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Dirhenium Compounds Containing the Diphosphine Ligands Ph2PCH2PPh2, Ph2PCH(CN)PPh2, or Ph2PCH(CH3)PPh2: A Comparative Study

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DIRHENIUM COMPOUNDS CONTAINING THE DIPHOSPHINE LIGANDS $Ph_2PCH_2PPh_2$, $Ph_2PCH(CN)PPh_2$, OR $Ph_2PCH(CH_3)PPh_2$: A COMPARATIVE STUDY

A Thesis

Submitted to the Faculty

of

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by

Hannah Arthur

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of

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To: John, the one who moved first.

ACKNOWLEDGMENTS

I would like to thank my family, friends, and professors who supported me through these four years and this thesis. I would like to especially thank Dr. Derringer, because without him I probably would never have been a chemistry major. Thank you all. I couldn’t have done it without you.

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LIST OF ABBREVIATIONS

Anal.	analysis
ATR	attenuated total reflection
Bu	butyl
ca.	approximately (circa; about)
Calcd	calculated
CV	cyclic voltammogram
d	day
DCM	dichloromethane
dppm	$Ph_2PCH_2PPh_2$
dppmCN	$Ph_2PCH(CN)PPh_2$
dppmMe	$Ph_2PCH(CH_3)PPh_2$
$E_{1/2}$	half-wave potential
$E_{p,a}$	anodic peak potential
$E_{p,c}$	cathodic peak potential
Et	ethyl
et al.	and others
g	gram
h	hour
IR	infrared
M	molar
Me	methyl
Mepy	methylpyridine

min	minute
mL	milliliter
mmol	millimole
n	normal
NMR	nuclear magnetic resonance
OAc	acetate
Pr	propyl
RT	room temperature
TBAH	tetra-n-butylammonium hexafluorophosphate
V	volt
vs.	versus

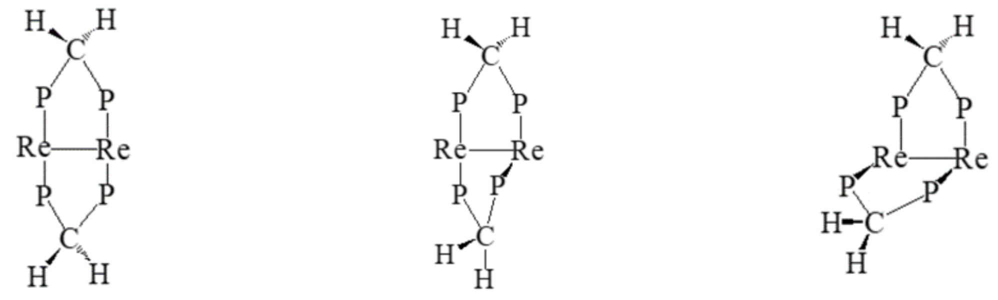
ABSTRACT

When M_2L_{10} complexes containing two rhenium(III) atoms in a quadruple bond react with an excess of the diphosphine ligand $Ph_2PCH_2PPh_2$, the bond order decreases, and the rhenium is reduced to rhenium(II). When two diphosphine ligands are bonded to the dirhenium center, they can adopt a *trans-trans*, *trans-cis,* or *cis-cis* configuration. NMR spectra of compounds that adopt the *cis-cis* arrangement show unusually large downfield shifts for one of the bridgehead methylene hydrogens (P-CH_2-P). To understand the unusual chemical shift, the hydrogens first have to be assigned. The strategy for making these assignments has been to try to make compounds where one of the hydrogens has been replaced with another group (e.g., CH_3 or CN). All efforts to make *cis-cis*-type compounds containing $Ph_2PCH(CH_3)PPh_2$ (dppmMe) or $Ph_2PCH(CN)PPh_2$ (dppmCN) have been unsuccessful. However, reactions of rhenium-containing starting materials with these derivatized ligands have produced compounds with unexpected chemical and physical properties. Furthermore, the work has allowed us to compare how the dirhenium chemistry of $Ph_2PCH(CH_3)PPh_2$ (dppmMe) and $Ph_2PCH(CN)PPh_2$ (dppmCN) differs from the well-established chemistry of the parent diphosphine, dppm. Finally, one reaction mixture may have produced a sample of a compound with a *trans-trans* configuration of diphosphine ligands.

