modes without empirical confirmation should be made very cautiously.

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Registry No. [PPN][HFe(CO)$_4$], 56791-54-9; [PPN][HRu(CO)$_4$], 81011-81-6; [PPN][HOs(CO)$_4$], 79408-53-0; deuterium, 16873-17-9.

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Reductive Coupling of Perrhenate To Form the Octachlorodirhenate(III) Anion: A New, Convenient, and High-Yield Synthetic Procedure

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The octachlorodirhenate(III) anion was the first complex to be formulated as containing a metal–metal quadruple bond,[1-3] and it remains to this day the key starting material for entry into the chemistry of multiply bonded dirhenium complexes.[4] The synthetic strategies utilized for its preparation have revolved around the following methods: (1) the high-pressure (autoclave) hydrogen reduction of KReO$_4$–hydrochloric acid mixtures;[1,5] (2) the hypophosphorous acid reduction of KReO$_4$;[1,6] (3) the disruption of Re$_3$Cl$_9$ by molten diethylammonium chloride.[7] The disadvantages of these methods are the often low and variable yields (usually only 40% or so at best), the inconvenience of using an autoclave in the H$_2$ reduction, and the need to synthesize Re$_3$Cl$_9$ (itself best prepared from quadruply bonded Re$_2$(O$_2$CCH$_3$)$_4$Cl$_2$).[8] In exploring alternative and more convenient methods which might be employed to reduce perrhenate to low-valent rhenium chlorides, we have discovered a remarkably simple and high-yield conversion of [ReO$_4$]$^-$ to [Re$_2$Cl$_8$]$^{2-}$. In view of the high cost of rhenium we feel that this procedure must now constitute the preferred method of preparing [(n-C$_4$H$_9$)$_4$N]$_2$Re$_2$Cl$_8$, the usual starting material for dirhenium chemistry.

Although KReO$_4$ is insoluble in benzoyl chloride (PhCOCl), prolonged reaction under reflux conditions affords a solution which upon addition of ethanol and tetra-n-butylammonium bromide produces [(n-C$_4$H$_9$)$_4$N]$_2$Re$_2$Cl$_8$ (**1**) in yields of ca. 50%. In this reaction, we find that there are two insoluble "intermediates" formed which can be readily separated and identified. When the reaction mixture which results from refluxing KReO$_4$ with PhCOCl for 5 h was filtered, a mixture of emerald green crystals (water insoluble) and yellow–green crystals (water soluble) was isolated. On the basis of microanalytical and spectroscopic data, the emerald green crystals were identified as Re$_2$(O$_2$CPh)$_2$Cl$_4$. This bis(carboxylate) complex is formulated as a dinuclear quadruply bonded complex similar in type to those of this stoichiometry which have been reported and characterized previously.[4,9,10] The yellow-green crystals were identified as K$_2$ReCl$_6$. This salt is completely insoluble in the reaction mixture and does not react further with PhCOCl, even after prolonged reflux, thereby explaining why the yields of **1** produced from KReO$_4$ were never greater than 60% since the K$_2$ReCl$_6$, once it is formed, does not react further due to its insolubility. On the other hand, Re$_2$(O$_2$CPh)$_2$Cl$_4$ is an intermediate on the way from KReO$_4$ to [Re$_2$Cl$_8$]$^{2-}$. Upon reaction with fresh PhCOCl and subsequent treatment with a HCl(g) saturated ethanol solution of [(n-C$_4$H$_9$)$_4$N]Br, it produces solutions from which **1** may be isolated in high yield. Thus the role of PhCOCl in these reactions is not only to reduce and chlorinate the metal centers but to couple them via the agency of benzoate bridges. The benzoate ligands are presumably formed from PhCOCl through oxygen transfer from the perrhenate starting material.

Although K$_2$ReCl$_6$ could not be converted into [Re$_2$Cl$_8$]$^{2-}$ by PhCOCl, this cannot be construed to mean that such rhenium(IV) species are inert to reduction by PhCOCl. We believe that it is only the extreme insolubility of K$_2$ReCl$_6$ which hinders its reaction. In accord with this interpretation we find that when the much more soluble tetra-n-butylammonium salt [(n-C$_4$H$_9$)$_4$N]$_2$ReCl$_6$ is reacted with PhCOCl, **1** can be produced in yields of 95%. This indicates that the solubility of the intermediates in the reaction mixture is crucial for the high-yield formation of **1**.

