-3,7-dienedirhodium(I), [{RhCl(TOND)}$_2$]

Freshly prepared [7] $[\{RhCl(C_2H_4)_2\}_2]$ (1.94 g, 0.005 mol) was suspended in 20 ml of ether and 3.64 g (0.020 mol) of TOND in 10 ml of ether was added with stirring. After 24 h the solvent was removed in vacuo and the resulting solid was washed with 30 ml of n-pentane to extract the unreacted TOND. Recrystallization of the residue from methylene chloride/n-heptane gave 3.08 g (96% yield) of a red-orange crystalline complex, m.p. 180—190°C (dec.) (Found: C, 37.32; H, 4.28; Cl, 11.00; mol.-wt. 630, osmometric in $CHCl_3$ $C_{20}H_{28}Cl_2O_6Rh_2$ calcd.: C, 37.46; H, 4.40; Cl, 11.06; mol.-wt. 641.2). The IR spectrum showed characteristic absorption bands at 1480 cm^{-1} (coordinated olefinic grouping) and 1235, 1220 cm^{-1} (unsaturated ether grouping).

Hydrolysis of coordinated TOND

To a solution of 0.45 g (0.001 mol) of [PtCl$_2$(TOND)] in 10 ml of methylene chloride, hydrate sodium carbonate was added at room temperature with stirring. After a few minutes a yellow solid began to precipitate. Stirring was continued for 1 h and the yellow precipitate was filtered off and dissolved in a few drops of water. Acetone was then added to precipitate the inorganic salts and the solution was filtered, and evaporated to dryness to give 0.3 g of a yellow product. The IR and ^{1}H NMR spectra of the product were identical to those reported [5] for the known $Na_2[Pt(acac)_2Cl_2]$ complex. Addition of dilute HCl to an aqueous solution of this material precipitated a green-yellow solid which was identified as the starting [PtCl$_2$(TOND)] complex.

Resolution of TOND via Rh(I)-complex

To a solution of 2.56 g (0.004 mol) of [{RhCl(TOND)}$_2$] in 20 ml of $CHCl_3$, 0.97 g (0.008 mol) of (*S*)-α-methylbenzenemethanamine dissolved in 10 ml of the same solvent was added dropwise with stirring at 0°C. After 0.5 h a 1 ml-aliquot of the solution was withdrawn. Evaporation of the solvent from this sample gave a yellow residue having $[\alpha]^{20}_D$ +8.5, $[\alpha]^{20}_{546}$ +14 (*c* 0.8, chloroform). The residual mother solution was diluted with an equal volume of n-heptane and after 2 h standing at 0°C, 1.7 g of a yellow solid was collected: $[\alpha]^{20}_D$ +243 (*c* 0.2, chloroform). This product was recrystallized from chloroform/n-heptane 1 : 1 until constant rotation was achieved. Finally, 1.35 g (40% yield) of the first diastereoisomer was obtained, $[\alpha]_D^{20}$ +270, $[\alpha]_{546}^{20}$ +330 (*c* 0.2, chloroform); m.p. 180—185°C (dec.) (Found: C, 48.80; H, 5.65; N, 3.06; mol.-wt. 425 osmometric in $CHCl_3$. $C_{18}H_{25}ClNO_3Rh$ calcd.: C, 48.94; H, 5.70; N, 3.17; mol.-wt 441.8).

The mother liquid was evaporated in vacuo and the resulting solid residue (1.3 g) had $[\alpha]_D^{20}$ −190 (*c* 0.2, chloroform). Attempts to achieve a better optical purity for this diastereoisomer by recrystallization failed because of its very high solubility in organic solvents. However, extraction of the crude product with five 10 ml-portions of n-heptane/benzene (20 : 1), followed by evaporation of the extract gave 0.85 g (25% yield) of a material having $[\alpha]_D^{20}$ −230, $[\alpha]_{546}^{20}$ −285 (*c* 0.2, chloroform).

Enantiomeric $[\{RhCl(TOND)\}_2]$

To a suspension of (+)$[RhCl(C_8H_{11}N)(TOND)]$ (1.10 g, 0.0025 mol) in 15 ml of methylene chloride was added 15 ml of 0.2 *N* aqueous HCl. Upon vigorous shaking the complex dissolved completely to give a red solution. The aqueous layer was removed, the methylene chloride solution washed with 5 ml of water, then dried over Na_2SO_4. Subsequently 10 ml of n-heptane was added, and the solution was concentrated in vacuo until crystallization occurred. Filtration gave red crystals of (+)$[\{RhCl(TOND)\}_2]$ (0.75 g, 93% yield), m.p. 190—195°C (dec); $[\alpha]_D^{20}$ +260, $[\alpha]_{546}^{20}$ +225 (*c* 0.2, chloroform).

