REACTIONS OF COORDINATED MOLECULES

XX *. AN UNEXPECTED ROUTE TO THE PREPARATION OF HYDROXYCARBENOID AND FORMYLRHENIUM(I) HALIDE COMPLEXES

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Summary

When $BrMn(CO)_5$ and the rhenium complexes, $XRe(CO)_5$ (where X is H, Cl, Br or I) are treated with one equivalent of methyllithium the corresponding *cis*-halo- or hydrido-acetylmetalate complexes, $Li[cis-(OC)_4(X)MC(O)CH_3]$, are formed unexpectedly. The protonation of the halo-anions affords the hydroxycarbenoid complexes. When the halopentacarbonylrhenium complexes are treated with $Li[BEt_3H]$ the corresponding formylmetalate complexes are formed. The reaction chemistry of these anions and of the analogous formyl- and acetyl-metalate anion is discussed briefly.

Introduction

When the metallaacetylacetone complex, *cis*-$(OC)_4Re[C(CH_3)O\cdots H\cdots OC-(CH(CH_3)_2)]$, was inadvertently subjected to presumably very strongly acidic conditions, we isolated a pale-yellow complex. The IR spectrum of this compound was consistent with its formulation as a chlororhenium analogue to either the known manganese bromohydroxycarbenoid complex, *cis*-$(OC)_4Mn(Br)[C(CH_3)(OH)]$ (I) [2] or the manganese boroxycarbenoid complex, *cis*-$(OC)_4Mn(Br)[C(CH_3)(OBBr_2)]$ (II) [3]. Although the subsequent repetition of the initial reaction was questionable, we undertook an independent preparation of the rhenium analogue to I.

After determining that the synthetic procedure used to prepare I failed for the rhenium analogue, we discovered that at —78°C methyllithium would add to a carbonyl carbon atom in the pentacarbonylrhenium halide complexes, XRe-

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* For Part XIX see ref. 1.

(CO)$_5$, where X is Cl, Br or I, which is *cis* to the halo ligand affording the corresponding haloacetylrhenate anions. This procedure could be used to prepare the known bromoacetylmanganate anion, also. This nucleophilic attack at the carbonyl carbon atom rather than at the metal atom to afford methylpentacarbonylrhenium is unexpected since such halide displacement reactions are a common route to alkyl-organometallic complexes [4].

The resulting haloacetyl-rhenate and -manganate anions can be protonated to give the corresponding hydroxycarbenoid complexes. In an attempt to prepare a stable hydroxymethylene complex utilizing the known intramolecular hydrogen bonding of complex I, we prepared the formyl analogues to the haloacetylrhenate anions using LiBEt$_3$H in place of the methyllithium. Although these formyl anions were prepared readily, the subsequent protonation led to decomposition. We wish to report the synthetic details of these and related reactions at this time.

Results and discussion

The known manganese complex I, and its iodo analogue II were prepared by Moss et al. by inducing "CO-insertion" with the corresponding lithium halide affording the *cis*-haloacetylmanganate anion followed by protonation [2].

(I)
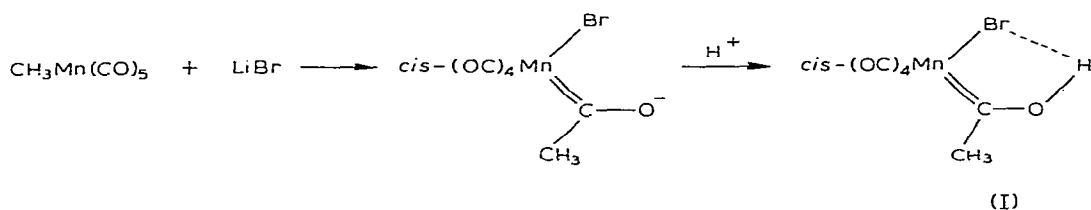
The analogous reaction with methylpentacarbonylrhenium failed presumably due to the greater stability of the rhenium—alkyl bond [5]. However, when the halopentacarbonylrhenium complexes are treated with one equivalent of methyllithium at —78°C, the *cis*-haloacetylrhenate anions are formed. These anions are thermally stable in solution at 25°C, and they can be protonated affording the *cis*-halohydroxycarbenoid complexes III—V. Complex I was prepared via this route to confirm the above procedure.

