

REDUCTION OF COBALT CHELATES OF BIS(SALICYLALDEHYDE)ETHYLENEDIIMINE AND SYNTHESIS OF ORGANOCOBALT DERIVATIVES

G. COSTA, G. MESTRONI AND G. PELLIZER

Institute of Chemistry, University of Trieste, Trieste (Italy)

(Received July 17th, 1967)

INTRODUCTION

A new series of stable organocobalt chelates with planar tetradentate ligand systems, bis(acetylacetonate)ethylenediiminato dianion (BAE): $[\text{RCo}(\text{BAE})]$ or $[\text{RCo}(\text{BAE})\text{L}]^1$ and bis(salicylaldehyde)ethylenediiminato dianion (salen): $[\text{RCo}(\text{salen})]$ or $[\text{RCo}(\text{salen})\text{L}]^2$, (R = alkyl, aryl; L = donor ligand), were recently obtained by the appropriate Grignard reaction, from the complexes $[\text{XCo}^{\text{III}}(\text{BAE})\text{L}]$ or $[\text{Co}^{\text{III}}(\text{BAE})\text{L}_2]\text{X}$, and $[\text{XCo}^{\text{III}}(\text{salen})\text{L}]$ or $[\text{Co}^{\text{III}}(\text{salen})\text{L}_2]\text{X}$, respectively.

Stabilization of the cobalt-carbon bond was previously observed in the "alkylcobaloximes"³ $[\text{RCo}(\text{DH})_2\text{L}]$, containing the planar bis-bidentate ligand system bis-dimethylglyoximate dianion (DH)₂, which were proposed as model molecules for the vitamin B₁₂ group (alkylcobalamins).

In analogy with the alkylcobalamins⁴ and alkyl porphyrins⁵, the "cobaloximes" can be obtained also by reaction of the appropriate electrophiles with the reduction product (cobaloxime_s) of the parent complexes, $[\text{Co}(\text{DH})_2\text{LL}]^6$.

The reduction product was formulated as the Co^I derivative, H-Co(DH)₂L, containing the Co-H bond⁶.

Work on the reactivity of the Co-C bond and some aspects of the physical chemistry of the complexes of (BAE) and (salen) is still in progress in this laboratory, but we wish to report in the present paper the reduction of the chelates of (salen)⁷ and the preparation of several new organometallic derivatives by reaction of the reduction product with the appropriate electrophiles.

After our preliminary note⁷ was submitted for publication the reduction of $[\text{Co}^{\text{II}}(\text{salen})]$ and preparation of $[\text{CH}_3\text{Co}(\text{salen})\text{L}]$ (L = H₂O, pyridine) was independently reported⁸.

RESULTS

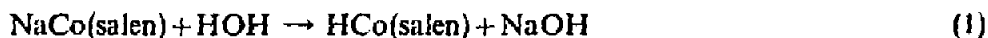
(1) When $[\text{XCo}^{\text{III}}(\text{salen})\text{L}]$ (X = Br; L = PPh₃), $[\text{Co}^{\text{III}}(\text{salen})\text{L}_2]^+\text{X}^-$ (L = py, benzylamine) or $\text{Co}^{\text{II}}(\text{salen})$ are reacted with metallic sodium or 1% sodium amalgam in anhydrous tetrahydrofuran (THF), an intense green solution is obtained. From this solution, the violet solid $\text{NaCo}^{\text{I}}(\text{salen})$ (I) can be isolated (see Table 1). The complex is highly sensitive to air and moisture but is stable at room temperature in an inert atmosphere.