INTRODUCTION

Considerable attention has been given to complexes that contain two metal atoms held together by strong metal-metal bonds. Interest in these species stems from their unusual electrochemical, spectroscopic, and structural properties. The element that has been most closely associated with this chemistry is rhenium.[1]

For many years, Dr. Derringer and other researchers have been interested in the spectroscopic properties of dirhenium(II) compounds that contain two bridging $Ph_2PCH_2PPh_2$ (dppm) ligands. Complexes of this type can adopt a *trans-trans* arrangement of the diphosphines[2-7] a *trans-cis* arrangement,[8] or a *cis-cis* arrangement.[2,3,8-14] Representations of these arrangements are shown in Figure 1.



trans-trans *trans-cis* *cis-cis*

Figure 1. Arrangements of two diphosphines bonded to a dirhenium center.

When the arrangement is *cis-cis*, one of the bridgehead methylene hydrogens of the dppm ligands ($P\text{-}CH_AH_M\text{-}P$) has an unusually large downfield chemical shift compared to the shifts observed for *trans-cis*- and the *trans-trans*-species. The following ranges have been observed: $\delta = 4.93\text{-}6.05$ ppm for *trans-trans*;[2-7] $\delta = 6.17\text{-}6.23$ ppm for *trans-cis*;[8] and $\delta = 6.40\text{-}6.63$ ppm for *cis-cis*.[2,3,8-14]

We would like to be able to explain why the shift for the *cis-cis* complexes is so far downfield. To do this, however, we must first assign the hydrogens. The work described here was undertaken to attempt to synthesize complexes that would help us make these assignments.

We set out to prepare complexes of the type *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppmR)_2$ (R = CN or CH_3). [Note: *Cis-cis* is normally simplified to *cis* alone, and *trans-trans* is simplified to *trans*.] We believe it might be possible to make the assignments if complexes of the following type can be prepared (see Figure 2).

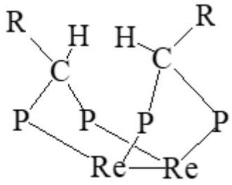


Figure 2. One possible arrangement of two dppmR ligands bonded to a dirhenium center.

To date, we have not been able to prepare any complexes we believe can be formulated as *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppmR)_2$. However, the work has allowed us to compare how the dirhenium chemistry of $Ph_2PCH(CH_3)PPh_2$ (dppmMe) and $Ph_2PCH(CN)PPh_2$ (dppmCN) differs from the well-established chemistry of the parent diphosphine, dppm.

EXPERIMENTAL SECTION

Starting Material

All solvents and the dirhenium starting material $[(\underline{n}\text{-Bu})_4N]_2Re_2Cl_8$ were purchased from commercial sources and used as received.

Reaction Procedures

Unless otherwise stated, all reactions were carried out under a nitrogen atmosphere, and all solvents were deaerated with N_2 gas before use. The diphosphine ligands dppmCN and dppmMe were synthesized as described previously.[15,16] The dirhenium compounds $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$, $Re_2(O_2CCH_3)_2Cl_4(4\text{-Mepy})_2$, and $Re_2(O_2CCH_3)_4Cl_2$ were prepared as described in the literature.[3,17]

A. <u>Synthesis of $Re_2(O_2CCH_3)Cl_4(dppmMe)_2$</u>

A mixture of $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ (0.0935 g, 0.140 mmol) and dppmMe (0.1478 g, 0.3714 mmol) was stirred in refluxing EtOH (15 mL) for ca. 22 min. The bright yellow solid product was filtered off and dried *in vacuo*; yield, 0.0525 g (51.4%). Note: When the reaction time was ca. 35 min, the yield was 82.3%. Anal. Calcd $C_{54}H_{51}Cl_4O_2P_4Re_2$: C, 47.3%; H, 3.72%. Found: C, 46.60%; H, 4.09%.