(I : M = Mn , X = Br ;
III : M = Re , X = Cl ;
IV : M = Re , X = Br ;
V : M = Re , X = I)
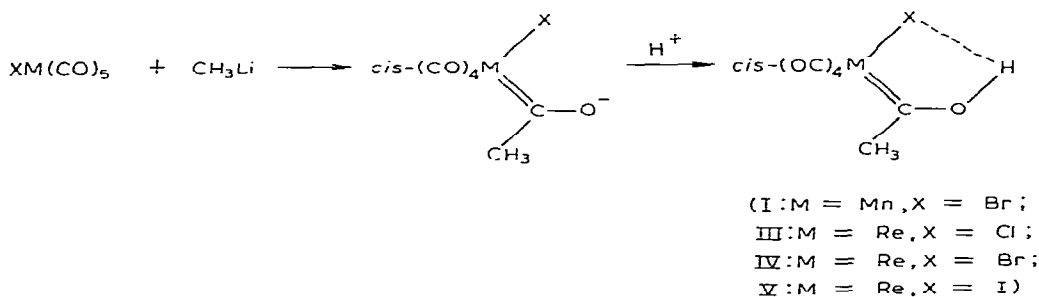
The reaction with methyllithium is followed easily by IR. The C—O stretching bands of the terminal carbonyl ligands of the acetylrhenate anions appear at ca. 70 cm^{-1} below those of the neutral halopentacarbonyl complexes, and the acetyl

C—O stretching vibrations appear at ca. 1565 cm^{-1}. Protonation of these anions affords the corresponding neutral hydroxycarbenoid complexes with the expected shift of the terminal carbonyl C—O stretching vibrations to higher energy. As found for the manganese anions [2], the alkylation of the rhenium anions with either [Et$_3$O]BF$_4$ or [Me$_3$O]BF$_4$ did not afford isolable products. Quite unexpectedly, there is no evidence that the methyllithium displaces the halide ligand to form CH$_3$Re(CO)$_5$ [4,6].
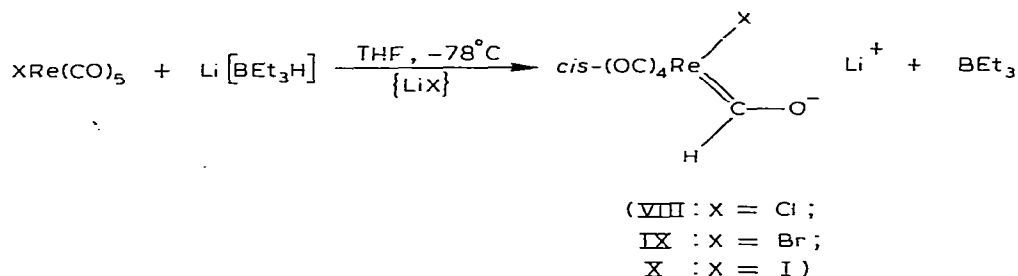
The rhenium complexes III—V are isolated as crystalline solids. Although the chloro and bromo complexes have excellent thermal and air stability, the iodo complex is less stable thermally which results in a poor elemental analysis. The ^{1}H NMR spectra show a singlet for the methyl group at ca. δ 3.13 ppm (CDCl$_3$). The hydroxy proton is not observed, presumably due to intra- or intermolecular exchange [2]. The methyl resonance exhibits a pronounced solvent dependence. This resonance shifts ca. 0.95 ppm upfield in going from CDCl$_3$ to C$_6$H$_6$ for all four hydroxycarbene complexes.

When HRe(CO)$_5$ is treated similarly with one equivalent of methyllithium, the corresponding hydridoacetylrhenate anion, cis-(OC)$_4$(H)ReC(O)CH$_3^-$ (VI) is formed. The IR spectrum shows a band at 1548 cm^{-1} for the acetyl ligand, and the ^{1}H NMR spectrum shows methyl and hydrido singlets (3/1) at δ 2.32 and —4.66 ppm, respectively. Since the pK_a of methane is presumably much greater than that of HRe(CO)$_5$, this reaction appears to be kinetically controlled rather than thermodynamically controlled. The protonation of this anions does not afford the corresponding hydroxycarbenoid complex.

Based on the excellent work of Casey [7] and Gladysz [8] in preparing and isolating salts of the rhenium-formyl anion, cis-(OC)$_9$Re$_2$C(O)H$^-$ (VII), we attempted the preparation of the formyl derivatives of the haloacetylrhenate anions mentioned above. We wanted to test the hypothesis that other one-electron ligands can be substituted for the (OC)$_5$Re group in the anion VII, and to determine if the presence of a cis-halo ligand in such a formyl anion could stabilize the resulting hydroxymethylene complexes which would result from protonation. At present, all attempts to protonate formyl ligands of this type have led to decomposition.

