COMMUNICATION

ISOLATION OF THE COMPLEXES $(n-Bu_4N)_2[(Re_2Cl_7)_2\{\mu-(L-L)\}]$, WHERE L---L = Ph₂PC==CPPh₂ OR *TRANS*-Ph₂PCH==CHPPh₂. THE FIRST EXAMPLES OF QUADRUPLY BONDED DIRHENIUM(III) ANIONS OF THE TYPE [Re₂Cl₇L]⁻

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(Received 23 March 1987; accepted 27 May 1987)

Abstract—The reactions of $(n-Bu_4N)_2Re_2Cl_8$ with the bidentate bridging phosphine ligands $(L-L) = Ph_2PC = CPPh_2$ or *trans*-Ph_2PCH=CHPPh_2 in methanol-conc. HCl give the salts $(n-Bu_4N)_2[(Re_2Cl_7)_2\{\mu-(L-L)\}]$, the first examples of quadruply bonded dirhenium(III) anions of the type $[Re_2Cl_7L]^-$. Their spectroscopic properties and reactivity have been examined.

The octahalodirhenate(III) anions $[\text{Re}_2X_8]^{2^-}$ (X = Cl or Br) react with monodentate phosphine ligands (PR₃) to form the neutral quadruplybonded species $\text{Re}_2X_6(\text{PR}_3)_2$, and from thence to the lower valent complexes $\text{Re}_2X_5(\text{PR}_3)_3$ (Re—Re bond order 3.5) or $\text{Re}_2X_4(\text{PR}_3)_4$ (Re—Re bond order 3) depending upon the reducing propensity of the phosphine ligand.¹ In no instance has a salt of the intermediate monoanionic mono-substituted type $[\text{Re}_2X_7(\text{PR}_3)]^-$ been isolated. We report for the first time the isolation of such species as present in the salts $(n-\text{Bu}_4\text{N})_2[(\text{Re}_2\text{Cl}_7)_2\{\mu-(\text{L}-\text{L})\}]$ (1), in which L—L is the bidentate bridging phosphine $\text{Ph}_2\text{PC}=C\text{PPh}_2(\text{dpa})$ or *trans*-Ph_2PCH=CHPPh_2 (*t*-dppee).

§ When the reaction which gave this complex was carried out in methanol in the absence of conc. HCl, a brown solid precipitated. Although this product has not yet been fully characterized, it is not $\text{Re}_2\text{Cl}_6(\text{dpa})_2$. $(n-Bu_4N)_2[Cl_4ReReCl_3{\mu-(L-L)}Cl_3ReReCl_4]$

 $L-L = Ph_2PC \equiv CPPh_2$ (1a)

 $L-L = trans-Ph_2PCH=CHPPh_2$ (1b)

A representative recipe is as follows.[‡] A mixture of $(n-Bu_4N)_2Re_2Cl_8^2$ (0.20 g, 0.175 mmol), dpa (0.09 g, 0.228 mmol) and 10 cm³ of methanol, to which 10 drops of conc. HCl had been added, was stirred at room temperature for one day. The resulting insoluble purple precipitate was filtered off, washed with methanol, hexanes, diethyl ether and dried *in vacuo*; yield 0.17 g (91%). Found: C, 34.1; H, 4.6; Cl, 22.9. Calc. for C₅₈H₉₂Cl₁₄N₂P₂Re₄: i.e. $(n-Bu_4N)_2[(Re_2Cl_7)_2\{\mu-(Ph_2PC=CPPh_2)\}]$: C, 32.9; H, 4.4; Cl, 23.4. The slightly high C and H microanalyses reflect the difficulty of purifying such an insoluble complex.§

A similar procedure gave $(n-Bu_4N)_2[(Re_2Cl_7)_2 {\mu-(trans-Ph_2PCH=CHPPh_2)}]$ as a green solid in a yield of 86%.

Although both complexes display very limited solubility properties we were, nonetheless, able to adequately characterize them although neither could be obtained in single crystal form. We favor a structure such as that depicted below in which the individual dirhenium units retain the eclipsed

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[‡]Bis(diphenylphosphino(acetylene (dpa) and *trans*-1,2-bis(diphenylphosphino)ethylene (*t*-dppee) were purchased from Strem Chemicals and used as received. Solvents used in the preparation of complexes were of commercial grade and were thoroughly deoxygenated prior to use. All reactions were performed in a nitrogen atmosphere using standard vacuum line techniques.

rotational geometry of the parent $[\text{Re}_2\text{Cl}_8]^{2-}$, ¹ (see Structure 1).



The electronic absorption spectrum of 1a, recorded as a Nujol mull, has a band at \sim 740 nm, assigned to the $\delta \rightarrow \delta^*$ transition, weak absorptions at \sim 540 and 480 nm, and more intense features at 390 and 325 nm. In CH₂Cl₂ solution, the spectrum is very similar to this, with absorptions (relative intensities in parentheses) at 730(9), \sim 540(2), \sim 470(2), 380sh(13) and 315(34) nm. The Nujol mull spectrum of (1b) shows the $\delta \rightarrow \delta^*$ transition at 735 nm, a weak band at \sim 570 nm, a shoulder at ~ 410 nm and an intense absorption at 290 nm. Although (1a) and (1b) decompose in CH₃CN (vide infra), the ¹H NMR spectrum of a freshly prepared solution of (1a) in CD₃CN shows proton resonances due to the dpa ligand and n- Bu_4N^+ cation in the expected intensity ratio of 1 : 2.

