

- (9) H. A. Kuska, *J. Am. Chem. Soc.*, **97**, 2289 (1975).
- (10) B. W. Levitt and L. S. Levitt, *Coord. Chem.*, **3**, 187 (1973).
- (11) J. W. Warren, *Nature (London)*, **164**, 810 (1950).
- (12) F. A. White, "Mass Spectrometry in Science and Technology", Wiley, New York, N.Y., 1968, pp 343-345.
- (13) H. H. Jaffe, D. L. Beveridge, and M. Orchin, *J. Chem. Educ.*, **44**, 383 (1967).
- (14) H. G. Brittain and R. Disch, *J. Electron Spectrosc.*, **7**, 475 (1975).
- (15) C. Cauletti and C. Furlani, *J. Electron Spectrosc.*, **6**, 465 (1975).
- (16) K. N. Houk, L. P. Davis, G. R. Newkome, R. E. Duke, Jr., and R. V. Nauman, *J. Am. Chem. Soc.*, **95**, 8364 (1973).
- (17) J. P. Fackler, Jr., and F. A. Cotton, *Inorg. Chem.*, **2**, 102 (1963).
- (18) R. L. Lintvedt and L. K. Kernitsky, *Inorg. Chem.*, **9**, 491 (1970).
- (19) J. Del Bene and H. H. Jaffe, *J. Chem. Phys.*, **48**, 1807, 4050 (1968); **49**, 1221 (1968); **50**, 1126 (1969); Program QCPE 174, Quantum Chemistry Program Exchange, Indiana University.

Contribution from the Department of Chemistry,
Purdue University, West Lafayette, Indiana 47907

A High-Yield Synthesis of Rhenium(III) Iodide and the Isolation and Characterization of β -Molybdenum(II) Iodide¹

H. D. Glicksman and R. A. Walton*

Received July 27, 1977

We have recently demonstrated² that the metal acetates $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{X}_2$, where $\text{X} = \text{Cl}$ or Br , and $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4$ exhibit different reactivities toward gaseous hydrogen chloride and hydrogen bromide. While $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ reacts to afford $\beta\text{-MoX}_2$, and $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{X}_2$ are converted to the trinuclear halides Re_3X_9 , the related reactions of $\text{Rh}_2(\text{O}_2\text{CCH}_3)_4$ result in disproportionation to RhX_3 and rhodium metal. To complete our current studies on the reactions of the solid metal acetates with the gaseous hydrogen halides, we now report details of the reactions of hydrogen iodide with $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ and $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$. This work has led to a convenient high-yield synthesis of Re_3I_9 and the isolation of the new molybdenum iodide phase $\beta\text{-MoI}_2$.

Experimental Section

Starting Materials. Molybdenum hexacarbonyl, potassium perchlorate, tertiary phosphines, and pyridine together with all reagent-grade solvents and gases were obtained from commercial sources. All solvents were deoxygenated by purging with nitrogen gas for at least 1 h prior to use.

Molybdenum(II) acetate, $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, was prepared by the standard literature procedure,³ while $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ was prepared from $\text{ReOCl}_3(\text{PPh}_3)_2$ using our slight modification² of the method described by Rouschias and Wilkinson.⁴

Synthetic Procedures. (A) **Reactions of Metal Acetates with Hydrogen Iodide.** (i) $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$. Finely ground molybdenum(II) acetate (0.5 g), contained in a porcelain boat, was treated with hydrogen iodide gas for 6 h at 300 °C. The resulting dark brown powder was reground and reheated at 300 °C in a flow of HI gas for a further 6 h. The final product (0.8 g) was analytically pure $\beta\text{-MoI}_2$. Anal. Calcd for MoI_2 : I, 72.6; Mo, 27.4. Found: I, 72.5; Mo, 27.9. Yield >95%.

(ii) $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$. Using a procedure similar to that described previously to prepare Re_3Cl_9 and Re_3Br_9 ,² the reaction of rhenium(III) acetate with hydrogen iodide gas for 5 h at 300 °C afforded black Re_3I_9 . Anal. Calcd for Re_3I_9 : I, 67.15. Found (for separate preparative samples): I, 66.8, 66.85. Yield ~80%.