The preceding observation prompted us to use [(n-C$_4$H$_9$)$_4$N]ReO$_4$ in place of KReO$_4$ in these reactions with PhCOCl. The conversion proceeds smoothly without the obvious precipitation of any insoluble intermediates, and **1** can now be formed in yields up to 95% (a yield of 90% was typical). However, the most critical factor which we found determined the yield was the reaction temperature. With a mercury bubbler, which ensured a higher pressure in the system, we found that the boiling point of PhCOCl was close to 209 °C. With a mineral oil bubbler and a boiling point of 198 °C, the yield of **1** decreased dramatically from ca. 90% to 60%.

An alternative starting material for the synthesis of **1** with PhCOCl is the rhenium(V) complex ReOCl$_3$(PPh$_3$)$_2$, which is itself prepared (in high yield) from perrhenate. The reaction proceeds through the red *trans*-ReCl$_4$(PPh$_3$)$_2$ which can be isolated. The overall conversion of ReOCl$_3$(PPh$_3$)$_2$ to **1** can be accomplished in yields of ca. 70%.

Na$_2$MoO$_4$·2H$_2$O, K$_2$MoO$_4$, H$_2$MoO$_4$·4H$_2$O, MoO$_2$(acac)$_2$, Na$_2$WO$_4$·2H$_2$O, WO$_3$, and MoO$_3$ were all checked for their reactivity toward PhCOCl in hopes that these systems could be used to produce dimolybdenum and ditungsten complexes. In only two cases were we able to isolate any identifiable products. MoO$_2$(acac)$_2$ and K$_2$MoO$_4$ both yielded [(n-C$_4$H$_9$)$_4$N]MoOCl$_4$ in yields of 76% and 84%, respectively. Thus, in the case of molybdenum and tungsten, the formation of high oxidation state oxo halide species predominates.

Experimental Section

Starting Materials. KReO$_4$ was purchased from ROC/RIC Chemicals. PhCOCl was obtained from Aldrich Chemical Co. and distilled under vacuum prior to use. All other chemicals were purchased from commercial sources and used as received. All solvents were thoroughly deoxygenated prior to use.

[(n-C$_4$H$_9$)$_4$N]ReO$_4$ was prepared in 98% yield from KReO$_4$ by the slow addition of a hot aqueous (n-C$_4$H$_9$)$_4$NBr solution to one of KReO$_4$. The resulting white precipitate was washed with water and dried in vacuo. [(n-C$_4$H$_9$)$_4$N]$_2$ReCl$_6$ was prepared in 80% yield by

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(9) The formation of Re$_2$(O$_2$CPh)$_2$Cl$_4$ is also in accord with the results of Shtemenko et al.,[10] who found that the H$_2$ reduction of mixtures of KReO$_4$ (or K$_2$ReCl$_6$), HCl, and CH$_3$CO$_2$H produces Re$_2$(O$_2$CCH$_3$)$_2$Cl$_4$·2H$_2$O in 80% yield. However, these workers[10] did not exploit these findings as a means of preparing salts of [Re$_2$Cl$_8$]$^{2-}$ in high yield.

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the addition of an aqueous $[(n\text{-}C_4H_9)_4N]Cl$ solution to an aqueous solution of K_2ReCl_6 at room temperature. The resulting pale green precipitate was washed with water and dried in vacuo. $ReOCl_3(PPh_3)_2$ was prepared by the method of Chatt and Rowe.[11] All reactions were carried out under a positive pressure of nitrogen with a mercury bubbler system so as to increase the boiling point of PhCOCl to 209 °C. The bubbler consisted of a cylindrical glass reservoir (22-mm internal diameter) containing 40 mL of mercury and fitted with a 4-mm diameter gas inlet tube extending 95 mm into the mercury pool.

