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Synthesis and Protonation of the Dithioformato Complex $OsH(\eta^2\text{-}S_2CH)(CO)(P\textit{i}Pr_3)_2$

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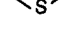
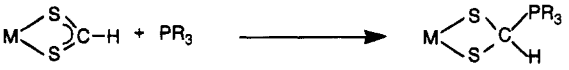
Summary: The reaction of the complex $OsHCl(CO)(PiPr_3)_2$ *(**1**) with nBuLi in hexane affords* $OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(PiPr_3)_2$ *(**2**) which reacts with* CS_2 *to give* $OsH(\eta^2\text{-}S_2CH)(CO)(PiPr_3)_2$ *(**3**). The reaction of **3** with* $HBF_4{\cdot}OEt_2$ *leads to two different derivatives depending upon the nature of the solvent used. The dihydrogen compound* $[Os(\eta^2\text{-}S_2CH)(\eta^2\text{-}H_2)(CO)(PiPr_3)_2]BF_4$ *(**4**) is formed in dichloromethane-*d_2*, while the methanedithiolate complex* $[OsH(\eta^2\text{-}S_2CH_2)(CO)(PiPr_3)_2]BF_4$ *(**5**) is obtained in diethyl ether.*

Introduction

Mononuclear metal hydrido complexes react with CS_2 to form complexes containing the dithioformato group by transferring the hydrido ligand to the CS_2 molecule (eq 1).[1]


(1)

The reactivity of dithioformato complexes toward nucleophiles has been studied in recent years, and it has been demonstrated that the central carbon atom of the S_2CH group is an electrophile. Thus, it undergoes attack by nucleophiles like tertiary phosphines (eq 2).[2] Indeed, the carbon atom of a variety of 1,1-dithio acid ligands is an electrophilic center, susceptible to attack by nucleophiles, which either add to the dithio ligand or replace the primary substituent on the carbon atom.[3]


(2)

The analogue reactions toward electrophiles have however received less attention. Following our previous work on the chemistry of the five-coordinated complexes $OsHCl(CO)(P\textit{i}Pr_3)_2$ (**1**),[4] we have now prepared the hydrido–olefin compound $OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P\textit{i}Pr_3)_2$ (**2**), which reacts with CS_2 to give the dithioformato complex $OsH(\eta^2\text{-}S_2CH)(CO)(P\textit{i}Pr_3)_2$ (**3**). In this paper, we report the synthesis and characterization of **2** and **3** and the reactivity of **3** toward HBF_4.

Results and Discussion

The complex $OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(P\textit{i}Pr_3)_2$ (**2**) was prepared by reaction of $OsHCl(CO)(P\textit{i}Pr_3)_2$ (**1**) with *n*BuLi in hexane at room temperature (Scheme 1). The reaction most probably involves the replacement of the Cl^- anion by a butyl group to give $OsH(Bu)(CO)(P\textit{i}Pr_3)_2$, which by a subsequent hydrogen β-elimination affords **2**.

Complex **2** was isolated as a colorless oil in quantitative yield and characterized by ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopies. The ^1H NMR spectrum in benzene-d_6 shows in the hydrido region two doublet of triplets at −9.8 and −11.6 ppm with P−H coupling constants of 31.0 and 23.9 Hz, respectively, and H−H coupling constants of 5.5 Hz. The vinylic protons of the coordinated 1-butene olefin appear at 3.0 and 2.5 ppm. In the $^{13}C\{^1H\}$ NMR spectrum the vinylic carbon atoms are observed as broad signals at 46.5 and 34.8 ppm. In agreement with the stereochemistry shown in Scheme 1, the $^{31}P\{^1H\}$ NMR spectrum of **2** exhibits an AB splitting pattern.

Previously, we have reported the synthesis of $OsH_2(\eta^2\text{-}CH_2{=}CHPh)(CO)(P\textit{i}Pr_3)_2$ comparable in structure to **2**. This complex was obtained by reaction of the hydrido–dihydrogen–alkynyl complex $OsH(C_2Ph)(\eta^2\text{-}H_2)(CO)(P\textit{i}Pr_3)_2$ with molecular hydrogen.[5]

Complex **2** reacts with CS_2 in hexane at room temperature to give, after 30 min, the dithioformato complex $OsH(\eta^2\text{-}S_2CH)(CO)(P\textit{i}Pr_3)_2$ (**3**), which was isolated as an orange solid in 68% yield.