B. <u>Attempted Synthesis of $Re_2(O_2CCH_3)Cl_4(dppmCN)_2$</u>

A mixture of $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ (0.0934 g, 0.140 mmol) and dppmCN (0.1474 g, 0.360 mmol) was stirred in refluxing EtOH (15 mL) for ca. 35 min. The bright yellow solid product was filtered off and dried *in* vacuo; yield, 0.0466 g. Note: When the reaction time was ca. 1 h, the yield was 0.0684 g.

C. Synthesis of $Re_2Cl_4(dppmMe)_2$

A mixture of $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ (0.1049 g, 0.157 mmol) and dppmMe (0.1611 g, 0.404 mmol) was stirred in refluxing EtOH (25 mL) for ca. 5 d. The reddish-purple solid product was filtered off and dried *in vacuo*; yield, 0.0534 g (50.9%). Note: When the reaction time was ca. 1 d with the same solvent, the yield was 0.0915 g. When the reaction time was ca. 1 d and the solvent was n-PrOH, the yield was 0.1339 g.

D. Synthesis of $Re_2Cl_4(dppmCN)_2$

A mixture of $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ (0.1045 g, 0.156 mmol) and dppmCN (0.1603 g, 0.392 mmol) was stirred in refluxing EtOH (25 mL) for ca. 5 d. The brownish-purple solid product was filtered off and dried *in vacuo*; yield, 0.0959 g (91.8%). Note: When the reaction time was ca. 1 d with the same solvent, the yield was 0.0640 g. When the reaction time was ca. 1 d and the solvent was n-PrOH, the yield was 0.0797 g.

E. Attempted Synthesis of *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppmR)_2$ (R = CN or Me)

(i). From $Re_2(O_2CCH_3)_4Cl_2$ and dppmCN in MeOH

A mixture of $Re_2(O_2CCH_3)_4Cl_2$ (0.0750 g, 0.110 mmol) and dppmCN (0.300 g, 0.732 mmol) was stirred in refluxing MeOH (20 mL) 2 d. After 2 d, an orange solid resembling the starting material was filtered off and dried *in vacuo*. Analysis showed the solid product was unreacted $Re_2(O_2CCH_3)_4Cl_2$.

(ii). From $Re_2(O_2CCH_3)_2Cl_4(4\text{-Mepy})_2$ and dppmCN in MeOH

A mixture of $Re_2(O_2CCH_3)_2Cl_4(4\text{-Mepy})_2$ (0.0421 g, 0.0580 mmol), dppmCN (0.1343 g, 0.328 mmol), and LiOAc (0.4091 g, 6.2 mmol) was stirred in refluxing MeOH (20 mL) for ca. 2 d. Additional MeOH (10 mL) was added 1 d into the reaction. This was done to ensure the complete dissolution of LiOAc. The solvent was removed by rotary evaporation. IR spectroscopy revealed that the solid residue, which was insoluble in acetone and DCM, contained unreacted LiOAc. No rhenium-containing product was identified.

(iii). From $Re_2(O_2CCH_3)_2Cl_4(4\text{-Mepy})_2$ and dppmMe in MeOH

A mixture of $Re_2(O_2CCH_3)_2Cl_4(4\text{-Mepy})_2$ (0.0433 g, 0.0597 mmol), dppmMe (0.1358 g, 0.344 mmol), and LiOAc (0.4040 g, 6.12 mmol) was stirred in refluxing MeOH (20 mL) for ca. 2 d. Additional MeOH (10 mL) was added 1 d into the reaction. This was done to ensure the complete dissolution of LiOAc. The solvent was removed by rotary evaporation. IR spectroscopy revealed that the solid residue, which was insoluble in acetone and DCM, contained unreacted LiOAc. No rhenium-containing product was identified.