TABLE I
ANALYSES (%) OF (SALEN) COMPLEXES OF COBALT

No.	Formula	C		H		N		
		Calcd.	Found	Calcd.	Found	Calcd.	Found	
(I)	NaCo(salen)	55.19	55.71	4.05	4.61	8.04	7.52	dark-green crystals from THF
(II)	CH ₃ COC ₂ Co(salen)	58.70	58.77	4.65	4.66	7.61	7.70	red crystals from CH ₂ Cl ₂ /C ₆ H ₆
(III)	CH ₃ OCOC ₂ Co(salen)H ₂ O	53.74	53.62	4.76	4.89	6.96	7.10	orange-yellow crystals from methanol/water
(IV)	C ₂ H ₅ OCOC ₂ Co(salen)H ₂ O	54.81	55.00	5.08	5.21	6.73	6.83	orange-yellow crystals from ethanol/water
(V)	CH ₂ =CHCo(salen)H ₂ O	58.39	58.15	5.17	5.21	7.56	7.49	orange-yellow crystals from methanol/water
(VI)	CNCH ₂ CH ₂ Co(salen)H ₂ O	57.44	57.61	5.07	4.99	10.58	10.31	orange-yellow crystals from methanol/water
(VII)	Br(CH ₂) ₄ Co(salen)	52.08	52.12	4.80	5.46	6.07	5.99	red-brown crystals from methanol/water
(VIII)	CH ₃ COC ₂ Co(salen)C ₃ H ₅ N	61.75	61.75	4.95	5.12	9.39	9.50	orange-yellow crystals from pyridine-ether-petroleum ether
(IX)	CH ₃ OCOC ₂ Co(salen)C ₃ H ₅ N	59.61	59.02	4.78	4.95	9.03	8.97	orange-yellow crystals from pyridine-ether-petroleum ether
(X)	C ₂ H ₅ OCOC ₂ Co(salen)C ₃ H ₅ N	60.38	61.00	5.06	5.41	8.80	8.87	orange-yellow crystals from pyridine-ether-petroleum ether
(XI)	CH ₂ =CHCo(salen)C ₃ H ₅ N	64.03	64.83	5.14	5.29	9.74	9.65	orange-yellow crystals from pyridine-ether-petroleum ether
(XII)	CNCH ₂ CH ₂ Co(salen)C ₃ H ₅ N	62.88	63.31	5.06	5.10	12.22	12.27	orange-yellow crystals from pyridine-ether-petroleum ether

Conductivity measurements on solutions of (I) in THF show that dissociation takes place yielding the species $[\text{Co}(\text{salen})]^-$.

Solutions of (I) in THF react with de-aerated water in an inert atmosphere to give green solutions assumed to contain the hydride, $\text{HCo}^{\text{I}}(\text{salen})$ (II), which, in turn, appears to be slowly decomposed yielding, eventually, orange-red solutions of $[\text{Co}^{\text{II}}(\text{salen})]$.



Reaction (2) can be followed quantitatively by measurement of the hydrogen evolved when excess water is added to a concentrated solution of (I) in THF.

Both (I) and (II) are powerful nucleophilic species reacting readily with several electrophilic centres RX ($\text{X} = \text{Cl}, \text{Br}$)



On the other hand, only (I) reacts with unsaturated halides such as $\text{CH}_2=\text{CHCl}$ with retention of the double bond



while (II) adds to acetylene and to activated double bonds.

(2) Reaction of (I) with electrophiles

A number of stable, diamagnetic organometallic derivatives were prepared by reaction (3).

When the products are crystallized by the addition of water and slow evaporation of THF from the reaction solutions, and recrystallized from methanol-water, either the orange-yellow crystalline six-coordinated complexes $[\text{RCo}(\text{salen})\text{H}_2\text{O}]$ ($\text{R} = \text{CH}_3, \text{C}_3\text{H}_7, \text{CH}_2=\text{CH}, \text{CH}_3\text{OCO}, \text{C}_2\text{H}_5\text{OCO}$) or complexes consistent with the formula $[\text{RCo}(\text{salen})]$ ($\text{R} = \text{Br}(\text{CH}_2)_4$: brown crystals; C_2H_5 : brown crystals) are obtained (see Table I).