(B) **Reactions of $\beta\text{-MoI}_2$ with Pyridine and Tri-*n*-propylphosphine.** (i) **Pyridine.** $\beta\text{-MoI}_2$ (0.3 g) and 20 mL of pure dry pyridine were refluxed together for 5 days. The reaction mixture was then cooled and filtered and the filtrate evaporated to dryness in vacuo. The resulting brown residue was washed with diethyl ether and dried. Microanalytical data showed that this was not a pure sample of $\text{Mo}_2\text{I}_4(\text{py})_4$. Anal. Calcd for $\text{C}_{20}\text{H}_{20}\text{I}_4\text{N}_4\text{Mo}_2$: C, 23.6; H 2.0; I, 50.0. Found: C, 25.85; H, 2.3; I, 46.2. However, the infrared spectrum of this product in the 4000–400- cm^{-1} region was identical with that of the complexes $\text{Mo}_2\text{X}_4(\text{py})_4$, where $\text{X} = \text{Cl}$ or Br .² In the far-infrared

region (400–200- cm^{-1}) bands at 252 (m) and 240 (w) cm^{-1} [probably assigned to $\nu(\text{Mo-N})$] have counterparts in the spectra of $\text{Mo}_2\text{Cl}_4(\text{py})_4$ and $\text{Mo}_2\text{Br}_4(\text{py})_4$ at 247 (m-w) and 240 (m) cm^{-1} , respectively.^{2,5} The diffuse-reflectance and solution (pyridine) electronic absorption spectra exhibit a low-energy absorption at ~740 nm, in keeping with the trend established by $\text{Mo}_2\text{Cl}_4(\text{py})_4$ and $\text{Mo}_2\text{Br}_4(\text{py})_4$ which possess related low-energy bands at 560 and 680 nm, respectively.^{2,5} Since the x-ray powder pattern of this product is not the same as that reported by Brencic et al.⁶ for a sample of $\text{Mo}_2\text{I}_4(\text{py})_4$ prepared by the reaction of pyridine with $(\text{picH})_2\text{Mo}_2\text{I}_6(\text{H}_2\text{O})_2$, where $\text{picH} = 4\text{-methylpyridinium}$, these two products may be different structural isomers.

(ii) **Tri-*n*-propylphosphine.** $\beta\text{-MoI}_2$ (0.3 g) was added to 15 mL of dry acetone followed by 1.0 mL of tri-*n*-propylphosphine and the resulting reaction mixture was refluxed for 1 day and then filtered while hot. The blue crystals of the complex $\text{Mo}_2\text{I}_4(\text{P-}n\text{-Pr}_3)_4$ (0.07 g) were washed with ethanol and diethyl ether and then dried in vacuo. Anal. Calcd for $\text{C}_{36}\text{H}_{84}\text{I}_4\text{P}_4\text{Mo}_2$: C, 32.3; H, 6.3; I, 37.9. Found: C, 32.2; H, 6.4; I, 37.9. Yield 12%.

(C) **Reactions of Re_3I_9 with Tri-*n*-propylphosphine and Heterocyclic Tertiary Amines.** (i) **Tri-*n*-propylphosphine.** Re_3I_9 (0.6 g) was dissolved in 15 mL of dry acetone. A small quantity of tri-*n*-propylphosphine (~1 mL) was added and the resulting solution was gently heated for 20 min and then cooled. The insoluble gray powder (0.19 g) was filtered off and washed with ethanol and diethyl ether and dried in vacuo. Anal. Calcd for $\text{C}_{36}\text{H}_{84}\text{I}_4\text{P}_4\text{Re}_2$: C, 28.4; H, 5.5; I, 33.4. Found: C, 27.9; H, 5.6; I, 33.5. Yield 24%. A molecular weight determination in benzene confirmed the dimeric nature of this complex. Calcd for $\text{Re}_2\text{I}_4(\text{P-}n\text{-Pr}_3)_4$: 1520. Found: 1645. The spectroscopic properties of this complex were identical in all respects with those exhibited by a complex of this same stoichiometry prepared by an alternative procedure.⁷

(ii) **Pyridine, 4-Methylpyridine, and Pyrazine.** Although chloride and bromide derivatives of the types $\text{Re}_3\text{X}_9\text{L}_3$ and $[\text{Re}_3\text{X}_6\text{L}_3]_n$ have been prepared from the direct reaction of Re_3X_9 ,^{8,9} treatment of acetone solutions of Re_3I_9 with pyridine, 4-methylpyridine, and pyrazine did not produce the corresponding iodide complexes. In the case of the reactions with pyridine and 4-methylpyridine, infrared spectral data on the resulting impure brown solids support the formation of rhenium(V) species of the type ReO_2L_4^+ ($\nu(\text{O}=\text{Re}=\text{O})$ at ~820 cm^{-1}).¹⁰

Physical Measurements and Analytical Procedures. These were carried out as described previously.²

Results and Discussion

The reaction of $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$ with hydrogen iodide at 300 °C to afford rhenium(III) iodide in high yield (~80%) is the most direct synthetic route available for this halide. This preparation offers considerable advantages over other literature methods,^{11–16} in terms of both the reproducibility and simplicity of our procedure and the high product yield which is obtained. Also, since this same rhenium(III) acetate starting material can also be used for the synthesis of Re_3Cl_9 and Re_3Br_9 ,² this synthetic procedure is of quite general applicability.