(iv). From $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ and dppmMe in EtOH

A mixture (1:6 starting material/ligand) of $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ (0.0847 g, 0.127 mmol) and dppmMe (0.3024 g, 0.759 mmol) were refluxed in EtOH (20 mL) in the presence of a boiling stick for ca. 1 d. The dark solid product was filtered off and dried *in vacuo*. The solid was examined under a microscope and found to be a mixture of bright yellow microcrystals and dark purplish-brown microcrystals. The purplish-brown compound was soluble in DCM while the yellow compound was not. The yellow compound was also insoluble in acetone and in acetonitrile.

(v). From From $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ and dppmMe in acetone

A mixture (1:6 starting material/ligand) of $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ (0.0580 g, 0.0868 mmol) and dppmMe (0.2011 g, 0.505 mmol) was stirred in acetone (20 mL) at RT for ca. 2 h. After 2 hours, the reaction mixture was still blue (the color of $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$), so the solution was refluxed overnight. After ca. 1 d of reflux, the reaction mixture contained a greenish-yellow solid product, which was filtered off and dried *in vacuo*; yield, 0.0334 g.

F. Other Reaction Mixtures

(i). A sample of $Re_2Cl_4(dppmCN)_2$ (0.0303 g, 0.0227 mmol) was dissolved in DCM (ca. 75 mL). The purple solution was stirred at room temperature as CO_2 was bubbled into it. After ca. 8 h, the DCM was removed by forced evaporation. An analogous procedure was also performed using $Re_2Cl_4(dppmMe)_2$.

(ii). A mixture of the yellow compound from reaction A – the reaction which produced a possible *trans*-$[Re_2(O_2CCH_3)_2Cl_2(dppmCN)_2]^+$ complex – (0.0115 g) and LiOAc (0.0106 g, 0.161 mmol) was refluxed in EtOH (25 mL) in the presence of a boiling stick for ca. 5 d. The solvent was removed by evaporation. The grayish black residue that remained was shown to be insoluble in DCM and in acetone. No rhenium-containing product was identified.

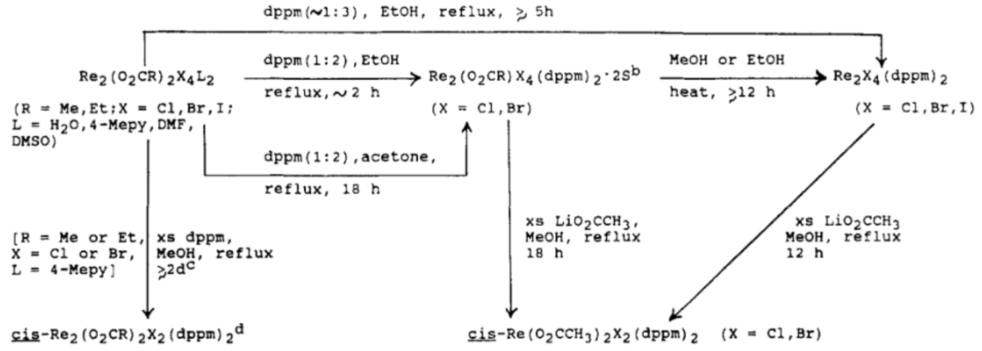
Physical Measurements

Fourier-transform infrared spectra in the region 4000-600 cm^{-1} were recorded using a Thermo Scientific Nicolet iS5 equipped with an ATR attachment.

Electrochemical measurements were made using a Digi-Ivy DY2100B voltammeter. The solvent was dry DCM that contained 0.1 M TBAH as supporting electrolyte. At Pt-disk working electrode and a Pt-wire auxiliary electrode were utilized. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to an Ag/AgCl reference electrode at room temperature and are uncorrected for junction potentials. Under our experimental conditions the ferrocenium/ferrocene couple is at $E_{1/2} = +0.47$ V vs. Ag/AgCl.

