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Scientific Review by Priestley Medalist

Highlights from Recent Work on Metal−Metal Bonds[†]

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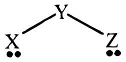
The study of transition metal compounds with metal−metal (M−M) bonds of various orders (from $^1/_2$ to 4) began in a coherent and productive way in 1964 with the recognition that a strong quadruple bond exists between the metal atoms in the $Re_2Cl_8^{2-}$ ion. For nearly 20 years the field grew exponentially, before settling back to a steady level of activity. While it is now a fairly mature field, it continues to provide scope, challenges, and new results that are often surprising. In this review I shall summarize a few new results, primarily from work in my own laboratory. The selection is somewhat arbitrary; there are other topics of comparable interest, but space is limited. To economize on space, references that may be found in *Multiple Bonds between Metal Atoms*, 2nd ed., by F. A. Cotton and R. A. Walton, will not be given here.

1. In Quest of the Perfect Ligand

Although unbridged quadruple and triple bonds between metal atoms are well-known for certain pairs of metal atoms[1] (Figure 1), it is generally helpful and often necessary to have suitable bridging ligands in order to render compounds containing such bonds stable. By suitable bridging ligands we most often mean those that may be generically represented as in **1**. These are uninegative, bent, trinuclear anions with X−Z distances similar to the M−M distances across which they are intended to form a pair of approximately parallel X−M and Z−M bonds.



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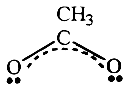

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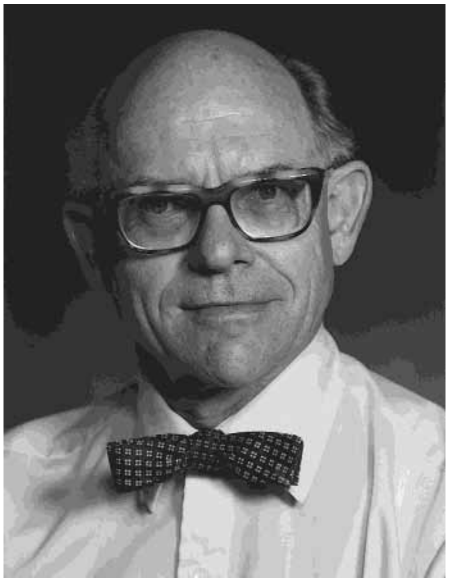
The first ligand of this type was the acetate anion, **2**, as in $Mo_2(O_2CCH_3)_4$, and, indeed, carboxylate anions have permitted the preparation of $M_2(O_2CR)_4$ or $M_2(O_2CR)_4L_2$ compounds of many elements, particularly Cr, Mo, W (hard to make and relatively unstable), Tc, Re, Ru, Os, Rh, and (only recently and with difficulty) Pt. However, in the cases of V, Nb, Co, and Ir, no one has succeeded in making such molecules. Three



F. A. Cotton was born in Philadelphia, PA, in 1930. His undergraduate education was obtained at Drexel and Temple Universities (A.B., 1951) and his Ph.D. at Harvard University (1955). He joined the MIT faculty as an instructor in 1955 and became a full professor in 1961. In 1972 he moved to Texas A&M University, where he is now Doherty-Welch Distinguished Professor. His research interests have been principally in preparative and structural chemistry of transition metal compounds, especially those with metal−metal bonds, but he has worked in organometallic and metal carbonyl chemistry, theory, and protein structure. Over 100 Ph.D. recipients and an even larger number of postdoctoral visitors have worked with him. He is a member of the NAS, The Royal Society, the French Academy, and numerous other major scientific academies and holds 23 honorary doctorates. Among his awards are the Priestley Medal, the Welch Prize, the AIC Gold Medal, the King Faisal Prize, and the Paracelsus Medal. His current research group numbers 20 people from seven different countries.

[†] This paper is to commemorate scientific achievements of the author, who received the Priestley Medal at the 215th National Meeting of the American Chemical Society, Dallas, TX, March 31, 1998. The text of the Priestley Award Address has been separately published in *Chem. Eng. News*, March 30, 1998, pp 43−46.

(1) This is true for Mo_2^{4+}, W_2^{4+}, MoW^{4+}, Tc_2^{4+}, Tc_2^{6+}, Re_2^{4+}, Re_2^{6+}, and Os_2^{6+} in species of the types $M_2X_8^{n-}$ and $M_2X_4L_4$, and also for $Cr_2(tmtaa)_2$. There are also some $M_2(porph)_2$ and $MM'(porph)_2$ molecules that have been made and studied in great detail by J. P. Collman and co-workers.