There is good agreement between the x-ray powder pattern for Re_3I_9 prepared by our method and that reported by Bennett et al.¹⁷ for a sample of this halide obtained by an alternative synthetic route. The x-ray photoelectron spectrum (ESCA) of this phase ($\text{Re } 4f_{5/2,7/2}$ binding energies at 43.7 and 41.3 eV and $\text{I } 3d_{3/2,5/2}$ energies at 630.7 and 619.2 eV) shows that it possesses considerably lower Re 4f binding energies than the analogous chloride and bromide phases.² This trend reflects the greater charge density at the metal center in Re_3I_9 , relative to Re_3Cl_9 and Re_3Br_9 , presumably a consequence of the lower electronegativity of iodine ($\text{I} < \text{Br} < \text{Cl}$).

As noted previously,¹⁷ Re_3I_9 forms very few compounds. In the present work we have been unable to form complexes of the type $\text{Re}_3\text{I}_9\text{L}_3$ by direct reaction of this halide with either heterocyclic tertiary amines or tertiary phosphines. In contrast to the related behavior of Re_3Cl_9 and Re_3Br_9 ,^{8,9,18,19} the decomposition of the Re_3I_9 cluster appears to be very rapid. In spite of this, the reactions of Re_3I_9 resemble those of the related chloride and bromide in one respect, namely, the formation of dimeric metal-metal bonded complexes of the type

$\text{Re}_2\text{X}_4(\text{PR}_3)_4$. 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, $\text{Re}_2\text{I}_4(\text{P-}n\text{-Pr}_3)_4$, has been isolated.⁷

The formation of $\beta\text{-MoI}_2$ from the reaction between $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$ and hydrogen iodide completes the series of $\beta\text{-MoX}_2$ phases ($\text{X} = \text{Cl}, \text{Br}, \text{or I}$) which may be prepared by this synthetic procedure. The low magnetic moment of this phase ($\mu_{\text{eff}} = 0.66 \mu_{\text{B}}$ at room temperature) resembles the related magnetic behavior of $\beta\text{-MoCl}_2$ and $\beta\text{-MoBr}_2$ ($\mu_{\text{eff}} = 0.49$ and $0.60 \mu_{\text{B}}$, 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 $\beta\text{-MoI}_2$, with $\text{Mo } 3d_{3/2,5/2}$ binding energies at 231.5 and 228.4 eV, is characteristic of a molybdenum(II) halide.²²

Although $\beta\text{-MoI}_2$ reacts with refluxing pyridine, the pure complex $\text{Mo}_2\text{I}_4\text{py}_4$ could not be isolated from this reaction mixture. In contrast to this, upon reacting $\beta\text{-MoI}_2$ with a refluxing acetone solution of tri-*n*-propylphosphine, the blue crystalline complex $\text{Mo}_2\text{I}_4(\text{P-}n\text{-Pr}_3)_4$ was obtained. This latter reaction is analogous to that of $\beta\text{-MoCl}_2$ and $\beta\text{-MoBr}_2$ with this phosphine and supports the formulation of $\beta\text{-MoI}_2$ as $[\text{Mo}_2\text{I}_4]_m$ containing a very strong metal-metal bond and being the parent halide of the as yet unknown $\text{Mo}_2\text{I}_8^{4-}$ anion.

The complex $\text{Mo}_2\text{I}_4(\text{P-}n\text{-Pr}_3)_4$ 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 $\text{Mo}_2\text{Br}_4(\text{P-}n\text{-Pr}_3)_4$ 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 $\text{Mo } 3d_{3/2,5/2}$ binding energies (231.7 and 228.6 eV) which are typical of a molybdenum(II) complex of the type $\text{Mo}_2\text{X}_4\text{L}_4$.²²

Acknowledgment. We thank the National Science Foundation (Grant CHE74-12788A02) for generous research support.