All the above complexes give green solutions in non-coordinating solvents ($\text{CH}_2\text{Cl}_2, \text{CHCl}_3$). The solutions are assumed to contain the five-coordinated species, $[\text{RCo}(\text{salen})]$. Brown complexes, consistent with this formula were obtained by crystallization from CH_2Cl_2 ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, \text{Br}(\text{CH}_2)_4$).

The acetyl derivative $[\text{CH}_3\text{COCo}(\text{salen})]$ can be obtained as red-violet crystals by crystallization from $\text{CH}_2\text{Cl}_2/\text{C}_6\text{H}_6$. The complex shows a single IR band in the CO-stretching vibration region.

The phenyl derivative could not be prepared by the above reaction. It has been obtained (also the methyl and ethyl derivatives) as a stable compound by the Grignard reaction from $[\text{BrCo}(\text{salen})\text{PPh}_3]^2$.

(3) Reaction of (II) with acetylenes and activated ethylenes

The addition of (II) to double and triple bonds was carried out in THF solution:

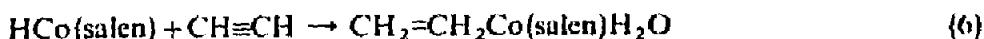
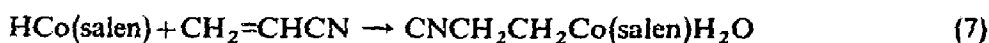


TABLE 2
 ULTRAVIOLET AND VISIBLE ABSORPTION FREQUENCIES AND INTENSITIES OF (SALEN) COMPLEXES OF COBALT
 Frequencies of absorption bands revealed as shoulders, are estimated; intensities are given for the absorption curve at the estimated frequency of the underlying band

Formula	Frequencies ($\text{cm}^{-1} \cdot 10^{-3}$) and $\log \epsilon_{\text{max}}$ (in brackets)		Solvent
NaCo(salen)	28.4	22.0 sh	THF
$\text{Br}(\text{CH}_2)_2\text{Co}(\text{salen})$	29.1 (3.97)	22.0 sh (3.19)	CH_2Cl_2
$\text{CNCH}_2\text{CH}_2\text{Co}(\text{salen})\text{H}_2\text{O}$	29.0 (4.14)	22.7 sh (3.44)	CH_2Cl_2
$\text{CNCH}_2\text{CH}_2\text{Co}(\text{salen})\text{C}_3\text{H}_5\text{N}$	28.7 (3.97)	23.3 sh (3.61)	$\text{EtOH}/\text{C}_3\text{H}_5\text{N}$
$\text{CH}_2=\text{CHCo}(\text{salen})\text{H}_2\text{O}$	29.4 (4.14)	22.7 sh (3.47)	CH_2Cl_2
$\text{CH}_2=\text{CHCo}(\text{salen})\text{C}_3\text{H}_5\text{N}$	28.8 (3.94)	23.2 (3.65)	$\text{EtOH}/\text{C}_3\text{H}_5\text{N}$
$\text{CH}_3\text{COCO}(\text{salen})$		23.5 sh (3.52)	CH_2Cl_2
$\text{CH}_3\text{COCo}(\text{salen})\text{C}_3\text{H}_5\text{N}$	26.3 sh (3.77)	obs	$\text{EtOH}/\text{C}_3\text{H}_5\text{N}$
$\text{CH}_3\text{OCOCO}(\text{salen})\text{H}_2\text{O}$	26.8 sh (3.97)	obs	CH_2Cl_2
$\text{CH}_3\text{OCOCO}(\text{salen})\text{C}_3\text{H}_5\text{N}$	25.8 sh (3.71)		$\text{EtOH}/\text{C}_3\text{H}_5\text{N}$
$\text{C}_2\text{H}_5\text{OCOCO}(\text{salen})\text{H}_2\text{O}$		23.8 (3.79)	CH_2Cl_2
$\text{C}_2\text{H}_5\text{OCOCO}(\text{salen})\text{C}_3\text{H}_5\text{N}$	26.0 sh (3.66)	23.8 (3.79)	$\text{EtOH}/\text{C}_3\text{H}_5\text{N}$
		21.6 (3.49)	
		20.7 sh (3.32)	
		17.7 (3.17)	
		16.4 (3.31)	
		16.4 (3.24)	
		15.0 (2.93)	
		14.8 (3.09)	
		14.0	



The products are stable orange-yellow crystalline compounds.