A. Reactions of $KReO_4$ with PhCOCl. (i) $Re_2(O_2CPh)_2Cl_4$. $KReO_4$ (1.0 g, 3.5mmol) was refluxed in PhCOCl (15 mL, 13 mmol) for 5 h. The resulting solid was filtered off and washed with PhCOCl and petroleum ether and dried. It was then washed several times with water to dissolve the yellow-green component K_2ReCl_6 (vide infra). The resulting emerald green solid was finally washed with propanol and petroleum ether and dried in vacuo; yield 50% (0.65 g). Anal. Calcd for $C_{14}H_{10}Cl_4O_4Re_2$: C, 22.23; H, 1.33. Found: C, 21.86; H, 1.48. IR data (cm^{-1}): $\nu(Re\text{–}Cl) = 327$ (s), $\nu(COO) = 1416$ (vs, br). Electronic absorption spectral data in methanol (nm): 815 (w), 630 (w), 355 (m), 314 (s, sh), 287 (vs).

(ii) K_2ReCl_6. The water washings from preparation i were collected and evaporated to dryness. The resulting yellow-green crystals were then washed with EtOH and diethyl ether and finally dried in vacuo; yield 43% (0.71 g). The spectral properties of this compound were identical with those of an authentic sample of K_2ReCl_6.

(iii) $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$. $KReO_4$ (1.0 g, 3.5 mmol) was refluxed in PhCOCl (15 mL, 13 mmol) for 5 h, the reaction mixture was cooled, and a HCl(g) saturated solution of $[(n\text{-}C_4H_9)_4N]Br$ (3.0 g, 9.6 mmol) dissolved in ethanol (50 mL) was added. This mixture was refluxed for an additional 1 h, the solution evaporated to low volume and diethyl ether (100 mL) added. The resulting solid was filtered off and washed with ethanol and diethyl ether. So that the K_2ReCl_6 which is present could be removed, the product was added to hot methanol and the mixture filtered into concentrated hydrochloric acid. The blue solution was then evaporated by boiling until blue crystals of $[n\text{-}C_4H_9)_4N]_2Re_2Cl_8$ formed. These were filtered off, washed with ethanol (10 mL) and diethyl ether, and dried in vacuo; yield 56% (1.1 g). Anal. Calcd for $C_{32}H_{72}Cl_8N_2Re_2$: C, 33.69; H, 6.36. Found: C, 33.86; H, 6.12. [IR data: $\nu(Re\text{–}Cl) = 335\ cm^{-1}$ (s).] The electronic absorption spectrum of a methanol solution of this complex was identical with that reported in the literature.[1]

B. Reaction of $[(n\text{-}C_4H_9)_4N]ReO_4$ with PhCOCl. $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$. In a typical reaction, $[(n\text{-}C_4H_9)_4N]ReO_4$ (3.0 g, 6.1 mmol) was refluxed with PhCOCl (30 mL, 26 mmol) for 1.5 h and cooled, and an HCl(g) saturated solution of $[(n\text{-}C_4H_9)_4N]Br$ (5.0 g, 16 mmol) dissolved in ethanol (75 mL) was added. After a reflux period of 1 h, the solution was evaporated to approximately half-volume under a stream of nitrogen. The resulting blue crystals were filtered off, washed with 10 mL portions of ethanol and then with diethyl ether, and dried in vacuo; yield 92% (3.19 g). The product so obtained is of sufficient purity that it can be used without further recrystallization. The spectral properties of this complex were identical with those described in the literature.[1] Anal. Calcd for $C_{32}H_{72}Cl_8N_2Re_2$: C, 33.69; H, 6.36. Found: C, 33.97; H, 6.12.

C. Reactions of $ReOCl_3(PPh_3)_2$ with PhCOCl. (i) *trans*-$ReCl_4(PPh_3)_2$. $ReOCl_3(PPh_3)_2$ (1.0 g, 1.2 mmol) was refluxed in PhCOCl (15 mL, 13 mmol) for 5 min. The deep red solution was filtered, and the resulting insoluble red solid was washed with diethyl ether and dried in vacuo; yield 43%. The spectral properties of this compound were identical with those reported previously.[12]

(ii) $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$. $ReOCl_3(PPh_3)_2$ (1.0 g, 1.2 mmol) was reacted with PhCOCl as described in preparation iii of section A; yield 70% (0.48 g).

