Journal of Organometallic Chemistry, 105 (1976) 231—237

REACTIONS OF COORDINATED MOLECULES

III *. ALKOXY SUBSTITUENT EXCHANGE REACTIONS ON A CYCLIC LIGAND

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(Received July 22nd, 1975)

Summary

The extraction of an ethoxide anion from a β-diethylacetal-acyl ligand of a neutral organometallic molybdenum complex affords a cationic complex having a cyclic ligand which is described best as a metal-stabilized oxonium ion. This ligand has an unusually reactive saturated carbon atom which reacts with a variety of alcohols and with ethanethiol via an alkoxy group exchange reaction affording a differently substituted cyclic ligand. The oxidization of the metal—ligand bond in the initial complex forms 4-ethoxy-γ-butyrolactone and, therefore, it is a precursor for the preparation of a variety of 4-substituted-γ-butyrolactones. The reaction of this complex with sodium methoxide and dimethyl sulfoxide is discussed, also.

Introduction

We wish to report the preparation of a transition metal complex II, possessing an unusually reactive site on a coordinated molecule. Although this reactive carbon center is not bonded directly to the metal atom, its reactivity toward nucleophilic attack is enhanced, apparently, from the stabilization of one of its substituents as a leaving group by the transition metal atom. The complex is described best as a metal-stabilized oxonium ion.

This report discusses the reaction of this complex with a variety of alcohols, ethanethiol, sodium methoxide and dimethyl sulfoxide. The oxidation of the metal—ligand bond affording the corresponding 4-alkoxy-γ-butyrolactone is demonstrated for one of these complexes.

* For Part II see ref. 8.

Results and discussion

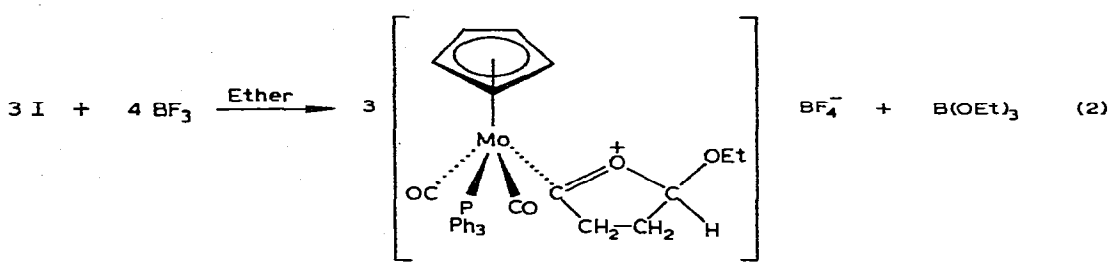
The acyl-acetal complex I was prepared by treating β-iodopropionaldehyde diethyl acetal with $NaCpMo(CO)_3$ in tetrahydrofuran solution at 25°C followed by a triphenylphosphine induced "CO insertion" reaction in acetonitrile solution at 25°C:

$$NaCpMo(CO)_3 + ICH_2CH_2C(OEt)_2H \xrightarrow[(2)\ PPh_3,\ CH_3CN]{(1)\ THF} \textit{trans}\text{-}CpMo(CO)_2(PPh_3)C(O)CH_2CH_2C(OEt)_2H \quad (1)$$

(I)

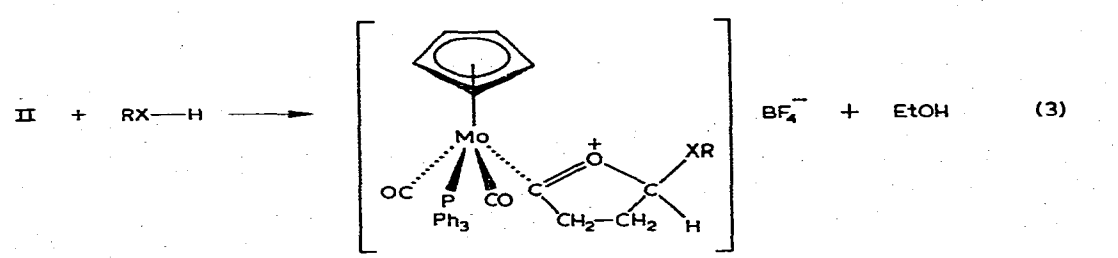
The stereochemistry of complex I is determined from the IR and PMR spectra [1].