(4) *Reactions of (I) with unsaturated compounds in the presence of water*

Reactions (6) and (7) also take place when THF solutions of (I) are reacted with water, and (II) is formed as intermediate, in the presence of unsaturated compounds.

(5) The six-coordinated complexes, $[\text{RCo(salen)(py)}]$, were prepared as representative of $[\text{RCo(salen)L}]$ (L = nitrogen Lewis base).

(6) All the organometallic derivatives II–XII are photolabile and are thermally decomposed (200° under vacuum) giving $[\text{Co}^{\text{II}}(\text{salen})]$.

(7) All the compounds are diamagnetic as expected. A comparatively low diamagnetism was observed which may be attributed to a rather high T.I.P. term associated with Co^{III} ¹⁰ (see Table 3).

TABLE 3

MOLAR MAGNETIC SUSCEPTIBILITIES

Compound	$-\chi_M \cdot 10^6$
Salen	151 ± 2
Zn(salen)	150 ± 2
Co(salen)PPh ₃ Br	292.5 ± 6
$[\text{Co(salen)(NH}_3)_2]\text{BrH}_2\text{O}$	163 ± 4
$\text{CH}_3\text{Co(salen)H}_2\text{O}$	111 ± 2
$\text{C}_2\text{H}_3\text{Co(salen)H}_2\text{O}$	114.5 ± 4
$\text{C}_2\text{H}_3\text{Co(salen)}$	96 ± 2
$\text{C}_3\text{H}_7\text{Co(salen)H}_2\text{O}$	117.5 ± 4
$\text{CH}_3\text{OCOCo(salen)H}_2\text{O}$	119 ± 4
$\text{CH}_3\text{COCOC(salen)}$	103 ± 8

Good agreement is found between the experimental value of (salen) susceptibility and the value calculated for its eno-form by Pascal's constants.

(8) Ultraviolet spectra and visible absorptions of several five- and six-coordinated (salen) complexes are reported in Table 2 (see also ref. 2).

DISCUSSION

The reduction of cobalt complexes of salen reported in the present paper appears to take place in much the same way as for the (BAE) complexes⁹. The stability of the organometallic derivatives obtained by reaction of reduction products were briefly discussed in the preceding paper. The reduction reaction and general chemical behaviour of the reduction products further confirm the analogy with the complexes of the vitamin B₁₂ group. Among the various aspects of the physico-chemical properties of the latter and its model molecules, the oxidation state of the cobalt atom is of interest.

In the diamagnetic organometallic complexes, $[\text{RCo}(\text{salen})\text{L}]$ or $[\text{RCo}(\text{BAE})]$, (as in the cobaloximes or alkylcobalamins) the organic group can be regarded as a carbanion and thus the formal oxidation state of the cobalt atom is +3, but the actual oxidation state depends on the nature of the conjugate chelate rings and of the cobalt-carbon bond. The effect of different organic groups on the electronic structure around the cobalt atom is revealed by the position of the absorption band in the 14.5–18 kk region, which is shifted by π -acceptor groups towards higher frequencies (see Table 2). On the other hand, in the $\text{NaCo}(\text{salen})$ and $\text{NaCo}(\text{BAE})$ complexes, as in the alkali metal derivatives of cobaloximes³, the $[\text{Co}(\text{salen})]^-$ species containing Co^1 is considered to be present.

Two electrons/mole are involved in the reduction of $[\text{RCo}(\text{salen})]$ and of alkyl cobaloximes to deeply coloured solutions identical with those obtained with sodium amalgam followed by treatment with water¹¹.