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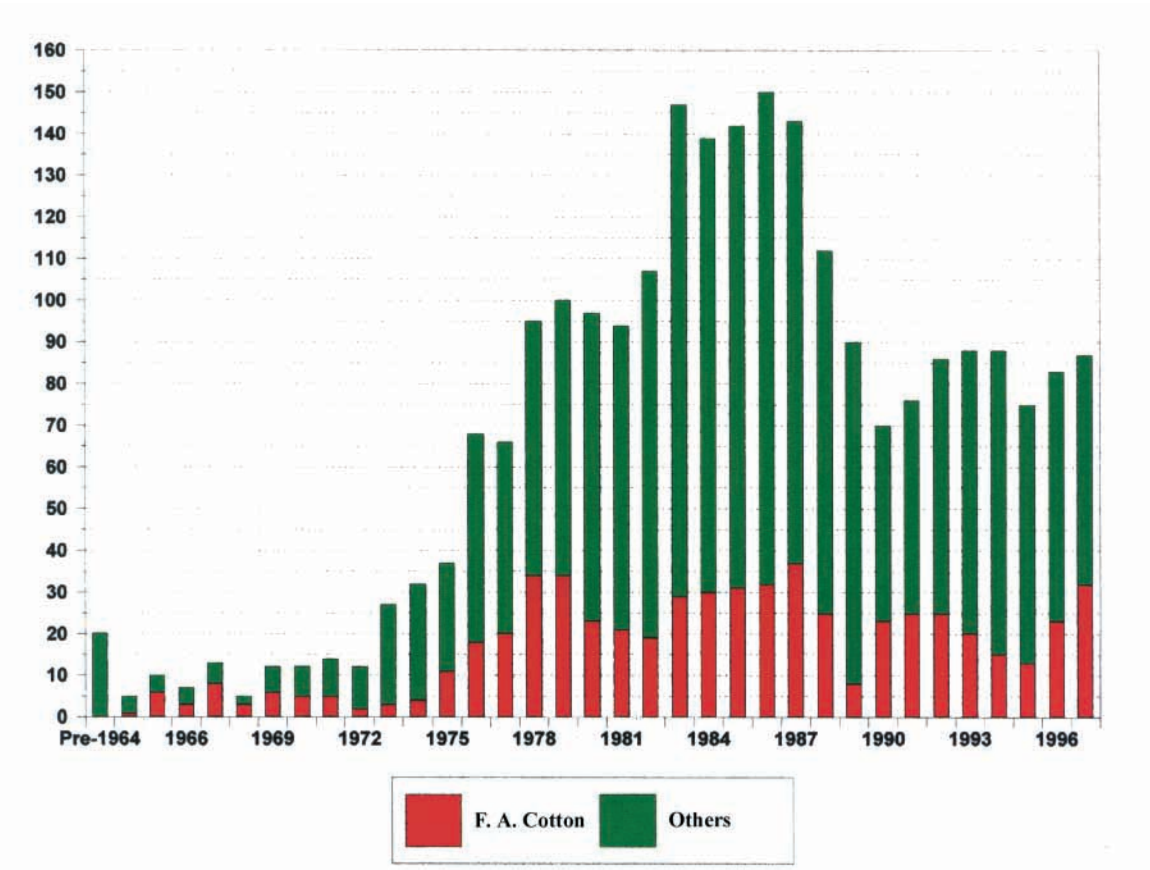
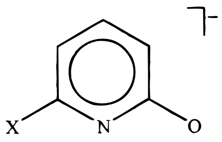


Figure 1. The per annum number of publications on metal−metal bonds up to 1997. Only those bonds in the L_3MML_3 and L_4MML_4 structural classes are included.

reasons for seeking other ligands are (1) to extend the range of M_2^{n+} chemistry to other elements and other oxidation states, (2) to have greater ease of preparation and greater stability, and (3) to obtain compounds with a range of properties such as redox potentials.

A promising way ahead[2] was long ago recognized to be to use ligands in which one or both oxygen atoms that form bonds to the metal atoms are replaced by nitrogen atoms. The oxopyridinate, **3**, and amidopyridinate, **4**, types were studied early. The use of 6-methyl-2-hydroxypyridine provided access to the first complete group of congeneric compounds by the simple reactions I as well as to the first mixed species by reactions II.