When complex I is treated with boron trifluoride etherate in ether at 25°C the metal-stabilized oxonium salt II is formed in 91% yield (eq. 2).



(II)

The conversion of the expected $[BF_3OEt]^-$ anion into the BF_4^- anion and triethylborate in the presence of boron trifluoride is a well known transformation [2,3]. The ionic nature of II is confirmed by a metathetical exchange of the BF_4^- anion by the BPh_4^- anion. The presence of the cyclic five-membered ring is substantiated by the absence of an acyl stretch in the IR spectrum and by the observation of a highly diastereotopic ($\Delta\tau$ 0.51) methylene group in the PMR spectrum. The low-field chemical shift of the methine proton relative to that value observed in complex I is a strong indication of ring formation, also. The oxidation of complex II with pyridine-*N*-oxide in methylene chloride solution at 25°C affords 4-ethoxy-γ-butyrolactone. In addition, the IR and PMR spectra of II indicate

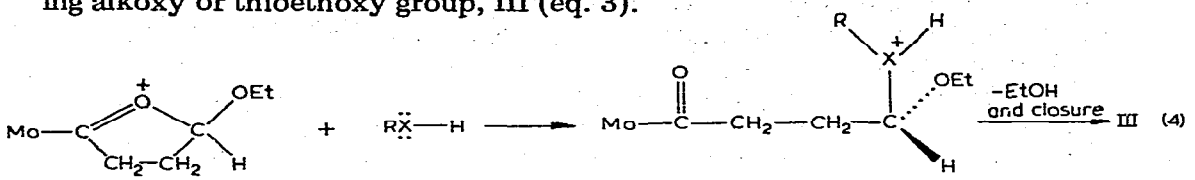


(III)

(IIIa) RX = OMe, (IIIb) RX = O-n-Pr, (IIIc) RX = O-i-Pr, (IIId) RX = O-t-Bu, (IIIe) RX = SEt

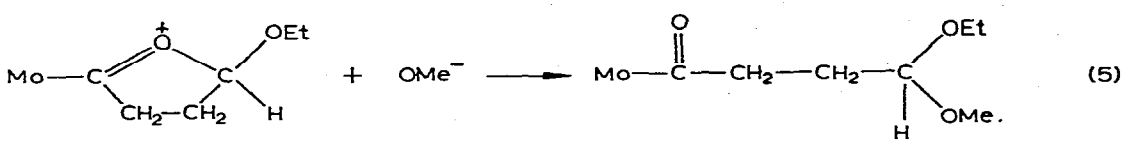
that the molybdenum atom is conjugated with a positive charge [1].

The dissolution of complex II in the presence of excess alcohols or excess ethanethiol leads to the exchange of the ethoxy substituent for the corresponding alkoxy or thioethoxy group, III (eq. 3).



(II)

Apparently, the high reactivity of the alkoxy-substituted carbon atom in II toward these weak nucleophiles can be attributed to the oxonium ion character of the coordinated cyclic molecule [4]. This saturated carbon atom reacts as though it possesses an extremely good leaving group. In fact, this leaving group is an acyl complex. The alcohol or ethanethiol molecule then bonds to the straight-chain carbonium ion forming an oxonium ion which then eliminates ethanol [2]. The five-membered ring closes and forms the exchanged complex III (eq. 4). The positive charge is localized on the ethoxy-substituted carbon

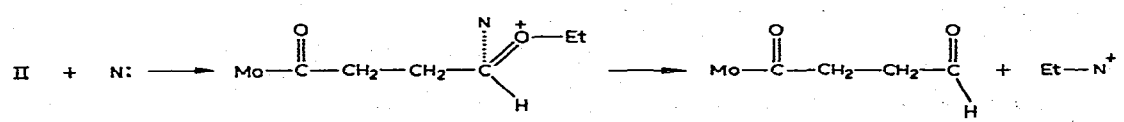


(II) (IV)

atom only through such a ring-opening reaction. The repetition of this process in the presence of excess nucleophile leads to the total exchange of the ethoxy group of complex II. Since the oxidation of the metal—ligand bond in the exchanged complexes IIIa—IIIe is expected to be as facile as with complex II, complex II is considered to be a convenient precursor to a variety of 4-alkoxy- or thioalkoxy-γ-butyrolactones [5].