Although direct evidence for the Co-H bond has so far not been obtained, chemical behaviour (*e.g.*, reaction with $\text{CH}\equiv\text{CH}$ yielding the vinyl derivatives) can be explained either by the addition of the hydrides, $\text{HCo}(\text{salen})$, $\text{HCo}(\text{BAE})$ or $\text{HCo}(\text{DH})_2\text{L}$ to the unsaturated compound or, alternatively, by the reaction of the Co^1 complex anion with the unsaturated compound to give a carbanion.

EXPERIMENTAL

$\text{NaCo}(\text{salen})$ (I)

$[\text{Co}^{\text{II}}(\text{salen})]$ (3.25 g, 10 mmole) dissolved in anhydrous THF was reduced with excess Na or 1% Na(Hg) in an inert atmosphere. The green solution was filtered and evaporated under vacuum at room temperature. A bright violet solid was obtained.

Reaction of (I) with water. $\text{NaCo}(\text{salen})$ (1.81 mmole) in anhydrous THF (150 ml) was treated with de-aerated water (5 ml) at room temperature. During one hour, 20.8 ml of H_2 (S.T.P.) was evolved (calcd. for $\text{HCo}(\text{salen})$, 20.25 ml). The orange-yellow solution was concentrated under vacuum and $[\text{Co}^{\text{II}}(\text{salen})]$ quantitatively recovered. The product was identical with an authentic sample (IR spectra).

$[\text{RCo}(\text{salen})\text{H}_2\text{O}]$, ($\text{R} = \text{CH}_3, n\text{-C}_3\text{H}_7$) and $\text{RCo}(\text{salen})$ ($\text{R} = \text{C}_2\text{H}_5$)

$[\text{Co}^{\text{II}}(\text{salen})]$ (3.25 g, 10 mmole) or $[\text{BrCo}(\text{salen})\text{PPh}_3]$ (6.67 g, 10 mmole) dissolved in anhydrous THF (150 ml) were reduced in an inert atmosphere with 1% Na(Hg). The amalgam was withdrawn from the green solution which was then treated at low temperature (-50°) with the stoichiometric amount of the appropriate alkyl halide RX ($\text{X} = \text{Br}, \text{I}$) giving immediately a deep orange solution. The reaction mixture was poured in water (100 ml). Evaporation under vacuum produced orange-yellow ($\text{R} = \text{CH}_3, n\text{-C}_3\text{H}_7$) or red-brown ($\text{R} = \text{C}_2\text{H}_5$) crystals. The compounds were recrystallized from methanol-water (80% yield), and were identical with those obtained from the Grignard reaction².

$[\text{Br}(\text{CH}_2)_4\text{Co}(\text{salen})]$ (III)

Obtained as above from 1,4-dibromobutane as red-brown crystals (70% yield).

$[\text{CH}_3\text{OCOCo}(\text{salen})\text{H}_2\text{O}]$ (IV); $[\text{C}_2\text{H}_5\text{OCOCo}(\text{salen})\text{H}_2\text{O}]$ (V)

Obtained as above from ClCOOR ($\text{R} = \text{CH}_3, \text{C}_2\text{H}_5$) as orange-yellow crystals (80% yield).

$[CH_3COCo(salen)]$ (VI)

Obtained as above from CH_3COCl or $(CH_3CO)_2O$. Recrystallized from $CH_2Cl_2C_6H_6$ as red crystals (50% yield).

 $[CH_2=CHCo(salen)H_2O]$ (VII)

Obtained (a) by treatment of a THF solution of (I) with $CH_2=CHCl$ at room temperature; after standing (12 h), the reaction mixture was poured into water and evaporated under vacuum (10% yield); (b) after reaction of a THF solution of (I) with water, the solution was saturated with acetylene; (c) by bubbling acetylene through a cooled (-80°) solution of (I) in THF, followed by the addition of water.

The compound was recrystallized from methanol-water. The THF solution of $NaCo(salen)$ did not react with acetylene until water was added.