Registry No. $\beta\text{-MoI}_2$, 14055-74-4; Re_3I_9 , 15622-42-1; $\text{Mo}_2\text{I}_4(\text{py})_4$, 59610-42-3; $\text{Mo}_2\text{I}_4(\text{PPr}_3)_4$, 64508-28-7; $\text{Re}_2\text{I}_4(\text{PPr}_3)_4$, 64508-27-6; $\text{Mo}_2(\text{O}_2\text{CCH}_3)_4$, 14221-06-8; $\text{Re}_2(\text{O}_2\text{CCH}_3)_4\text{Cl}_2$, 14126-96-6; HI, 10034-85-2.

References and Notes

- (1) Part 13 of the series entitled "Studies on Metal Carboxylates".
- (2) Part 12: H. D. Glicksman, A. D. Hamer, T. J. Smith, and R. A. Walton, *Inorg. Chem.*, **15**, 2205 (1976).
- (3) T. A. Stephenson, E. Bannister, and G. Wilkinson, *J. Chem. Soc.*, 2538 (1964).
- (4) G. Rouschias and G. Wilkinson, *J. Chem. Soc. A*, 465 (1966).
- (5) J. San Filippo, Jr., H. J. Sniadoch, and R. L. Grayson, *Inorg. Chem.*, **13**, 2121 (1974).
- (6) J. V. Brencic, D. Dobnik, and P. Segedin, *Monatsh. Chem.*, **107**, 395 (1976).
- (7) We have recently succeeded in preparing the octaiododirhenate(III) anion (as its Bu_4N^+ salt) and found that this is an excellent starting material for the synthesis of tertiary phosphine complexes of the type $\text{Re}_2\text{I}_4(\text{PR}_3)_4$. Full details of this study will be published at a later date.
- (8) D. G. Tisley and R. A. Walton, *Inorg. Chem.*, **12**, 373 (1973).
- (9) H. D. Glicksman and R. A. Walton, *Inorg. Chim. Acta*, **19**, 91 (1976).
- (10) N. P. Johnson, C. J. L. Lock, and G. Wilkinson, *J. Chem. Soc.*, 1054 (1964).
- (11) R. D. Peacock, A. J. E. Welch, and L. T. Wilson, *J. Chem. Soc.*, 2901 (1958).
- (12) L. Malatesta, *Inorg. Synth.*, **7**, 185 (1963).
- (13) G. W. Watt and R. J. Thompson, *Inorg. Synth.*, **7**, 187 (1963).
- (14) V. G. Tronev and R. A. Dovlyatshina, *Azerb. Khim. Zh.*, 116 (1965); *Chem. Abstr.*, **64**, 9210d (1966).
- (15) M. A. Bush, P. M. Druce, and M. F. Lappert, *J. Chem. Soc., Dalton Trans.*, 500 (1972).

- (16) D. V. Drobot and L. G. Mikhailova, *Russ. J. Inorg. Chem.*, **18**, 15 (1973).
- (17) M. J. Bennett, F. A. Cotton, and B. M. Foxman, *Inorg. Chem.*, **7**, 1563 (1968).
- (18) F. A. Cotton, S. J. Lippard, and J. T. Mague, *Inorg. Chem.*, **4**, 508 (1965).
- (19) F. A. Cotton and J. T. Mague, *Inorg. Chem.*, **3**, 1094 (1964).
- (20) J. R. Ebner and R. A. Walton, *Inorg. Chem.*, **14**, 1987 (1975).
- (21) G. B. Allison, I. R. Anderson, and J. C. Sheldon, *Aust. J. Chem.*, **22**, 1091 (1969).
- (22) R. A. Walton, "Proceedings of the Second International Conference on the Chemistry and Uses of Molybdenum", P. C. H. Mitchell, Ed., Climax Molybdenum Co. Ltd., London, 1976, p 34.

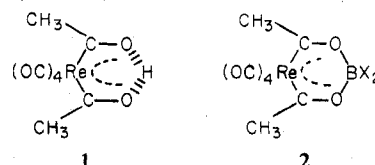
Contribution from the Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235

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

C. M. Lukehart* and L. T. Warfield

Received July 21, 1977

The preparation and structure determination of the first example of a metallo- β -diketonate molecule were reported recently.¹ This molecule, **1**, exists as the symmetrical structural



analogue of the enol tautomer of acetylacetonate, 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 -diketonate molecules to that of the nonmetallo analogues is being pursued actively.

We wish to report that complex **1** reacts with boron trihalides, BX_3 (where $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{or I}$), 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 $[\text{cis}-(\text{OC})_4\text{Re}(\text{CH}_3\text{CO})_2\text{IBX}_2]$ (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