When THF solutions of the halopentacarbonylrhenium complexes are treated at —78°C with Li[BEt$_3$H] and then warmed to 0°C, halide displacement occurs affording HRe(CO)$_5$ and the haloformylrhenate anions in an ca. 60/40 yield. However, if this reaction is conducted in THF solution at —78°C in the presence of added lithium halide, then the corresponding haloformylrhenate anions VIII—X are formed in a spectroscopically quantitative yield. Solutions of the haloformylrhenate anions are thermally stable even at +32°C. The lithium halide could be added as such or generated from another equivalent of Li[BEt$_3$H] and the corresponding acid, HX. Additional iodide was not added in the IRe(CO)$_5$ reaction. Presumably, the presence of free halide ion is needed to reduce the effective Lewis acidity of the generated triethylborane. This observation has been noted previously [9]. Although the generation of lithium halide using another equivalent of Li[BEt$_3$H] and the acid, HX, does not produce a net increase of free halide ion relative to the triethylborane in the system, the presence of free halide ion may inhibit halide ligand abstraction by the triethyl-borane by shifting complex equilibria. Recent evidence has demonstrated the

participation of the triethylborane Lewis acid in the hydride transfer reactions of anionic formyl complexes which were formed using Li[BEt$_3$H] [10].

$$\text{XRe(CO)}_5 \;+\; \text{Li[BEt}_3\text{H]} \xrightarrow[\{\text{LiX}\}]{\text{THF}, -78°C} \quad \textit{cis}\text{-(OC)}_4\text{Re}\overset{\displaystyle X}{\underset{\displaystyle \underset{H}{C}-O^-}{\big<}} \quad \text{Li}^+ \;+\; \text{BEt}_3$$

$$(\underline{\text{VIII}} : X = Cl ;$$
$$\underline{\text{IX}} : X = Br ;$$
$$\underline{X} : X = I)$$

The formyl complexes VIII—X were formed in spectroscopically quantitative yield and were characterized by IR and ^{1}H NMR (at +32°C) [7,8]. The terminal carbonyl C—O stretching vibrations appeared at the frequencies expected for an anionic complex and exhibited the relative intensity pattern consistent with the *cis*-(OC)$_4$Re geometry. The formyl C—O stretch occurs at ca. 1570 cm^{-1}. The formyl proton resonances appear as sharp singlets at ca. δ 15.07 ppm. The corresponding resonance for VII appears at δ 15.78 ppm which apparently reflects the greater electronegativity of the Re(CO)$_5$ substituent. Repeated attempts to isolate these formyl anions as the PPN or as the lithium salts gave only analytically impure solids. However, solutions of these anions could be handled very easily.

The attempted protonation of the bromo- and iodo-formyl anions IX and X at 25°C in both THF and ether solution led to decomposition. Protonation on a synthetic scale at —78°C failed, also. Using a variable temperature ^{1}H NMR probe, the protonation reaction of both of these anions was observed at ca. —30°C in THF-d_8 solution. Using HCl or acetic acid the formyl resonances disappeared upon adding the acid without the appearance of any new proton resonances in the spectrum. Presumably the protonation proceeded directly to the evolution of hydrogen gas [7,8].

Since the *cis*-halo ligand failed to stabilize the expected hydroxymethylene ligand, we attempted to stabilize the formyl anion further by forming the metalla-formylacetonate anion. Acetylpentacarbonylrhenium was treated with one equivalent of Li[BEt$_3$H] in THF at —78°C. The metalla-formylacetonate anion, *cis*-(OC)$_4$Re(CH$_3$CO)(HCO)$^-$ (XI) was formed upon warming the reaction solution to 0°C. The formyl C—O band appeared at 1580 cm^{-1} and the methyl and formyl proton resonances (3/1) appeared at δ 2.46 and 14.31 ppm, respectively. Related manganese anions have been reported earlier [11]. This anion appears to be even less stable than the haloformylrhenate anions. The rate of decomposition of XI, as measured by ^{1}H NMR, in THF solution at 32°C was 1.43×10^{-3} sec^{-1} assuming a first-order process. The half-life was measured to be 8.1 min, and the decomposition was quantitative as measured by ^{1}H NMR.

The product of this decomposition was identified by IR and ^{1}H NMR as the hydridoacetyl anion VI which was prepared by the above independent method. Although the mechanism of this reaction was not investigated in detail, it may represent the decarbonylation of a formyl ligand similar to the mechanism proposed for the decarbonylation of the formyl ligand in the presumed intermediate HC(O)Mn(CO)$_4$ [12].

When the ^{1}H NMR spectrum of XI was recorded in CDCl$_3$ solution, the anion reacted with the solvent affording acetylpentacarbonylrhenium, CHDCl$_2$ and, presumably, lithium chloride. Apparently, this anion also acts as a good hydride donor [7,8,11].