Complex II reacts with sodium methoxide in methylene chloride solution at 25°C affording the rather unique mixed methoxy—ethoxy acetal complex IV. This reaction proceeds probably via nucleophilic attack on the ethoxy-substituted carbon atom of complex II followed by carbon—oxygen bond formation (eq. 5).

When complex II is treated with a nucleophile which would not be expected to add to the reactive carbon atom, the acyl-aldehyde complex V is formed. The reaction of II with dimethyl sulfoxide affords complex V in good yield, while reaction with triethylamine produces complex V in a much lower yield. In this reaction the straight-chain carbonium ion acts, apparently, as an oxonium ion and alkylates the nucleophilic reagent which is present in large excess.



(N = DMSO, Et_3N) (V)

Experimental

All reactions were performed under dry, prepurified nitrogen at 25°C. The following special reagents were purchased: β-chloropropionaldehyde diethyl acetal (Columbia Organic Chemicals Co.), $[CpMo(CO)_3]_2$ (Pressure Chemical Co.) and ethanethiol (Aldrich Chemical Co.).

Infrared spectra were recorded on a Perkin—Elmer 727 spectrometer as methylene chloride solutions in 0.10 mm sodium chloride cavity cells using the solvent as a reference and polystyrene as a calibration standard. Peak frequencies are reported in cm^{-1}. Proton NMR spectra were obtained on a Jeol MH-100 NMR spectrometer using TMS as a reference.

Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Preparation of trans-$CpMo(CO)_2PPh_3C(O)CH_2CH_2C(OEt)_2H$ (I)

β-chloropropionaldehyde diethyl acetal was converted to the iodo compound by a Finkelstein halide interchange reaction using sodium iodide in acetone solution [6]. To 8.0 g (48 mmol) of the chloro compound dissolved in 15 ml of acetone was added a solution of 7.5 g (50 mmol) of NaI in 25 ml of acetone. The reaction mixture was stirred for 2 h, then filtered, and the acetone removed at reduced pressure. The residue was extracted with 75 ml of ether, then filtered, and the solvent removed at reduced pressure. The resulting neat liquid was passed through an alumina column (3 cm × 1 cm) affording 5.40 g (21 mmol, 43%) of the iodo compound as a yellow liquid which darkened appreciably over 15 min at 25°C.

The iodo acetal was added to a solution of $NaCpMo(CO)_3$ in 50 ml of freshly distilled THF prepared by sodium amalgam reduction of 5.12 g (10.5 mmol) of $[CpMo(CO)_3]_2$. The reaction solution was stirred for 16 h and then the solvent was removed at reduced pressure. The residue was extracted with 75 ml of methylene chloride and filtered. Removal of the solvent at reduced pressure afforded 5.42 g of a red liquid which could not be purified by column chromatography. An infrared spectrum indicated the nearly total presence of a $CpMo(CO)_3$–alkyl complex. Therefore, the liquid was dissolved in 4 ml of acetonitrile and was treated with 7.70 g of triphenylphosphine. The reaction solution was stirred for 2 h, and then the solvent was removed at reduced pressure. The reaction residue was crystallized from 200 ml of methylene chloride:hexane (1:5) by slowly reducing the volume of the solution at reduced pressure affording 6.68 g of the crude product. This solid was recrystallized from ether at —20°C affording 4.10 g (31% based on Mo) of I as a yellow-orange solid: m.p. 123.5—125.0°; IR ν(CO) 1940s, 1850vs, ν(acyl), 1618 m; ^1H NMR ($CDCl_3$); τ 8.88 (triplet, 6, CH_3), 8.32 (triplet, 2, $C(O)CH_2$), 6.95 (quartet, 2, CH_2), 6.56 (quintet, 4, OCH_2), 5.67 (triplet, 1, methine H), 5.08 [doublet, $J(P—H) \approx 1.3$ Hz, 5, C_5H_5], 2.65 (multiplet, 15, PPh_3). (Found: C, 62.20; H, 5.61; P, 4.71. $C_{33}H_{35}O_5PMo$ calcd.: C, 62.07; H, 5.53; P, 4.85%.)