By a similar procedure, a binuclear complex with $[\alpha]_D^{20}$ −250 (*c* 0.2, chloroform) was obtained from the diastereoisomer with $[\alpha]_D^{20}$ −230.

Enantiomeric TOND by cyanide treatment

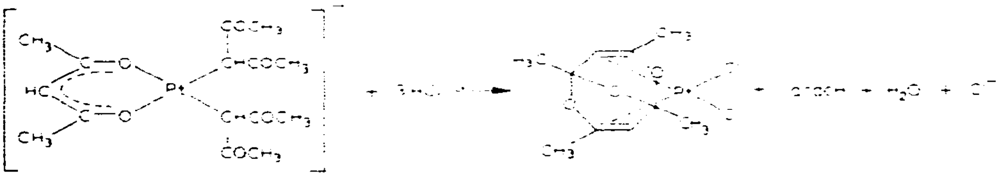
To a solution of 0.49 g (0.010 mol) of NaCN in 10 ml of water, 10 ml of n-pentane and (+)$[\{RhCl(TOND)\}_2]$ (0.64 g, 0.001 mol) were added at 0°C. The mixture was stirred until dissolution was complete. The organic layer was removed and the aqueous solution was extracted twice with 5 ml of n-pentane. The combined extracts were washed with 5 ml of water and dried over Na_2SO_4. Removal of n-pentane in vacuo gave a white solid, which was purified by sublimation at room temperature (0.05 mmHg). Pure (+)TOND (0.070 g, 20% yield), identified by IR and ^1H NMR spectra, was obtained: $[\alpha]_D^{20}$ +85; $[\alpha]_{546}^{20}$ +110 (*c* 0.3, carbon tetrachloride).

Enantiomeric TOND by COD treatment

(−)$[\{RhCl(TOND)\}_2]$ (0.32 g, 0.0005 mol) was dissolved in the minimum amount of methylene chloride and 1,5-cyclooctadiene (0.11 g, 0.001 mol) was added at room temperature. After 0.5 h stirring the solvent was removed in vacuo and the resulting solid was extracted with 10 ml of n-pentane. The residual yellow-orange solid was identified as the $[\{RhCl(COD)\}_2]$ complex by comparison of its IR and ^1H NMR spectra with those of an authentic sample. Work-up of the n-pentane solution as above described gave (−)TOND in a nearly quantitative yield: $[\alpha]_D^{20}$ −84; $[\alpha]_{546}^{20}$ −108 (*c* 0.3, carbon tetrachloride).

Results and discussion

Coordinated TOND is formed [2] by condensation * in presence of HCl or HBr of the two acetylacetonate (acac) units [9] σ-bound through the γ-carbon to Pt(II) in the $[Pt(acac)_3]^-$ complex:



This type of Pt(II)-promoted condensation reaction, the mechanism of which is not yet fully understood, is known for unsaturated alcohols [10] and halides [11].

Free TOND

The TOND can be almost quantitatively removed from the complex by mild treatment with acqueous sodium cyanide and purified by sublimation. Analytical and structural data, i.e. elemental analysis, IR, ^{1}H NMR and mass spectrum parameters, of isolated TOND point to a structure identical with that of coordinated TOND [3], indicating that removal from the metal does not induce any substantial structural modification.

TOND is a white crystalline solid with a camphor-like smell. It is rather stable at room temperature and is not reduced by $NaBH_4$. Catalytic hydrogenation did not lead to the isolation of the corresponding saturated derivative, a complex mixture of products being formed.

Free TOND is readily hydrolyzed by dilute acids at room temperature, but is not affected by dilute base. Conversely, coordinated TOND is quite stable in a mild acidic medium but is readily hydrolyzed by bases. Thus on addition of hydrated sodium carbonate to a dichloromethane solution of $[PtCl_2(TOND)]$, a yellow-green compound is precipitated; its IR spectrum is identical with that of the known [5] $Na_2[PtCl_2(acac)_2]$. It is noteworthy that this reaction is reversible, since the original $[PtCl_2(TOND)]$ complex is formed on treatment of $Na_2[PtCl_2(acac)_2]$ with HCl.

