$Re_2X_4(PR_3)_4$. These are obtained[9,20] upon heating Re_3X_9 with certain tertiary phosphines in acetone or alcohol solvents. In the present work, the first rhenium(II) iodide complex of this type, $Re_2I_4(P\text{-}n\text{-}Pr_3)_4$, has been isolated.[7]

The formation of β-MoI_2 from the reaction between $Mo_2(O_2CCH_3)_4$ and hydrogen iodide completes the series of β-MoX_2 phases (X = Cl, Br, or I) which may be prepared by this synthetic procedure. The low magnetic moment of this phase ($\mu_{eff} = 0.66\ \mu_B$ at room temperature) resembles the related magnetic behavior of β-$MoCl_2$ and β-$MoBr_2$ (μ_{eff} = 0.49 and 0.60 μ_B, respectively),[2,21] and like the latter phases it possesses a characteristic x-ray powder diffraction pattern. However, these three halides are not isomorphous with one another. The ESCA spectrum of β-MoI_2, with Mo $3d_{3/2,5/2}$ binding energies at 231.5 and 228.4 eV, is characteristic of a molybdenum(II) halide.[22]

Although β-MoI_2 reacts with refluxing pyridine, the pure complex $Mo_2I_4py_4$ could not be isolated from this reaction mixture. In contrast to this, upon reacting β-MoI_2 with a refluxing acetone solution of tri-*n*-propylphosphine, the blue crystalline complex $Mo_2I_4(P\text{-}n\text{-}Pr_3)_4$ was obtained. This latter reaction is analogous to that of β-$MoCl_2$ and β-$MoBr_2$ with this phosphine and supports the formulation of β-MoI_2 as $[Mo_2I_4]_n$, containing a very strong metal–metal bond and being the parent halide of the as yet unknown $Mo_2I_8^{4-}$ anion.

The complex $Mo_2I_4(P\text{-}n\text{-}Pr_3)_4$ exhibits moderate air stability, although it shows obvious signs of decomposition if kept in the air for more than a day. Its solutions are even more sensitive to oxygen; in dichloromethane a rapid color change from blue to yellow-brown occurs upon aerial oxidation. The infrared spectrum of this complex in the region between 4000 and 400 cm^{-1} is virtually identical with that of $Mo_2Br_4(P\text{-}n\text{-}Pr_3)_4$[2] and its Nujol mull electronic absorption spectrum (λ_{max} at 645 (s), 530 (w), 475 (vw)?, 408 (s) nm) reveals a strikingly similar spectral profile to that of the bromide complex.[2] The identity of this complex as an authentic derivative of molybdenum(II) is further supported by ESCA measurements which show that it possesses Mo $3d_{3/2,5/2}$ binding energies (231.7 and 228.6 eV) which are typical of a molybdenum(II) complex of the type $Mo_2X_4L_4$.[22]

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Registry No. β-MoI_2, 14055-74-4; Re_3I_9, 15622-42-1; $Mo_2I_4(py)_4$, 59610-42-3; $Mo_2I_4(PPr_3)_4$, 64508-28-7; $Re_2I_4(PPr_3)_4$, 64508-27-6; $Mo_2(O_2CCH_3)_4$, 14221-06-8; $Re_2(O_2CCH_3)_4Cl_2$, 14126-96-6; HI, 10034-85-2.

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Reactions of Coordinated Molecules. 13. The Reaction of the Rhenium Tetracarbonyl Metalloacetylacetone Complex with Boron Trihalides

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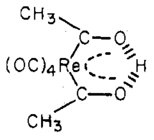
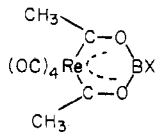
The preparation and structure determination of the first example of a metallo-β-diketone molecule were reported recently.[1] This molecule, **1**, exists as the symmetrical structural analogue of the enol tautomer of acetylacetone, and several derivatives of this molecule having various substituents on the chelate ring as well as a different metallo moiety have been prepared.[2] The comparison of the chemical reactivity of these metallo-β-diketone molecules to that of the nonmetallo analogues is being pursued actively.



1



2

We wish to report that complex **1** reacts with boron trihalides, BX_3 (where X = F, Cl, Br, or I), upon mixing in pentane solution at −35 °C, affording neutral (metallo-β-diketonate)BX_2 compounds, **2**, in high yield.