RESULTS AND DISCUSSION

Much of our work was based on the chemistry summarized in the scheme shown in Figure 3. This figure was taken from a paper published by Cutler et al.[3]



[a] Numbers in parentheses refer to the stoichiometric ratios of reagents (i.e., dirhenium complex:dppm). [b] S = EtOH or $(CH_3)_2CO$. [c] In the presence of excess LiO_2CCH_3 or NaO_2CCH_3 these reactions proceed much more rapidly (~7 h) to give exclusively *cis*-$Re_2(O_2CR)_2X_2(dppm)_2$. [d] A small amount of $Re_2(O_2CR)X_4(dppm)_2$ was also isolated in the case of R = Me and X = Cl.

Figure 3. A scheme showing how *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$ can be prepared from $Re_2(O_2CCH_3)Cl_4L_2$ (L = H_2O, 4-Mepy).

Cutler et al. observed that mixtures of $Re_2(O_2CCH_3)_2X_4(H_2O)_2$ (X = Cl, Br) and dppm (1:2 mole ratio) in refluxing EtOH produced $Re_2(O_2CCH_3)X_4(dppm)_2$ after 2h.[3] One of the ways they identified the product was by cyclic voltammetry. A cyclic voltammogram (CV) of $Re_2(O_2CCH_3)Br_4(dppm)_2$ is shown in Figure 4.

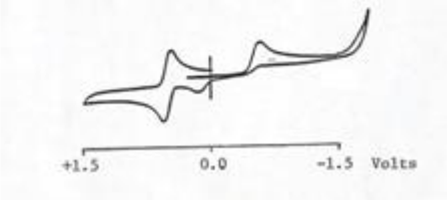


Figure 4. A CV of $Re_2(O_2CCH_3)Br_4(dppm)_2$.[18]

Our work has revealed that $Re_2(O_2CCH_3)Cl_4(dppmMe)_2$ can be prepared from mixtures of $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ and dppmMe in refluxing EtOH in shorter time: ca. 20 min compared to 2 h for dppm. A CV of $Re_2(O_2CCH_3)Cl_4(dppmMe)_2$ is shown in Figure 5. The electrochemical parameters are as follows: $E_{1/2}$ = + 0.48 V; $E_{p,c}$ = – 0.58 V.

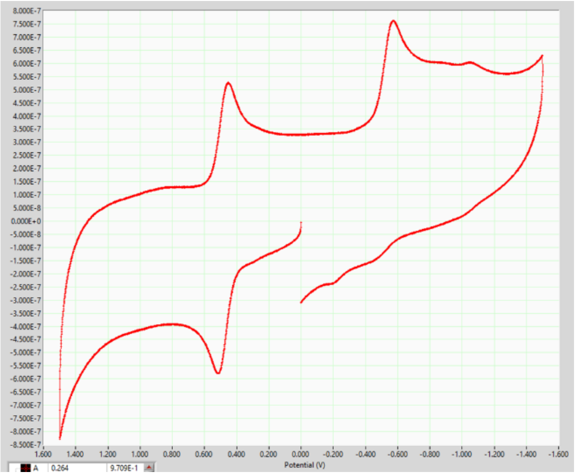


Figure 5. A CV of $Re_2(O_2CCH_3)Cl_4(dppmMe)_2$.