The dithioformato ligand is formulated as bidentate on the basis of the IR spectrum in Nujol, which shows bands at 1248 (ν(HCS)) and 925 ($\nu(CS_2)_{asym}$) cm^{-1}, in accordance with those found for related osmium compounds.[6] The ^1H NMR spectrum in benzene-d_6 has the expected resonances for the hydrido and the dithioformato ligands. The hydrido ligand appears as a doublet of triplets at −12.8 ppm with $^4J_{H-H}$ and $^2J_{P-H}$ coupling constants of 2.4 and 21.4 Hz, respectively. The proton of the dithioformato ligand is also observed as a doublet of triplets at 12.7 ppm with $^4J_{H-H}$ and $^4J_{P-H}$ coupling constants of 2.4 and 3.9 Hz, respectively.

The $^{31}P\{^1H\}$ NMR spectrum in benzene-d_6 shows a singlet at 33.6 ppm, indicating the two phosphine ligands are equivalent and are mutually trans disposed.

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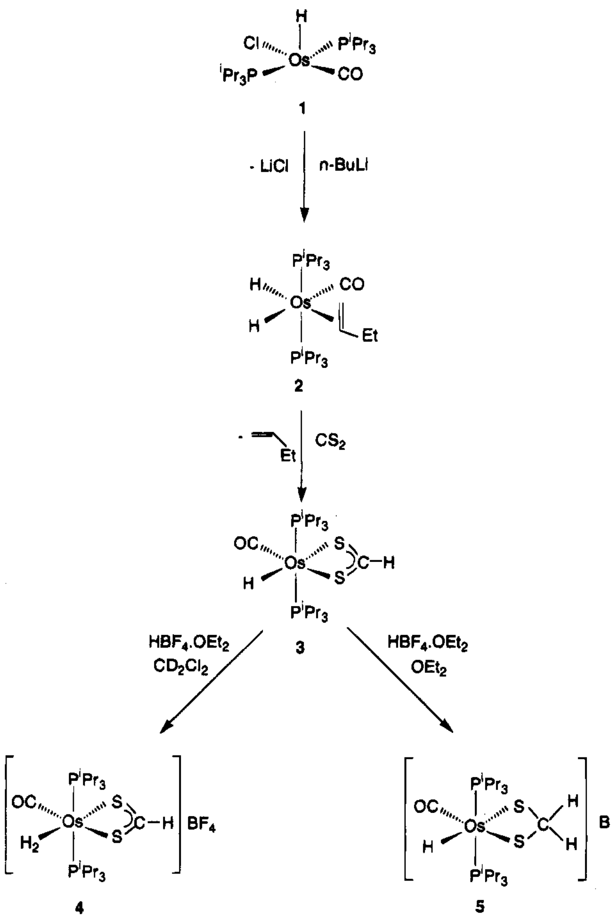
Scheme 1



The dithioformato complex **3** reacts with HBF_4. The addition of 1 equiv of $HBF_4{\cdot}OEt_2$ to a solution of **3** in dichloromethane-d_2 leads, after a few seconds, to the dihydrogen complex **4** (Scheme 1).

The ^1H NMR spectrum of **4** has the typically broad dihydrogen signal at −7.5 ppm and the resonance of the dithioformato at 12.9 (t, $^4J_{P-H}$ = 4.2 Hz) ppm. A variable temperature 300-MHz T_1 study of the dihydrogen peak of **4** gives a T_1 (min) of 8 ms at 203 K. This T_1(min) value corresponds to a hydrogen–hydrogen distance of 0.79 Å (fast spinning) or 1.00 Å (slow spinning).[7] The H–D coupling constant, J_{H-D}, of 25.1 Hz in $[Os(\eta^2\text{-}S_2CH)(\eta^2\text{-}HD)(CO)(PiPr_3)_2]^+$ suggests that the 1.00-Å hydrogen–hydrogen distance is the more likely one.[8]

The $^{31}P\{^1H\}$ NMR spectrum shows a singlet at 26.5 ppm in agreement with the structure shown in Scheme 1.