Experimental Section

All reactions and other manipulations were performed under dry prepurified nitrogen at 25 °C unless otherwise stated. Diethyl ether and pentane were dried over Na/K alloy under a nitrogen atmosphere and were distilled before use. Methylene chloride was distilled from P_2O_5 prior to use. Gaseous boron trifluoride and boron trichloride were purchased from K & K Labs and Matheson Gas Products, respectively, while boron tribromide and boron triiodide were purchased from Alfa Products. Complex **1** was prepared by a literature procedure.[1]

Infrared spectra were recorded on a Perkin-Elmer 727 spectrometer as solutions in 0.10-mm sodium chloride cavity cells using the solvent as a reference and a polystyrene film as a calibration standard. Band frequencies are reported in cm^{-1}. ^1H NMR spectra were obtained on a Joel MH-100 NMR spectrometer using Me_4Si as an internal reference. Mass spectra were obtained on a LKB 9000 spectrometer.

General Preparation of the Complexes [*cis*-$(OC)_4Re(CH_3CO)_2$]BX_2 (3–6). A solution of 0.10–0.25 g of complex **1** in 30 mL of pentane was cooled to −35 °C. To this solution was added 2 molar equiv of the appropriate boron trihalide as a gas (BF_3 and BCl_3), liquid (BBr_3), or solid (BI_3). The product formed within 5 s of the mixing of the reagents as a white to yellow powder. The reaction mixture was stirred at −35 °C for an additional 20 min and then was allowed to warm to 25 °C. After 20 min of stirring at room temperature, the solvent was removed at reduced pressure, affording the crude product in 76–90% yield. The reaction residue was extracted with a minimum

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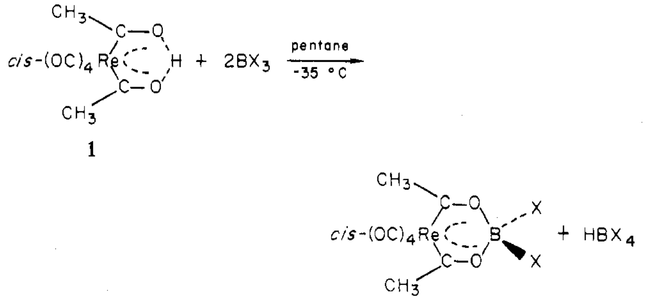
Scheme I



3, X = F
4, X = Cl
5, X = Br
6, X = I

volume of diethyl ether. The resulting mixture was filtered, and the filtrate was placed at −20 °C for 16 h, affording the product complexes as single crystals, except for the iodide complex which underwent slow decomposition. The detailed characterization of each complex is provided below.

[*cis*-$(OC)_4Re(CH_3CO)_2$]BF_2 (3). Colorless crystals (90%); mp 149–150 °C; IR (CH_2Cl_2) ν(CO) 2120 (m), 2045 (vs), 2025 (vs), 1990 (s); ν(C$\overset{\cdots}{-}$O) 1475 (m); ^{1}H NMR ($CDCl_3$) τ 6.95 (singlet, methyl groups). Anal. Calcd for $C_8H_6O_6BReF_2$: C, 22.18; H, 1.39; B, 2.49; F, 8.55. Found: C, 22.20; H, 1.44; B, 2.63; F, 8.55.

[*cis*-$(OC)_4Re(CH_3CO)_2$]BCl_2 (4). Pale lemon crystals (87%); mp 125–128 °C (dec); IR (CH_2Cl_2) ν(CO) 2120 (m), 2040 (vs), 2020 (vs), 1987 (s); ν(C$\overset{\cdots}{-}$O) 1447 (m); ^{1}H NMR ($CDCl_3$) τ 6.85 (singlet, methyl groups); MS, parent *m/e* 466. Anal. Calcd for $C_8H_6O_6BReCl_2$: C, 20.61; H, 1.30; B, 2.32; Cl, 15.44. Found: C, 20.76; H, 1.41; B, 1.63; Cl, 15.03.

[*cis*-$(OC)_4Re(CH_3CO)_2$]BBr_2 (5). Pale lemon crystals (76%); dec 100–125 °C; IR (CH_2Cl_2) ν(CO) 2105 (m), 2040 (vs), 2020 (vs), 1985 (s); ν(C$\overset{\cdots}{-}$O) 1455 (m); ^{1}H NMR ($CDCl_3$) τ 6.85 (singlet, methyl groups). Anal. Calcd for $C_8H_6O_6BReBr_2$: C, 17.32; H, 1.09; B, 1.95; Br, 28.81. Found: C, 17.48; H, 1.11; B, 2.02; Br, 28.35.

[*cis*-$(OC)_4Re(CH_3CO)_2$]BI_2 (6). Yellow powder; IR (CH_2Cl_2) ν(CO) 2115 (m), 2040 (vs, br), 1990 (vs); ^{1}H NMR ($CDCl_3$) τ 6.82 (singlet, methyl groups).