Under similar reaction conditions, mixtures of $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ and dppmCN, did not produce $Re_2(O_2CCH_3)Cl_4(dppmCN)_2$. We base this conclusion on the results of electrochemical investigations (see Figure 6). We would expect the CV of $Re_2(O_2CCH_3)Cl_4(dppmCN)_2$ to resemble the one for $Re_2(O_2CCH_3)Cl_4(dppmMe)_2$ (see Figure 5), but it does not. Instead, it resembles the CV of *trans*-$[Re_2(O_2CCH_3)_2Cl_2(dppm)_2]PF_6$ (see Figure 7).[3,18] Therefore, we believe we may have prepared *trans*-$[Re_2(O_2CCH_3)_2Cl_2(dppmCN)_2]^+$. The electrochemical parameters are as follows: $E_{1/2}$ (1) = + 0.78 V; $E_{1/2}$ (2) = – 0.29 V. Based on what is present in the reaction mixture, the most likely counterion is Cl^-. However, there is no evidence in CV this ion is present.

Figure 6. A CV of what may be a salt of *trans*-$[Re_2(O_2CCH_3)_2Cl_2(dppmCN)_2]^+$.

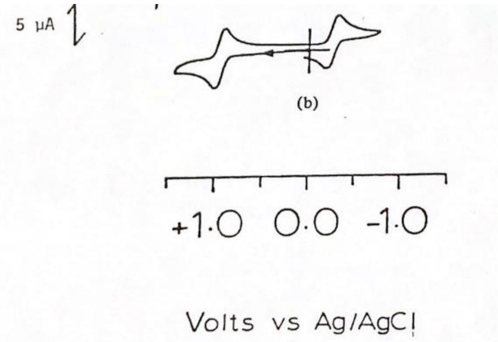


Figure 7. A CV of *trans*-$[Re_2(O_2CCH_3)_2Cl_2(dppm)_2)]PF_6$.[3,19]

Elemental analysis (%C and %H) of a sample of the "*trans* cation" was consistent with the calculated %C and %H for the complex $[Re_2(O_2CCH_3)_2Cl_2(dppmCN)_2]Cl$. It should be noted that %C and %H values of $Re_2(O_2CCH_3)Cl_4(dppmCN)_2$ are almost the same as the %C and %H for the proposed $[Re_2(O_2CCH_3)_2Cl_2(dppmCN)_2]Cl$ complex. As our focus was on obtaining the *cis* isomer, the possible formation of a *trans* cation was set on the back burner in favor of exploring novel reaction conditions which could lead to the formation of the *cis* isomer, but further study of this possible *trans* cation is warranted.

Cutler et al. showed that $Re_2X_4(dppm)_2$ (X = Cl, Br) forms when mixtures of $Re_2(O_2CCH_3)_2X_4(H_2O)_2$ and dppm are refluxed in EtOH for more than 5 h (see Figure 3).[3] A CV of $Re_2Br_4(dppm)_2$ is shown in Figure 8.

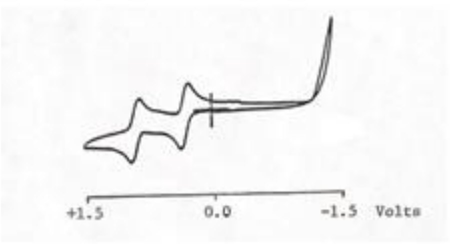


Figure 8. A CV of $Re_2Br_4(dppm)_2$.[18]

Our work has shown that $Re_2Cl_4(dppmR)_2$ (R = CN, Me) can be prepared from mixtures of $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ and dppmR in refluxing EtOH but longer reaction times are required: ca. 1-5 d (for the dppmR ligands) compared to ca. 5 h (for the dppm derivative). A CV of $Re_2Cl_4(dppmMe)_2$ is shown in Figure 9. The $E_{1/2}$ values for the most intense couples are as follows: $E_{1/2}$ (1) = + 0.18 V; $E_{1/2}$ (2) = + 0.87 V. It is important to note that even after a day or more, these reactions did not produce products that were exclusively $Re_2Cl_4(dppmR)_2$. Efforts to purify $Re_2Cl_4(dppmR)_2$ by standard methods (e.g., recrystallization and chromatography) were unsuccessful.

Figure 9. A CV that shows $Re_2Cl_4(dppmMe)_2$ may be present.