Further evidence for the identity of these salts as derivatives of the quadruply bonded Re_2^{6+} core was obtained from reactions with monodentate phosphines. (1a) reacts with PEt₃ in ethanol to form $Re_2Cl_4(PEt_3)_4$ in 55% yield, while PMePh₂ and PEtPh₂ under these same conditions form $Re_2Cl_5(PMePh_2)_3$ and $Re_2Cl_5(PEtPh_2)_3$, respectively, in yields of $\sim 80\%$. These yields are similar to those in which $\text{Re}_2\text{Cl}_5(\text{PMePh}_2)_3$ and Re_2Cl_5 (PEtPh₂)₃ are formed (90% and 75%, respectively) from $(n-Bu_4N)_2Re_2Cl_8$.³ (1b) shows this same reactivity behavior; it forms Re₂Cl₄(PEt₃)₄ in 68% yield and Re₂Cl₅(PMePh₂)₃ in 85% yield. These products, which are the ones expected from such a quadruply bonded Re⁶⁺₂ starting material,³ were identified on the basis of their spectroscopic and electrochemical properties.^{3,4}

Of special note is the reaction of (1a) with PPh₃ in hot ethanol. An excess of PPh₃ affords an almost quantitative yield of green insoluble $\text{Re}_2\text{Cl}_6(\text{PPh}_3)_2$ (94%), whereas 2 equivs of PPh₃ gives $\text{Re}_2\text{Cl}_6(\text{PPh}_3)_2$ (49%) and from the filtrate a mixture of dpa and $(n-\text{Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$.[†] These observations imply that the following reactions are

occurring:

(1)
$$[\operatorname{Re}_2\operatorname{Cl}_7(\mu-\operatorname{dpa})\operatorname{Re}_2\operatorname{Cl}_7]^{2-}$$

+2PPh₃ \rightarrow $\operatorname{Re}_2\operatorname{Cl}_6(\operatorname{PPh}_3)_2$
+ $(n-\operatorname{Bu}_4\operatorname{N})_2\operatorname{Re}_2\operatorname{Cl}_8$ +dpa

(2)
$$(n-\operatorname{Bu}_4 N)_2\operatorname{Re}_2\operatorname{Cl}_8 + 2\operatorname{PPh}_3$$

 $\rightarrow \operatorname{Re}_2\operatorname{Cl}_6(\operatorname{PPh}_3)_2 + 2n-\operatorname{Bu}_4\operatorname{NCl}.$

In this same context we have observed that (1a) reacts slowly with CH₃CN to give $(n-Bu_4N)_2Re_2Cl_8$ (36% yield of isolated product) together with an as yet unidentified blue Re_2^{6+} complex (λ_{max} at 656 nm for its $\delta \rightarrow \delta^*$ transition). When the latter reaction is carried out at room temperature in the presence of an excess of $n-Bu_4NCl$ for 2 h, the blue salt ($n-Bu_4N)_2Re_2Cl_8$ can be precipitated in quantitative yield upon the addition of an excess of diethylether. The yield of pure recrystallized product (from methanol/conc. HCl) was ~ 80%. These reactions not only confirm the structural identity of (1a) but, furthermore, demonstrate the lability of the μ -dpa ligand.

The cyclic voltammogram (CV) of (1a) in 0.1 M n-Bu₄NPF₆ (TBAH)-CH₂Cl₂ shows a pair of closely spaced couples at $E_{1/2} \simeq -0.31$ V and -0.43 V vs Ag/AgCl (Fig. 1) which signify that the reductions of the two dpa-coupled Re⁶⁺₂ cores occur at different potentials.⁵ A similar phenomenon is seen in the CV of (1b) with $E_{1/2}$ values of $\simeq -0.40$ V and -0.52 V vs Ag/AgCl. These potentials are, as expected, intermediate between those for the one-electron reductions of $\text{Re}_2\text{Cl}_6(\text{PR}_3)_2^{1,4}$ and $[\text{Re}_2\text{Cl}_8]^{2-.1,6,7}$ When acetonitrile is added to a solution of (1a) in 0.1 M TBAH-CH₂Cl₂, the CV changes with time and shows the formation of $[\text{Re}_2\text{Cl}_8]^{2-}$ (E_{1/2} \simeq +1.5 V and E_{1/2} \simeq -0.93 V vs $Ag/AgCl)^{6,7}$ together with a couple at $\simeq -0.7$ V which must be associated with another $\operatorname{Re}_{2}^{6+}$ species.

Studies on the chemistry of these systems



Fig. 1. Cyclic voltammogram (recorded at v = 200 mVs⁻¹ using a Pt-bead electrode) for a 0.1 M *n*-Bu₄NPF₆-CH₂Cl₂ solution of (n-Bu₄N)₂[(Re₂Cl₇)₂(μ -dpa)]. For each of the closely spaced couples at E_{1/2} = -0.31 V and -0.43 V, the peak separations ΔE_p (= $E_{p,a}$ - $E_{p,c}$) are $\approx 100 \text{ mV}$. Under our experimental conditions the ferrocenium/ferrocene reference standard had E_{1/2} = +0.47 V.

[†] The dissociation of dpa in this reaction under nonacidic conditions is in marked contrast to the reaction of $(n-Bu_4N)_2Re_2Cl_8$ with dpa in methanol to give (1a) which requires the presence of HCl.

are continuing. We note that the reaction of trans-dppee with $(n-Bu_4N)_2Re_2Cl_8$ in methanolconc. HCl to give (1b) is different from that with chelating *cis*-dppee. In the latter case, cleavage of the Re \equiv Re bond predominates to give *trans*-[ReCl₂(dppee)₂]Cl.⁸

Acknowledgement—We thank the National Science Foundation for support of this work (Grant No. CHE85-06702 to R.A.W.).

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