D. Reaction of $[(n\text{-}C_4H_9)_4N]_2ReCl_6$ with PhCOCl. $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$. $[(n\text{-}C_4H_9)_4N]_2ReCl_6$ (1.5 g, 1.7 mmol) was reacted as described in B; yield 95% (0.92 g).

E. Reaction of $ReCl_4(PPh_3)_2$ with PhCOCl. $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$. Following the procedure given in preparation iii of section A, *trans*-$ReCl_4(PPh_3)_2$ (0.50 g, 0.6 mmol) was converted to $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$ in 80% yield (0.26 g).

F. Reactions of Molybdenum Oxo Species with PhCOCl. (i) A mixture of $MoO_2(acac)_2$ (0.33 g, 1.0 mmol) and PhCOCl (15 mL, 13 mmol) was refluxed for 2 h. The solution was cooled, and an HCl(g)-saturated solution of $[(n\text{-}C_4H_9)_4N]Br$ (1.5 g, 4.7 mmol) dissolved in ethanol (35 mL) was added. An additional reflux period of 2 h produced a dark red solution which was evaporated to half-volume under a stream of nitrogen. An excess of diethyl ether (50 mL) was then added, and the green crystals of $[(n\text{-}C_4H_9)_4N]MoOCl_4$ were filtered off, washed with diethyl ether, and dried in vacuo; yield 76% (0.38 g). The spectroscopic properties of this product were identical with those reported in the literature.[13]

(ii) K_2MoO_4 (0.24 g, 1.0 mmol) when reacted as in preparation i above afforded $[(n\text{-}C_4H_9)_4N]MoOCl_4$ in 84% yield (0.42 g).

Physical Measurements. Infrared spectra were recorded from 4000 to 400 cm^{-1} with KBr plates and from 400 to 200 cm^{-1} with polyethylene on a Beckman IR 12 spectrophotometer. Electronic absorption spectra were obtained in the region from 900 to 300 nm with a Varian 634 spectrophotometer. Elemental microanalytical data were obtained by Dr. C. S. Yeh of this department.

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Registry No. $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$, 14023-10-0; $KReO_4$, 10466-65-6; PhCOCl, 98-88-4; $Re_2(O_2CPh)_2Cl_4$, 81011-79-2; $[(n\text{-}C_4H_9)_4N]ReO_4$, 16385-59-4; $ReOCl_3(PPh_3)_2$, 17442-18-1; *trans*-$ReCl_4(PPh_3)_2$, 34248-10-7; $[(n\text{-}C_4H_9)_4N]_2ReCl_6$, 71128-58-0; $MoO_2(acac)_2$, 17524-05-9; $[(n\text{-}C_4H_9)_4N]MoOCl_4$, 19341-30-1; K_2MoO_4, 13446-49-6.

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Solubility of Manganese Oxide in Molten Sodium Chloride and Sodium Sulfate

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Manganese is a reactive element that has potential for increasing the oxidation resistance of superalloys. Specifically, Mn is thought to reduce CrO_3 volatilization by formation of $MnCr_2O_4$ spinel.[3] The question of whether manganese might improve hot corrosion resistance was approached in the present work by measuring the solubility of manganese oxide in molten Na_2SO_4 and NaCl. Valuable insight concerning the hot corrosion resistance conferred by several metal constituents of superalloys was reported recently by measurement of the solubility of the oxides of these metals in molten Na_2SO_4 and NaCl.[4,5,8,9]

In previous solubility studies[4,5] of the oxides of nickel, cobalt, and yttrium we have used a coulometric titration technique[6,7] developed in our laboratory, in which a solution of the respective salt, e.g., $NiSO_4$ in Na_2SO_4, is titrated with oxide ion (O^{2-}) generated coulometrically at a stabilized zirconia electrode. However, this method proved to be unsuitable for

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