Since the first report by Kubas *et al.* on the coordination of molecular hydrogen to a transition metal,[9] a large family of dihydrogen complexes has been reported.[8] However, the number of complexes of this type containing S-donor ligands remains small. Recently, we have observed that the reactions of $OsH_2Cl_2(PiPr_3)_2$ with $K(EtOCS_2)$ and $K(CH_3COS)$ lead to the dihydrogen compounds $Os(\eta^2\text{-}S_2COEt)(\eta^1\text{-}SC(S)OEt)(\eta^2\text{-}H_2)(PiPr_3)_2$ and $Os(\eta^2\text{-}OSCCH_3)(\eta^1\text{-}SC(O)CH_3)(\eta^2\text{-}H_2)(PiPr_3)_2$, respectively.[10] Subsequently, Morris and co-workers reported that the reaction of $OsH(pyS)(CO)(PPh_3)_2$ (pySH = 2-pyridinethiol) with $HBF_4{\cdot}OEt_2$ affords $[Os(pyS)(\eta^2\text{-}H_2)(CO)(PPh_3)_2]^+$ as a mixture of two isomers.[11]

Complex **4** is stable in solution under argon at 20 °C for at least 24 h. However, the coordinated dihydrogen ligand in this complex is highly activated toward heterolytic cleavage, as demonstrated by deprotonation with very weak bases such as diethyl ether. This suggests that the pk_a of **4** is similar to the pk_a of the cation $[Ru(\eta^5\text{-}C_5Me_5)(\eta^2\text{-}H_2)(CO)_2]^+$, for which the estimated pk_a value is −2 in dichloromethane.[12]

When the reaction of the dithioformato complex **3** with $HBF_4{\cdot}OEt_2$ is carried out in diethyl ether as a solvent, a dark red-brown product is obtained in 43% yield after 5 h. The new product is formulated as the methanedithiolate complex $[OsH(\eta^2\text{-}S_2CH_2)(CO)(PiPr_3)_2]BF_4$ (**5**) (Scheme 1), on the basis of its IR and ^1H and $^{31}P\{^1H\}$ NMR spectra.

The IR spectrum in Nujol shows the absorption due to the $[BF_4]^-$ anion between 1030 and 1100 cm^{-1} with T_d symmetry, along with bands characteristic of the coordinated ligands. In particular, the absorptions at 2020, 1955, and 1245 cm^{-1} assigned to the hydrido, carbonyl, and methanodithiolate groups, respectively, must be mentioned. The ^1H NMR spectrum in chloroform-d_1 exhibits the signals corresponding to the $PiPr_3$ ligands together with a singlet at 5.5 ppm due to the S_2CH_2 group and a triplet at −10.7 ppm (J_{P-H} = 29.2 Hz) assigned to the hydrido ligand. The $^{31}P\{^1H\}$ NMR spectrum contains a singlet at 33.5 ppm, which under off-resonance conditions due to the P–H coupling, is split into a doublet.

Although the insertion reactions of CS_2 into the metal–hydrido bonds are common, the reduction of CS_2 to methanedithiolate has only been seen in a few cases and, as far as we know, never by reaction of a dithioformato complex with an acid.

Adams *et al.* have reported that the reactions of CS_2 with $H_2Os_3(CO)_{10}$ and $H_2Os_3(CO)_9(PMe_2Ph)$ afford dicluster complexes of formula $(\mu\text{-}S_2CH_2)[HOs_3(CO)_9L]_2$ (L = CO, PMe_2Ph).[13] DuBois and co-workers have observed that the deprotonation of $[CpMo(S)SH]_2$ with 2 equiv of sodium methoxide in the presence of excess dibromomethane results in the formation of the dimer $(\mu\text{-}S_2CH_2)[CpMoS]_2$, which contains a bridging methanedithiolate ligand.[14] Most recently, Jones *et al.* have prepared the complex $Rh(Cp^*)(\eta^2\text{-}S_2CH_2)(PMe_3)$ by reaction of $RhH_2(Cp^*)(PMe_3)$ with CS_2.[15]

Direct attack of H^+ at the CS_2 carbon of the S_2CH entity of **3**, to give **5**, does not seem likely in view of the electrophilicity of this atom. Hence it can be proposed that in diethyl ether solution **3** is in equilibrium with a nondetected $Os(\eta^2\text{-}S_2CH_2)(CO)(PiPr_3)_2$ isomer, which could undergo the attack of the acid. In good agreement