Cutler et al. showed that *cis*-$Re_2(OCCH_3)_2Cl_2(dppm)_2$ formed in ca. 7 h when an excess of LiOAc was present with $Re_2(O_2CCH_3)_2Cl_4(4\text{-}Mepy)_2$ and dppm in refluxing MeOH (see Figure 3).[3] Under similar conditions, albeit longer reaction times (1-2 d), no identifiable rhenium-containing product was observed by us when we used dppmCN or dppmMe. Although soluble in MeOH, our reaction products were insoluble in acetone and DCM, which is unfortunate, because we routinely use DCM as a solvent for cyclic voltammetry.

As far as we can tell, no *cis-cis* products formed in any of the mixture described in E(i.-v.) or F(ii.) above (see EXPERIMENTAL SECTION):

- Mixture E(i) used a different rhenium starting material, the light orange $Re_2(O_2CCH_3)_4Cl_2$.
- Mixtures E(ii.) and E(iii.) also used a different rhenium starting material, $Re_2(O_2CCH_3)_2Cl_4(4\text{-}Mepy)_2$, as well as an excess of lithium acetate. The change in starting material and addition of excess lithium acetate was the result of wanting to replicate a synthesis described in Cutler, et al., where a reaction with these reactants formed the *cis* isomer more rapidly and without the formation of

the monoacetate intermediate.[3] When these reaction conditions were replicated with dppmCN and dppmMe, no solid product was present in the reaction mixtures after multiple days, a departure from what was described.[3] When the solvents were removed *in vacuo*, the only solid product that could be isolated was a mixture of unreacted ligand, lithium acetate (both confirmed using IR), and an insoluble dark gray compound which could not be identified. No evidence could be found of any of the rhenium starting material in either the solvent or the mixture of solids. This procedure was replicated in reaction F(ii), with the yellow compound from reaction A (the possible *trans*-$[Re_2(O_2CCH_3)_2Cl_2(dppmCN)_2]Cl$ complex) used as a starting material, and it produced a very similar result, with no solid product in the reaction mixture and only a mixture of lithium acetate and an insoluble dark gray compound.

- Mixtures E(iv.) and E(v.) returned to using $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ as the rhenium starting material. The focus of E(iv.) was the stoichiometric ratio of ligand to starting material, as formation of the *cis* isomer is favored by longer reaction times and higher stoichiometric ratios.[3] A boiling stick was also placed in the flasks in these reactions to promote crystal growth and hopefully reduce contaminants in the final sample. The result of reaction E(iv.) was a mix of dark, purplish-brown microcrystals and bright yellow microcrystals (which were slightly larger than the dark ones) (see Figure 10). Surprisingly, while the dark microcrystalline sample was readily soluble in DCM, the yellow ones were not, nor were they soluble in acetone or in acetonitrile. While no electrochemical data were obtained for the yellow crystals, data for the dark crystals showed characteristics of the purple compound $Re_2Cl_4(dppmMe)_2$. IR data of both the crystal mixture and just the yellow crystals confirmed the presence of the dppmMe ligand in the sample but did not suggest any structural changes that would be detectable with IR.

Figure 10. Photo of purple/yellow microcrystalline mixture.

Reaction E(v.) kept the ligand, starting material, and ratios the same, but changed the reaction solvent from an alcohol to acetone to test the effect of the reaction solvent on the formation of the product. First, the mixture of ligand and starting material were stirred at room temperature to see if any reaction would proceed based on just the change in solvent. When there was no change after 2 hours, the reaction mixture was refluxed like all previous reactions. The solid that was isolated from the reaction mixture was a light yellowish-green color, a different color than any compound made previously. Although the color was different, the CV suggested that it was the same $Re_2(O_2CCH_3)Cl_4(dppmMe)_2$ compound as was synthesized in reaction B. In the IR spectrum of this compound, however, there was a peak around 1708 cm^{-1} that corresponded to acetone. While this may have been residual solvent in the sample, there is the possibility that acetone had been incorporated into the complex and caused the novel color.