Preparation of [trans-$CpMo(CO)_2PPh_3\overline{COCH_2CH_2C}(OEt)H]BF_4$ (II)

To 2.40 g (3.76 mmol) of I dissolved in 100 ml of ether was added 0.65 ml (5.17 mmol) of boron trifluoride etherate over a 5 min period. The reaction

mixture was stirred for 15 min more and then filtered through a glass frit. The solid was washed well with ether and dried under reduced pressure affording 2.34 g (91%) of II as a pale lemon-yellow solid: dec. 164—166°C; IR ν(CO) 1994s, 1915vs; ^{1}H NMR ($CDCl_3$); τ 8.70 (triplet, 3, CH_3), 8.25 (multiplet, 1, one diastereomeric H), 7.74 (multiplet, 1, one diastereomeric H), 6.14 (triplet, 2, CCH_2), 5.95 (multiplet, 2, OCH_2), 4.57 [doublet, J(P—H) ≈1.3 Hz, 5, C_5H_5], 3.65 (triplet, 1, methine H), 2.51 (multiplet, 15, PPh_3). (Found: C, 54.83; H, 4.50; P, 4.52; F, 11.66. $C_{31}H_{30}O_4BF_4PMo$ calcd.: C, 54.73; H, 4.45; P, 4.55; F, 11.17%.)

Preparation of the BPh_4^- salt of II

To 25 ml of an ethanol solution saturated with II was added a two-fold molar excess of $NaBPh_4$ dissolved in a minimum amount of ethanol. The reaction mixture was stirred at 0°C for 15 min and then was filtered through a glass frit. The collected solid was washed well with ether and dried at reduced pressure affording the pure BPh_4^- salt of II in high yield as a yellow solid: dec. 148—149°C; IR ν(CO) 1995s, 1915vs; ^{1}H NMR ($CDCl_3$); τ 8.81 (triplet, 3, CH_3), 8.55 (broad multiplet, 2, diastereomeric CH_2), 6.35 (triplet, 2, CCH_2), 6.14 (multiplet, 2, OCH_2), 4.99 [doublet, J(P—H) ≈1.3 Hz, 5, C_5H_5], 4.51 (triplet, 1, methine H), 3.2—2.6 (multiplet, 35, PPh_3 and BPh_4). (Found: C, 72.06; H, 5.49; P, 3.35. $C_{55}H_{50}O_4$ BPMo calcd.: C, 72.38; H, 5.52; P, 3.39%.)

General preparation of the complexes IIIb—IIIe

To a stirred solution of 0.20 g of II in 4 ml of acetone was added 2 ml of the appropriate alcohol or thiol. Within 2 h the yellow reaction solution turned orange at which time ether was added slowly to precipitate a light yellow solid. The solid was filtered in air, washed well with ether and dried under reduced pressure for 1 h. The product may be recrystallized from a methylene chloride: hexane solution.

Preparation of [trans-$CpMo(CO)_2PPh_3\overline{COCH_2CH_2C(OMe)H}]BF_4$ (IIIa)

To 0.20 g of II was added 5 ml of methanol forming a clear yellow solution. Within 2 min after dissolution a yellow solid precipitated. After 5 min more, the reaction mixture was filtered in air. The solid was washed with ether and dried under reduced pressure affording 0.11 g (56%) of a bright yellow solid: dec. 188—190°C; IR ν(CO), 1980s, 1914vs; ^{1}H NMR (CD_3CN), τ 7.59 (multiplet, 2, diastereomeric CH_2), 6.32 (singlet, 3, OCH_3), 6.18 (triplet, 2, CCH_2), 4.51 [doublet, J(P—H) ≈1.3 Hz, 5, C_5H_5], 3.90 (triplet, 1, methine H), 2.52 (multiplet, 15, PPh_3). (Found: C, 53.97; H, 4.29; P, 4.59. $C_{30}H_{28}O_4BF_4PMo$ calcd.: C, 54.08; H, 4.24; P, 4.65%.)