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with this assumption, Jia *et al.* ahve observed that the complex $RuH(\eta^2\text{-}S_2CH)(Cyttp)$ (Cyttp = $PhP(CH_2CH_2CH_2P(C_6H_{11})_2)_2$) is unstable in benzene solution and slowly isomerizes into $Ru(\eta^2\text{-}S_2CH_2)(Cyttp)$.[16]

In conclusion, the reaction of the dithioformato complex $OsH(\eta^2\text{-}S_2CH)(CO)(PiPr_3)_2$ with HBF_4 leads to two different derivatives depending upon the nature of the solvent used. The dihydrogen compound $[Os(\eta^2\text{-}S_2CH)(\eta^2\text{-}H_2)(CO)(PiPr_3)_2]BF_4$ is formed in dichloromethane-d_2, while the methanedithiolate complex $[OsH(\eta^2\text{-}S_2CH_2)(CO)(PiPr_3)_2]BF_4$ is obtained in diethyl ether. This complex is the first example of a mononuclear methanedithiolate osmium compound, and also is the first example of methanedithiolate complex obtained by reaction of a dithioformate compound with an acid.

Experimental Section

General Considerations. All reactions were carried out under an argon atmosphere by using Schlenk or NMR tube techniques. Solvents were dried and purified by known procedures and distilled under argon prior to use. The starting complex $OsHCl(CO)(PiPr_3)_2$ was prepared by a published method.[17]

Physical Measurements. NMR spectra were recorded on a Varian 200 XL or a Varian UNITY 300 spectrometer at room temperature. Chemical shifts are expressed in parts per million, upfield from $Si(CH_3)_4$ (^1H and $^{13}C\{^1H\}$ NMR spectra) and 85% H_3PO_4 {$^{31}P\{^1H\}$ NMR spectra). Coupling constants J and N ($N = J(HP) + J(HP')$) are given in hertz. The T_1 experiments were performed on a Varian UNITY 300 spectrophotometer with a standard 180°-τ-90° pulse sequence. T_1 values are given in miliseconds (ms). Infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer using Nujol mulls on polyethylene sheets. C and H analyses were carried out on a Perkin-Elmer 240C microanalyzer.

Preparation of $OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(PiPr_3)_2$ (2). A suspension of $OsHCl(CO)(PiPr_3)_2$ (**1**) (60 mg, 0.10 mmol) in 6 mL of hexane was treated with a hexane solution of *n*BuLi (0.06 mL, 0.10 mmol) at room temperature. The color of the mixture changed from red to white. Then the mixture was filtered through Kieselguhr and the filtrate was concentrated to dryness, leaving a colorless oil. ^1H NMR (300 MHz, C_6D_6): δ 3.0 (br, 1 H, =CH−), 2.5 (m, 2 H, CH_2=), 2.2 (m, 6 H, $PCHCH_3$), 1.6 (dq, 2 H, $J(HH) = 12.2$, $J(HH) = 6.3$, $CHCH_2$), 1.3, 1.2 (both dvt, each 18 H, $N = 12.7$, $J(HH) = 7.0$, $PCHCH_3$), 1.0 (t, 3 H, $J(HH) = 6.3$, CH_2CH_3), −9.8 (td, 1 H, $J(HP^a) \cong J(HP^b) = 31$, $J(HH) = 5.5$, OsH), −11.6 (td, 1 H, $J(HP^a) \cong J(HP^b) = 23.9$, $J(HH) = 5.5$, OsH). $^{31}P\{^1H\}$ NMR (80.98 MHz, C_6D_6: δ 32.6, 32.2 (AB system, $J(P^aP^b) = 142$). $^{13}C\{^1H\}$ NMR (75.33 MHz, C_6D_6): δ 188 (t, $J(CP) = 6.5$, CO), 46.5 (br, =CH), 34.8 (br, H_2C=), 29.8 (dd, $J(CP) = 19.7$ and 7.8, PCH), 28.8 (dd, $J(CP) = 19.8$ and 8.2, PCH), 27.2 (s, CH_2CH_3), 20.4 (s, CH_2CH_3), 20.8, 20.1, 19.7, 19.6 (all s, $PCHCH_3$).