Pd(II) and Rh(I) complexes

TOND shows a fairly good coordinating ability. Two new complexes with Pd(II) and Rh(I) were prepared from the corresponding ethylene complexes:

$$[PdCl_2(C_2H_4)]_2 + 2\ TOND \rightarrow 2[PdCl_2(TOND)] + 2\ C_2H_4$$

$$[\{RhCl(C_2H_4)_2\}_2] + 2\ TOND \rightarrow [\{RhCl(TOND)\}_2] + 4\ C_2H_4$$

The complex of TOND with Pd(II) is a stable crystalline mononuclear complex; its ^{1}H NMR data are given in Table 1. Treatment with CN^- regenerates unchanged TOND.

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* The condensation of acetylacetone in a reducing medium affords a tricyclic dimer having the nor-adamantane skeleton [8].

TABLE 1

^{1}H NMR DATA OF TOND AND RELATED METAL COMPLEXES [a]

Compound	H—C=C	CH_3—C=C	CH_3—C
TOND	4.68	1.78	1.56
$[PtCl_2(TOND)]$ [b]	4.42(82)	2.19(33)	1.73(4)
$[PdCl_2(TOND)]$	4.80	2.50	1.83
$[\{RhCl(TOND)\}_2]$ [c]	3.35(3)	2.08	1.60
	3.16(3)	1.87	1.55
$[RhCl(C_6H_5CH(CH_3)NH_2)(TOND)]$ [d]	3.5(un) [e]	2.10	1.48

[a] $CDCl_3$ solutions with TMS as internal standard; chemical shifts are given in δ (ppm) and are referred to the centers of gravity of the multiplets. [b] See also ref. 2; the $J^{195}Pt$—H coupling constants (in Hz) are reported in brackets. [c] The two sets of chemical shifts refer to the racemic and "*meso*" modification respectively; the *J*Rh—H coupling constants (in Hz) are reported in brackets. [d] The chemical shifts of the amine ligand are δ8.15 (C_6H_5); 4.2 (broad, $CH(CH_3)$); 1.73 ppm (doublet CH—CH_3). [e] un = unresolved.

The complex with Rh(I) is a stable binuclear compound which also yields free TOND upon treatment with cyanide ion.

Owing to the dissymmetric nature of TOND, the binuclear complex must be a mixture of two diastereoisomers, one (actually a racemic form) containing two diene molecules having the same absolute configuration, the other containing two diene molecules of opposite absolute configuration.

In absence of any asymmetric induction the two forms should be in a 1 : 1 ratio. In fact the ^{1}H NMR spectrum of $[\{RhCl(TOND)\}_2]$ (Fig. 1) shows two distinct resonance bands for each set of magnetically equivalent protons of the ligands, in the intensity ratio 7 : 3. The comparison of this spectrum with that

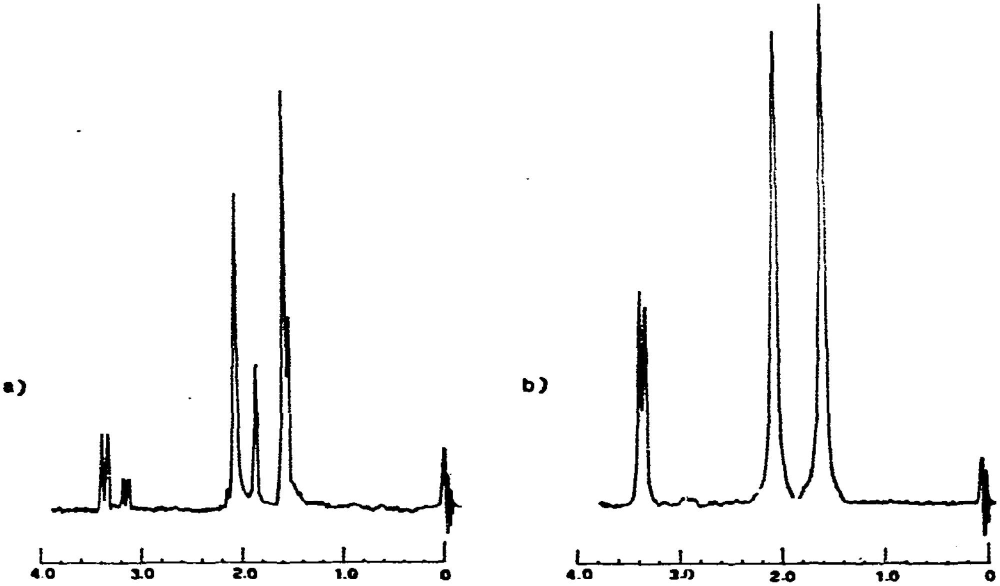


Fig. 1. ^{1}H NMR spectra of $[\{RhCl(TOND)\}_2]$ isomeric mixture (a) and resolved (+)$[\{RhCl(TOND)\}_2]$ (b).

of the isolated enantiomer (vide infra), (+)$[\{RhCl(TOND)\}_2]$, allows the identification of the minor component of the diastereoisomeric mixture and this reveals that the binuclear "*meso*" isomer is present in smaller amount, indicating that coordination of one TOND molecule favours the binding of another unit with the same absolute configuration.