Experimental

All reactions and other manipulations were performed under dry, prepurified nitrogen at 25°C, unless otherwise stated. Solvents were distilled from Na/K alloy before use. BrMn(CO)$_5$, ClRe(CO)$_5$, CH$_3$C(O)Re(CO)$_5$ and HRe(CO)$_5$ were prepared by literature methods [13—16]. A convenient procedure for preparing IRe(CO)$_5$ is reported. Methyllithium (Ventron Corp.), lithium triethyl-borohydride (Aldrich Chemical Co.) and all other reagents were purchased.

Infrared spectra were recorded on a Perkin—Elmer 727 spectrometer in 0.10 mm sodium chloride cavity cells using the solvent as a reference and poly-styrene film as a calibration standard. ^{1}H NMR spectra were recorded on a Jeol MH-100 spectrometer using TMS or solvent peaks as internal references. Mass spectra were recorded on a LKB 9000 spectrometer. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Preparation of IRe(CO)$_5$

A solution of 1.08 g (1.66 mmol) of Re$_2$(CO)$_{10}$ and 0.45 g (1.76 mmol) of I$_2$ in 20 ml of CCl$_4$ at 25°C was stirred for 72 h. After this time the solvent was removed from the reaction mixture at reduced pressure, and the solid residue was washed with 2 × 3 ml of hexane and then dried under reduced pressure for 2 h affording 1.08 g (72%) of IRe(CO)$_5$ as a fine white powder. The IR spectrum indicated that the product was pure enough for most purposes [14].

Preparation of cis-(OC)$_4$(Br)Mn[C(CH$_3$)(OH)] (I)

A solution of 1.07 mmol of methyllithium as an ether solution was added to a stirred solution of 0.29 g (1.07 mmol) of BrMn(CO)$_5$ in 10 ml of THF at —78°C. As the reaction solution warmed gradually to 0°C during a 1 h period a color change from yellow to orange was observed. An ether solution of 1.07 mmol of anhydrous HCl was then added to this solution at 0°C effecting an immediate color change back to yellow. The product was isolated by a pentane extraction (15 ml) followed by normal filtration and drying procedures. The IR, ^{1}H NMR and mass spectra of I were identical to the published data [2].

Preparation of the cis-(OC)$_4$(X)Re[C(CH$_3$)(OH)] complexes (III—V)

General procedure. To a stirred solution of 0.23—0.28 g of the appropriate halopentacarbonylrhenium complex in 10 ml of THF (65 ml for chloro com-plex) at —78°C was added dropwise one molar equivalent of methyllithium (low halide for the chloro complex) as an ether solution. As the temperature was increased gradually to 0°C, the colorless solution turned pale yellow. After stirring for 1 h, the solvent was removed under reduced pressure and the anionic complex was dissolved in 10 ml of ether (50 ml for chloro complex) and then cooled to 0°C. To this solution was added dropwise 1.5 molar equivalents of anhydrous HCl as an ether solution, and an immediate white precipitate of

LiCl formed. The reaction mixture was stirred at 25°C for 30 min. The ether was removed under reduced pressure and the mixture was extracted with 10 ml of hexane (30 ml for chloro complex) and then filtered. The pale yellow complexes crystallized from this solution when kept at −78°C for 16 h. Specific data for each reaction are provided below.

cis-(OC)₄(Cl)Re[C(CH₃)(OH)] (III). Using 0.28 g (0.77 mmol) of ClRe(CO)₅ afforded 57 mg (0.151 mmol, 19.6%) of III as fine tan crystals: m.p. 76—77°C; IR (hexane): ν(CO) 2124w, 2040s, 2027vs, 1949s cm⁻¹; ¹H-NMR (CDCl₃): τ 6.89 (singlet, 3, CH₃) ppm; the mass spectrum (calcd. for $C_6H_4{}^{37}ClO_5{}^{187}Re$: M^+, 380) possesses the correct three-peak isotopic pattern for the parent ions at m/e 376, 378 and 380 (*P*, 14%) and for subsequent fragmentation ions. Anal. Found: C, 18.90; H, 1.07. $C_6H_4ClO_5Re$ calcd.: C, 19.08; H, 1.07%.