Preparation of $OsH(\eta^2\text{-}S_2CH)(CO)(PiPr_3)_2$ (3). A solution of $OsH_2(\eta^2\text{-}CH_2{=}CHEt)(CO)(PiPr_3)_2$ (**2**) (ca. 124 mg, 0.21 mmol) in 5 mL of hexane was treated with CS_2 (15.5 μL, 0.26 mmol) at room temperature. The color of the solution turned to orange. The mixture was concentrated in vacuo to dryness. Addition of cold methanol to the resulting residue caused the formation of a solid. The mixture was decanted, and the resulting orange solid was washed with methanol and dried in vacuo: yield 84 mg (68%). Anal. Calcd for $C_{20}H_{44}OOsP_2S_2$: C, 38.94; H, 7.18. Found: C, 38.95; H, 7.79. IR (Nujol, cm^{-1}): ν(OsH) 2067, ν(CO) 1900, ν(HCS) 1248, ν(CS_2 asym) 925. ^1H NMR (300 MHz, C_6D_6): δ 12.7 (td, 1 H, $J(HP) = 3.9$, $J(HH) = 2.4$, S_2CH), 2.5 (m, 6 H, $PCHCH_3$), 1.2, 1.1 (both dvt, each 18 H, $N = 13.8$, $J(HH) = 7.2$, $PCHCH_3$), −12.8 (td, 1 H, $J(HP) = 21.4$, $J(HH) = 2.4$, OsH). $^{31}P\{^1H\}$ NMR (80.98 MHz, hexane/C_6D_6): δ 33.6 (s).

Reaction of $OsH(\eta^2\text{-}S_2CH)(CO)(PiPr_3)_2$ (3) with HBF_4 in Dichloromethane: Preparation of $[Os(\eta^2\text{-}S_2CH)(\eta^2\text{-}H_2)(CO)(PiPr_3)_2]BF_4$ (4). In an NMR tube a solution of $OsH(\eta^2\text{-}S_2CH)(CO)(PiPr_3)_2$ (**3**) (10 mg, 0.016 mmol) in 0.5 mL of dichloromethane-d_2 was treated with a stoichiometric amount of $HBF_4{\cdot}OEt_2$ (2.2 μL, 0.016 mmol). No color change was observed. The NMR tube was sealed under argon, and the reaction was followed by NMR. ^1H NMR (300 MHz, CD_2Cl_2): δ 12.9 (t, 1 H, $J(HP) = 4.2$, S_2CH), 2.7 (m, 6 H, $PCHCH_3$), 1.4 (dvt, 36 H, $N = 15.0$, $J(HH) = 7.0$, $PCHCH_3$), −7.5 (br, 2 H, $Os(\eta^2\text{-}H_2)$). $^{31}P\{^1H\}$ NMR (121.4 MHz, CD_2Cl_2): δ 26.5 (s). T_1 of $Os(\eta^2\text{-}H_2)$ (300 MHz, CD_2Cl_2) = 38 (293 K), 21 (253 K), 14 (233 K), 9 (213 K), 8 (203 K), 8 (193 K).

Reaction of $OsH(\eta^2\text{-}S_2CH)(CO)(PiPr_3)_2$ (3) with HBF_4 in Diethyl Ether: Preparation of $[OsH(\eta^2\text{-}S_2CH_2)(CO)(PiPr_3)_2]BF_4$ (5). A solution of $OsH(\eta^2\text{-}S_2CH)(CO)(PiPr_3)_2$ (**3**) (100 mg, 0.16 mmol) in 15 mL of diethyl ether was treated with $HBF_4{\cdot}OEt_2$ (44 μL, 0.32 mmol). After the mixture was stirred for 5 h at room temperature, a dark red-brown solid precipitated. The resulting red-brown solid was decanted, repeatedly washed with diethy ether, and dried in vacuo: yield 48 mg (43%). Anal. Calcd for $C_{20}H_{45}BF_4OOsP_2S_2$: C, 34.09; H, 6.44. Found: C, 33.90; H, 6.27. IR (Nujol, cm^{-1}): ν(OsH) 2020, ν(CO) 1955, ν(HCS) 1245, ν(BF) 1100−1030. ^1H NMR (300 MHz, $CDCl_3$): δ 5.5 (s, 2 H, S_2CH_2), 2.7 (m, 6 H, $PCHCH_3$), 1.4, 1.3 (both dd, each 18 H, $J(HP) = 16.7$, $J(HH) = 7.0$, $PCHCH_3$), −10.7 (t, 1 H, $J(HP) = 29.2$, OsH). $^{31}P\{^1H\}$ NMR (121.4 MHz, $CDCl_3$): δ 33.5 (s).

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