- An offshoot of the main body of work for this study was testing the reactivity of the purple $Re_2Cl_4(dppmR)_2$ complexes with CO_2 gas (Mixture F(i)). These complexes have two open coordination sites which could allow for the binding of CO_2 and open the door for further study into similar M_2L_8 complexes for future use in CO_2 filters. While these tests with CO_2 were unsuccessful, they were very limited in scope (done once for each complex, only at STP). Further work with these complexes and CO_2 could involve changing reaction temperatures, pressures, apparatuses, etc.

CONCLUSION

Although the dirhenium systems containing the derivatized dppmR ligands were expected to behave in similar ways to the dppm systems, this has not been the case thus far. The intermediate complexes $Re_2(O_2CCH_3)Cl_4(dppmR)_2$ and $Re_2Cl_4(dppmR)_2$ seem to form readily using similar stoichiometric ratios and reaction conditions as described in Culter, et al., the formation of *cis*-$Re_2(O_2CCH_3)_2Cl_2(dppmR)_2$ has been unsuccessful.^{3}

Particularly strange outcomes were observed for mixtures E(ii.), E(iii.), and F(ii.). In the dppm system, the addition of excess lithium acetate readily promoted the formation of the *cis* isomer, but when these same conditions were used in the dppmR systems, no rhenium product was isolated from the reaction mixtures at all. This was also the case in reaction F(ii.), where the initial formation of an intermediate was bypassed by using the monoacetate intermediate as a starting material. Even without the addition of lithium acetate in the reactions described in E(iv.) and E(v.), where only the dppmR ligands were in excess, the *cis* isomer still did not form. Noteworthy in E(iv.) was that the final product mixture was unexpectedly insoluble. Changing the reaction solvent, as described in E(v.), also produced a compound having characteristics of the monoacetate intermediate, but the difference in color and IR data suggested that acetone may have been incorporated into the complex.

It is possible the complex *trans*-$[Re_2(O_2CCH_3)_2Cl_2(dppmCN)_2]Cl$ formed under the conditions described in B above (see EXERIMENTAL SECTION), but beyond CV and elemental analysis, further study of this compound and its synthesis was not undertaken in favor of pursuing the *cis* isomer. The possibility of forming this complex, however, is exciting, as previous syntheses yielded *cis/trans* mixtures and not pure *trans*-$Re_2(O_2CCH_3)_2Cl_2(dppm)_2$.^{3} If this complex can be synthesized, there is the possibility of isolating only *trans*-$Re_2(O_2CCH_3)_2Cl_2(dppmR)_2$ and isomerizing it to the *cis* isomer.

There are many possibilities for future work with these compounds in addition to working with the *trans* complex described above. Investigating the changes in the reactions involving the addition of lithium acetate could give more insight into the mechanisms of the reactions in the dppmR systems, which in turn could explain the difficulties in forming the *cis* isomer. In that same vein, further analysis of the product of E(iv.), especially the insoluble yellow microcrystals, could be helpful in determining the differences between the dppm and dppmR systems, as the formation of those insoluble crystals suggests that the replacement of one of the methylene hydrogens in dppm affects the mechanistic actions of the dppmR ligands more than expected. Understanding these differences could lead to changes in reaction conditions to optimize the pathway to forming the *cis* isomer, or possibly working with dppm derivatives other than dppmCN and dppmMe.

In the case of the purple $Re_2Cl_4(dppmR)_2$ complexes, the free coordination sites could allow for the binding of other molecules such as CO_2. This binding potential could be investigated further and eventually give insights into CO_2 binding mechanisms. If this intermediate can be shown to reliably bind CO_2 under the right conditions, then derivatized versions or complexes with similar binding characteristics could eventually be used to advance the technology of CO_2 filters for use in research and industry to counteract the effects of climate change.

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