cis-(OC)₄(Br)Re[C(CH₃)(OH)] (IV). Using 0.28 g (0.69 mmol) of BrRe(CO)₅ afforded 44 mg (0.105 mmol, 15.3%) of IV as a pale yellow solid: m.p. 50—51°C; IR (hexane): ν(CO) 2120m, 2039s, 2030vs, 1950s cm⁻¹; ¹H NMR (CDCl₃): τ 6.87 (singlet, 3, CH₃) ppm; the mass spectrum (calcd. for $C_6H_4{}^{81}BrO_5{}^{187}Re$: M^+, 424) exhibited the correct three-peak isotopic pattern for the parent ions at m/e 420, 422 and 424 (*P*, 99%) and for subsequent fragmentation ions. Anal. Found: C, 16.73; H, 1.00. $C_6H_4BrO_5Re$ calcd.: C, 17.07; H, 0.96%.

cis-(OC)₄(I)Re[C(CH₃)(OH)] (V). Using 0.23 g (0.51 mmol) of IRe(CO)₅ afforded 96 mg (0.204 mmol, 40%) of V as a pale yellow solid: m.p. 35—36°C; IR (hexane): ν(CO) 2120m, 2040s, 2030vs, 1953s cm⁻¹; ¹H NMR (CDCl₃): τ 6.85 (singlet, 3, CH₃) ppm; the mass spectrum (calcd. for $C_6H_4IO_5{}^{187}Re$: M^+, 471) showed the correct isotopic pattern for the parent ions at m/e 469 and 471 (*P*, 21%), and for subsequent fragmentation ions. Anal. Found: C, 13.84; H, 0.81. $C_6H_4IO_5Re$ calcd.: C, 15.36; H, 0.86%.

Preparation of Li[cis-(OC)₄(H)ReC(O)CH₃] (VI)

To a stirred solution of 0.25 g (0.764 mmol) of HRe(CO)₅ in 10 ml of THF at −78°C was added 0.77 mmol of methyllithium as an ether solution. The temperature was increased gradually to 25°C while stirring for 1 h, and the colorless solution turned pale yellow. The anion VI was characterized in solution: IR (THF): ν(CO) 2055w, 1940vs(br), 1918s, ν(acyl) 1548m cm⁻¹; ¹H NMR (THF): τ 14.66 (singlet, 1, ReH); 7.68 (singlet, 3, CH₃) ppm.

Preparation of the Li[cis-(OC)₄(X)ReC(O)H] salts (VIII—X)

General procedure. To a stirred solution of 0.05—0.5 mmol of the appropriate halopentacarbonylrhenium complex in 15 ml tetrahydrofuran at −78°C was added one molar equivalent of the corresponding hydrohalic acid and two molar equivalents of lithium triethylborohydride, Li[BEt₃H], as a THF solution. The solution turned yellow upon warming to 25°C over a 45 min period. The reaction solution was concentrated to ca. 0.4 ml under reduced pressure for solution characterization.

Li[cis-(OC)₄(Cl)ReC(O)H] (VIII). Using 0.022 g (0.06 mmol) of ClRe(CO)₅ and 0.06 mmol of anhydrous HCl as an ether solution afforded the formyl complex VIII: IR (THF): ν(CO) 2090w, 1970vs(br), 1900s(br), ν(formyl) 1575m cm⁻¹; ¹H NMR (THF): τ −5.06 ppm.

Li[cis-(OC)₄(Br)ReC(O)H] (IX). Using 0.15 g (0.38 mmol) of BrRe(CO)₅

and 0.38 mmol of anhydrous HBr as an ether solution afforded the formyl complex IX: IR (THF): ν(CO) 2095w, 1970vs(br), 1910s(br), ν(formyl) 1575m;cm^{-1}; ^{1}H NMR (THF): τ —5.01 ppm.

Li[cis-(OC)$_4$(I)ReC(O)H] (X). Using 0.14 g (0.31 mmol) of IRe(CO)$_5$ and a slight excess of Li[BEt$_3$H] afforded the formyl complex X: IR (THF): ν(CO) 2093w, 1970vs(br), 1918s(br), ν(formyl) 1568m cm^{-1}; ^{1}H NMR (THF): τ —5.14 ppm.

Preparation of Li[cis-(OC)$_4$Re(CH$_3$CO)(HCO)] (XI)

To a stirred solution of 0.14 g (0.39 mmol) of CH$_3$C(O)Re(CO)$_5$ in 10 ml of THF at —78°C was added 0.40 mmol of Li[BEt$_3$H] as a THF solution. The reaction solution was warmed to 0°C over a 50 min period, affording the pale yellow metallaformylacetonate complex (XI): IR (THF): ν(CO) 2065w, 2035vs(br), 2015s(sh), ν(acylformyl) 1580m cm^{-1}; ^{1}H NMR (THF): τ 7.45 (singlet, 3, CH$_3$), —4.31 (singlet, 1, HCO) ppm.

Acknowledgements

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