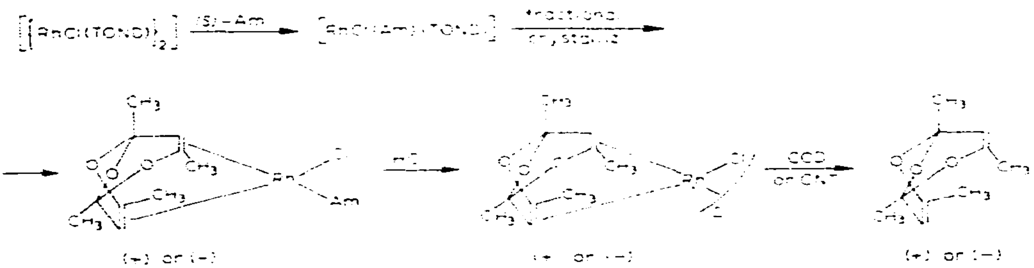
No change was observed in the ^{1}H NMR spectra over the temperature range —60 to +60° C indicating that the ratio of the optical isomers does not vary with temperature.

Resolution of TOND

As a further example of the use of transition metals complexes in the resolution of asymmetric dienes [12,13] we attempted the separation of the enantiomers of TOND via its complexes. In the early attempts we used Pt(II) and Pd(II) complexes of the diene, following the methods described for similar compounds [12,13]. These methods involve as the first step the transformation of the coordinated diene to a σ-alkyl derivative by a nucleophilic addition of base such as an alkoxide or an amine to one of the coordinated double bonds. In the case of the Pt(II) and Pd(II) complexes of TOND this procedure was unsuccessfull because of the instability of coordinated TOND towards base.

Satisfactory results (Scheme 1) were obtained by use of the binuclear chloro-bridged Rh(I) complex, which is directly suitable for a bridge-splitting reaction with a chiral amine. Thus treatment of the complex $[\{RhCl(TOND)\}_2]$ with (*S*)-α-methylbenzenemethaneamine (*S*-Am) in stoichiometric amount yielded a mixture of diastereoisomeric mononuclear complexes. The mixture was subjected to fractional crystallization from 1 : 1 chloroform/n-heptane to give the less soluble isomer with $[\alpha]_D^{20}$ +270. The second diastereoisomer is more soluble in organic solvents and its isolation is more difficult, but a product with $[\alpha]_D^{20}$ —230 was obtained.

SCHEME 1



The enantiomers of $[\{RhCl(TOND)\}_2]$ can be obtained by treatment of the crystallized diastereoisomers with a slight excess of HCl:

$$2[RhCl(S\text{-}Am)(TOND)] + 2\,HCl \rightarrow [\{RhCl(TOND)\}_2] + 2(S)\text{-}Am \cdot HCl$$

The ^{1}H NMR spectrum of the regenerated (+)$[\{RhCl(TOND)\}_2]$ ($[\alpha]_D^{20}$ +260) indicates an optical purity of > 95%.

Cyanide treatment of the binuclear complex yields the optically active TOND with $[\alpha]_D^{20}$ +85 but only in 20% yield, whereas with the Pt(II) complex the recovery is almost quantitative. The low yield in the case of the Rh(I) complex may be due to irreversible denaturation of coordinated TOND by the action of CN^- or by the water-soluble $Rh{-}CN^-$ complexes which are formed.

Almost quantitative yields were obtained when TOND was displaced from the (−) complex in dichloromethane solution by treatment with stoichiometric amounts of 1,5-cyclooctadiene (COD):

$$[\{RhCl(TOND)\}_2] + 2\ COD \rightarrow 2\ TOND + [\{RhCl(COD)\}_2]$$

Our work provides the first example of the resolution of an asymmetric diene by use of complexes of the type $[(diene)RhClL^*]$ (where L^* is an asymmetric ligand). This method is more convenient than that based on Pt(II) complexes [12] since in the latter case it is necessary to carry out and then reverse a nucleophilic addition.

Acknowledgements

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