 $[CNCH_2CH_2Co(salen)H_2O]$ (VIII)

Obtained by methods (b) and (c) above from $CNCH=CH_2$ as orange-yellow crystals.

 $[RCo(salen)(C_5H_5N)]$ ($R = CH_3OCO$ (IX), C_2H_5OCO (X), CH_3CO (XI), $CH_2=CH$ (XII), $CNCH_2CH_2$ (XIII))

Obtained by dissolving the corresponding *aquo* complexes or five-coordinated complexes in the minimum amount of pyridine. The compounds were precipitated with a mixture of petroleum-ether and ether as orange-yellow crystals.

Spectra

The UV and visible spectra were determined using a Unicam SP700 spectrophotometer. During all the operations, care was taken to avoid photochemical decomposition.

Infrared spectra were obtained using a Perkin-Elmer model 13C infrared spectrophotometer using KBr pellets.

Magnetic measurements

Magnetic measurements were made with the Gouy method at three magnetic field values. Redistilled water saturated with air was used for the calibration of the Gouy tube^{1,2}. Susceptibility values are corrected for the presence of air.

ACKNOWLEDGEMENTS

Financial assistance from the National Research Council and SNAM-Progetti is gratefully acknowledged.

SUMMARY

Complexes of Co^{III} and Co^{II} of the type $BrCo(salen)PPh_3$, $[Co(salen)L_2]^+X^-$ or $[Co(salen)]$ can be reduced to $NaCo^I(salen)$ by Na or 1% Na(Hg). The preparation of stable organocobalt complexes, $[RCo(salen)]$ and $[RCo(salen)H_2O]$ ($R = \text{alkyl, vinyl, acyl, carboxyalkyl}$), by reaction of $NaCo^I(salen)$ with RX is described.

The reactions of $NaCo(salen)$ with acetylene or acrylonitrile in the presence of

water yielding the vinyl and cyanoethyl compounds are reported.

The analogy with the chemical behaviour of Vitamin B₁₂s is confirmed.

REFERENCES

- 1 G. COSTA, G. MESTRONI, G. TAUZHER AND L. STEFANI, *J. Organometal. Chem.*, 6 (1966) 181.
 - 2 G. COSTA, G. MESTRONI AND L. STEFANI, *J. Organometal. Chem.*, 7 (1967) 493.
 - 3 G. N. SCHRAUZER AND J. KOHNLE, *Chem. Ber.*, 97 (1964) 3056.
 - 4 R. BONNET, *Chem. Rev.*, 63 (1963) 573.
 - 5 D. A. CLARKE, R. GRIGG AND A. W. JOHNSON, *Chem. Commun.*, (1966) 208.
 - 6 G. N. SCHRAUZER, R. J. WINDGASSEN AND J. KOHNLE, *Chem. Ber.*, 98 (1965) 3324.
 - 7 G. COSTA AND G. MESTRONI, *Tetrahedron Letters*, (1967) 1783.
 - 8 F. CALDERAZZO AND C. FLORIANI, *Chem. Commun.*, (1967) 139.
 - 9 G. COSTA AND G. MESTRONI, *J. Organometal. Chem.*, 11 (1968) 325.
 - 10 J. L. KERNAHAN AND M. J. SIENKO, *J. Am. Chem. Soc.*, 77 (1955) 1978; C. J. BALLHAUSEN AND R. W. ASMUSSEN, *Acta Chem. Scand.*, 11 (1957) 479; S. S. DHARMATTI AND C. R. KANEKAR, *J. Chem. Phys.*, 31 (1959) 1436; J. S. GRIFFITH AND L. E. ORGEL, *Trans. Faraday Soc.*, 53 (1957) 601.
 - 11 G. COSTA *et al.*, Unpublished results.
 - 12 B. N. FIGGIS, *J. Chem. Soc.*, (1964) 3423.
- J. Organometal. Chem.*, 11 (1968) 333-340