Preparation of [trans-$CpMo(CO)_2PPh_3\overline{COCH_2CH_2C(OPr)H}]BF_4$ (IIIb)

The above procedure afforded 0.11 g (55%) of a lemon-yellow solid: dec. 165—166.5°C; IR ν(CO) 1988s, 1913vs; ^{1}H NMR ($CDCl_3$), τ 9.08 (triplet, 3, $CH_2\underline{CH_3}$), 8.34 (multiplet, 3, $\underline{CH_2}CH_3$ + diastereomeric H), 7.74 (multiplet, 1, diastereomeric H), 6.17 (multiplet, 4, CCH_2 + OCH_2), 4.60 [doublet, J(P—H) ≈1.3 Hz, 5, C_5H_5], 3.69 (triplet, 1, methine H), 2.58 (multiplet, 15, PPh_3). (Found: C, 55.83; H, 4.52; P, 4.43. $C_{32}H_{32}O_4BF_4PMo$ calcd.: C, 55.36; H, 4.65; P, 4.46%.)

Preparation of [trans-CpMo(CO)$_2$PPh$_3$COCH$_2$CH$_2$C(O-i-Pr)H]BF$_4$ (IIIc)

The above procedure afforded 0.17 g (76%) of a light yellow solid: dec. 161—163°C; IR ν(CO) 1987s, 1914vs; ^{1}H NMR ($CDCl_3$), τ 8.70 (doublet of doublets, 6, CH_3), 8.31 (multiplet, 2, diastereomeric H), 7.71 (multiplet, 1, diastereomeric H), 6.17 (triplet, 2, CCH_2), 5.77 (multiplet, 1, i-Pr methine H), 4.6 [doublet, J(P—H) ≈1.3 Hz, 5, C_5H_5], 3.60 (triplet, 1, methine H), 2.58 (multiplet, 15, PPh_3). (Found: C, 55.17; H, 4.69; P, 4.33. $C_{32}H_{32}O_4BF_4PMo$ calcd.: C, 55.36; H, 4.65; P, 4.46%.)

Preparation of [trans-CpMo(CO)$_2$PPh$_3$COCH$_2$CH$_2$C(O-t-Bu)H]BF$_4$ (IIId)

The above procedure using 0.14 g of II afforded 0.05 g (40%) of a light solid: dec. 153—155°C; IR ν(CO) 1988s, 1909vs; ^{1}H NMR ($CDCl_3$), τ 8.61 (singlet, 9, CH_3), 8.37 (multiplet, 1, diastereomeric H), 7.83 (multiplet, 1, diastereomeric H), 6.18 (triplet, 2, CCH_2), 4.64 [doublet, J(P—H) ≈1.3 Hz, 5, C_5H_5], 3.42 (triplet, 1, methine H), 2.58 (multiplet, 15, PPh_3). (Found: C, 55.09; H, 4.70; P, 4.40. $C_{33}H_{34}O_4BF_4PMo$ calcd.: C, 55.96; H, 4.84; P, 4.37%.)

Preparation of [trans-CpMo(CO)$_2$PPh$_3$COCH$_2$CH$_2$C(SEt)H]BF$_4$ (IIIe)

The crude product was recrystallized with some difficulty from ca. 25 ml of methylene chloride:hexane (1:3) solution affording 0.03 g (15%) of bright yellow needles: dec. 142—144°C; IR ν(CO) 1992s, 1913vs; ^{1}H NMR ($CDCl_3$), τ 8.59 (triplet, 3, CH_3), 8.34 (multiplet, 1, diastereomeric H), 7.53 (multiplet, 1, diastereomeric H), 7.15 (quartet, 2, SCH_2), 6.14 (triplet, 2, CCH_2), 4.6 [doublet, J(P—H) ≈1.3 Hz, 5, C_5H_5], 3.54 (triplet, 1, methine H), 2.61 (multiplet, 15, PPh_3). (Found: C, 53.47; H, 4.44; S, 4.01. $C_{31}H_{30}O_3BF_4PSMo$ calcd.: C, 53.47; H, 4.34; S, 4.60%.)