Results and Discussion

When the rhenium metalloacetylacetone complex **1** is treated with a boron trihalide, the neutral (metallo-β-diketonate)BX_2 complexes **3**–**6** are formed immediately with, presumably, the elimination of the corresponding haloboric acid, HBX_4, as shown in Scheme I.

The BX_2 complexes, where X is F, Cl, and Br, have excellent thermal stability, and all three complexes show no air decomposition for at least 15 min. The fluoride and chloride complexes are air stable for at least 24 h. However, the reaction solution of the iodide complex turns pink upon warming to near 25 °C. This decomposition of the iodide complex is so sufficiently rapid at 25 °C that the attempted crystallization of complex **6** from a minimum volume of methylene chloride/ether solution (1:3) at −20 °C afforded only an orange oil and a small amount of a purple solid. Apparently, the iodide complex decomposes thermally by the elimination of iodine. The bromide complex may similarly eliminate bromine at temperatures near 125 °C, where a red-brown liquid phase is observed. All four complexes are soluble in benzene, and therefore they are considered to be covalent complexes.

The solution-phase infrared spectra for all four BX_2 complexes, **3**–**6**, are nearly identical. The terminal carbonyl stretching vibrations are consistent with a *cis*-$(OC)_4$Re moiety.[3] The $A_1{}^1$, B_1, and B_2 modes of these complexes appear at ca. 30 cm^{-1} to higher frequency than the same vibrational modes of the rhenium–enol complex **1**.[4] Presumably, the BX_2 unit is more electron withdrawing or a stronger Lewis acid than the enolic proton. Also, the vibrational mode assigned to the intraligand acyl C$\overset{\cdots}{-}$O stretching stretching vibration (1447–1475 cm^{-1}) occurs at least 40 cm^{-1} to lower frequency in the BX_2 complex than in complex **1**.[1] This shift is also consistent with a stronger coordination of the metallo-acac ligand to the BX_2 groups than to the enolic proton. The corresponding vibrational mode of (acac)BF_2 occurs at 1560 cm^{-1}.[5]

The ^{1}H NMR spectra of compounds **3**–**6** show only a single resonance for the equivalent methyl groups within the range τ 6.89 ± 0.07 in $CDCl_3$ solution. The corresponding resonances of the Re–enol complex **1** and the organic analogue (acac)BF_2 occur at τ 7.22 and 7.71, respectively.[1,6] The observed shift of the methyl resonance of **1** to lower field for complexes **3**–**6** is consistent with a greater withdrawal of electron density from the metallo-acac ligand toward the BX_2 group.

The spectroscopic, microanalytical, and solubility data for the complexes **3**–**6** indicate that the compounds are metallo analogues of the well-known β-diketonate complexes of BF_2.[7] These organic analogues are prepared by treating the neutral β-diketone molecule with BF_3. Solution molecular weight measurements of several (β-diketonate)BF_2 molecules[8] and the mass spectrum of complex **4** indicate strongly that these molecules are monomeric four-coordinate complexes of boron possessing a bidentate chelating β-diketonate ligand.

Complexes **3**–**6** are formed by a reaction which is similar to the use of BF_3·etherate to link the coordinated dimethylglyoxime ligands in both the bis-chelate Ni(II) complex[9] and the tris-chelate Co(III) complex.[10]

The chemical reactivity of complex **1** is both unique and intriguing. Although complex **1** reacts with all boron trihalides to afford the corresponding (metallo-acac)BX_2 complexes, acetylacetone reacts similarly only with BF_3. When acetylacetone is treated with BCl_3, the boronium ion $B(acac)_2{}^+Cl^-$ is formed.[11] The reactions of acetylacetone with BBr_3 and BI_3 are not reported; however, the formation of similar boronium salts is expected since the Lewis acidity of these boron trihalides is even greater. The stability of complexes **3**–**5** has prevented the preparation of boronium complexes having metallo-β-diketonate ligands. Similarly, complex **1** does *not* react with boron trihalides to eliminate a hydroxide ion, affording an acyl(methyl)carbyne complex of rhenium, as might be expected if it were to react as a carbenoid complex.[12]

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Registry No. 1, 64714-90-5; **3**, 64714-91-6; **4**, 64714-92-7; **5**, 64714-93-8; **6**, 64728-45-6; BF_3, 7637-07-2; BCl_3, 10294-34-5; BBr_3, 10294-33-4; BI_3, 13517-10-7.

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