Oxidation of II

To a stirred solution of 0.30 g of II in 1 ml of methylene chloride was added 5 equivalents of pyridine-*N*-oxide. The reaction solution turned red immediately. After stirring for 2 h the reaction solution was filtered and analyzed by preparative GLC using an areograph autoprep A-700 GLC having a 10-foot by 3/8 inch glass column containing 10% 80/100 chromasorb Q with a column temperature of 120°C and a flow rate of 60 ml/min. Collection of the appropriate band afforded 0.013 g (23% determined by weighing collected liquid) of 4-ethoxy-γ-butyrolactone: IR ν(C=O) 1776s; ^{1}H NMR ($CDCl_3$), τ 8.80 (triplet, 3, CH_3), 7.65 (multiplet, 4, CCH_2CH_2), 6.35 (doublet of quartets, 2, OCH_2), 4.54 (doublet of triplets, 1, methine H). The ^{1}H NMR agrees exactly with the published full spectrum of 4-ethoxy-γ-butyrolactone [7].

Preparation of trans-CpMo(CO)$_2$PPh$_3$C(O)CH$_2$CH$_2$C(OEt)(OMe)H (IV)

To 0.33 g (0.48 mmol) of II dissolved in 3 ml of methylene chloride was added 0.026 g (0.48 mmol) of sodium methoxide. The reaction mixture was stirred for 16 h and then the solvent was removed at reduced pressure. The reaction residue was extracted with 50 ml of ether and the resulting mixture was filtered and the solvent was removed at reduced pressure affording 0.12 g (40%) of IV as a yellow solid. The complex may be crystallized from 2:5 methylene chloride:hexane at —20°C as yellow needles: dec. 124—125°C; IR ν(CO) 1937s,

1850vs, ν(acyl) 1610m; ^{1}H NMR ($CDCl_3$); τ 8.88 (triplet, 3, CH_2CH_3), 8.29 (quartet, 2, CH_2CH_2), 6.97 (triplet, 2, CCH_2), 6.82 (singlet, 3, OCH_3), 6.54 (quintet, 2, OCH_2), 5.73 (triplet, 1, methine H), 5.08 [doublet, J(P—H) ≈1.3 Hz, 5, C_5H_5], 2.66 (multiplet, 15, PPh_3). (Found: C, 61.25; H, 5.38; P, 4.96. $C_{32}H_{33}O_5PMo$ calcd.: C, 61.54; H, 5.33; P, 4.96%.)

Preparation of trans-$CpMo(CO)_2PPh_3C(O)CH_2CH_2C(O)(H)$ (V)

To 0.20 g of II was added 4 ml of DMSO forming a cloudy yellow solution. After 4 min the reaction solution was transferred by syringe to a flask containing 30 ml of N_2 purged distilled H_2O and 75 ml of diethyl ether. The mixture was stirred vigorously for 5 min, during which time the ether layer became pale yellow. The ether layer was removed and dried over $MgSO_4$ for 30 min. The ether solution was then filtered under N_2 and the solvent was removed under reduced pressure. The orange residue was dissolved in 2 ml of benzene and purified by column chromatography using a 10 × 130 mm column of silica gel (60-200 mesh). A faint red band was washed off the column with benzene and discarded. The eluent was changed to 1:1 benzene/ether and the bright yellow band that came off was collected and dried under reduced pressure. The residue was washed twice with 2 ml of ether and dried under high vacuum to yield 0.042 g (25%) of a bright yellow solid: dec. 121—123°C; IR ν(CO) 1940s, 1855vs, ν(C=O) 1720m, ν(acyl) 1610m; ^{1}H NMR ($CDCl_3$), τ 7.62 (doublet of triplets, 2, $CH_2C(O)(H)$, J_1 7.5, J_2 2.1 Hz), 6.65 (triplet, 2, $C(O)CH_2$), 5.04 [doublet, J(P—H) ≈1.3 Hz, 5, C_5H_5], 2.61 (multiplet, 15, PPh_3), 0.39 [triplet, J_2 2.1 Hz, C(O)H]. (Found: C, 62.16; H, 4.71; P, 5.26. $C_{29}H_{25}O_4PMo$ calcd.: C, 61.84; H, 4.85; P, 5.26%.)

Acknowledgements

Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research and to the University Research Council of Vanderbilt University for a grant to C.M.L.

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