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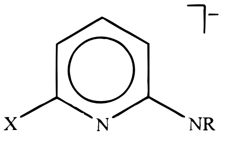

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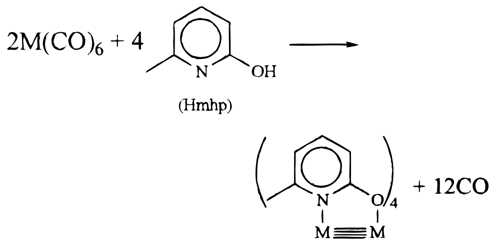
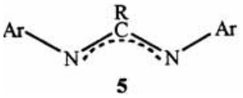


(I)

$$M(CO)_6 + M'(CO)_6 + 4Hmhp \longrightarrow MM'(mhp)_4 + 12CO \qquad (II)$$

M = Cr, Mo, W

For a number of reasons, favor has recently fallen strongly on the amidinate ligands, **5**, and particularly on the formamidinates, **6**, since they are easy to prepare and variation of the para substituents, X, allows control of redox potentials[3] and solubility.



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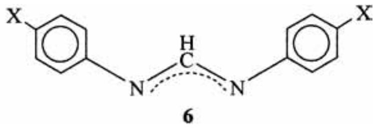

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A particularly satisfying result of using formamidinate ligands was that the preparation of the first compound containing a V≡V (triple) bond, $V_2[(p\text{-tolN})_2CH]_4$, Figure 2, was accomplished in this way by my colleague Carlos Murillo. Prior to this, large amounts of time had been invested by several people over

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(2) It should be noted that the list of ligands that conform to the generic type **1** is very long. It includes those with C−C−N, C−C−O, C−C−C, and C−P−C chains as well as many with O−C−N and N−C−N chains.

(3) Lin, C.; Ren, T.; Valente, E. J.; Zubkowski, J. D. *J. Chem. Soc., Dalton Trans*. **1998** and earlier work by Lin, Ren, et al. cited therein.

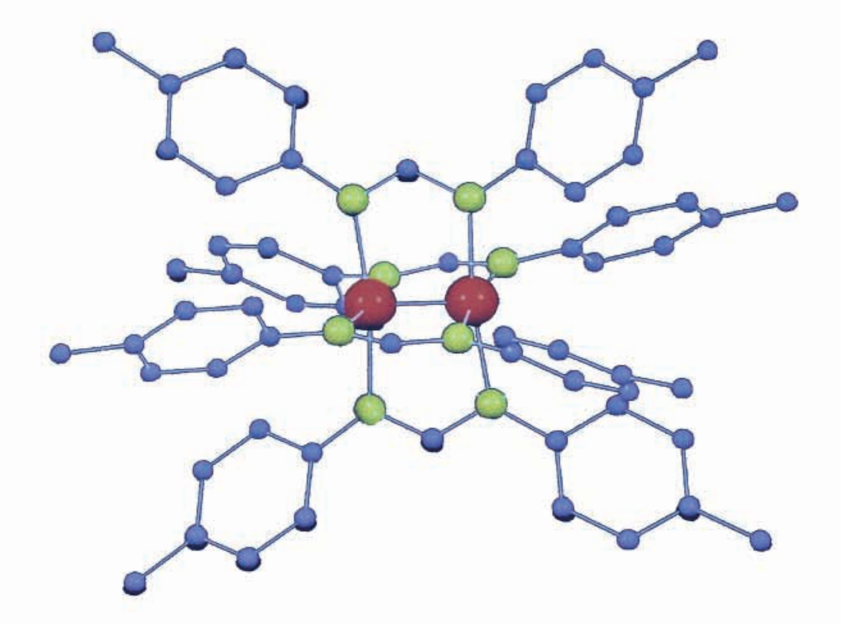


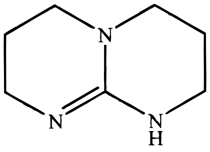
Figure 2. The first molecule with a V≡V bond, V_2(*N*,*N*′-di-*p*-tolylformamidinate)$_4$.

several years to make a V≡V compound by employing carboxylates and other ligands that contained oxygen. From all of this effort the only positive results obtained were a library of compounds containing oxo-centered V_3 triangles. The well-known oxophilicity of vanadium, especially V^{II}, had proved insuperable. Indeed, even the compounds of the V_2^{4+} core that can be made with "all nitrogen" ligands are hyper-reactive toward O_2.[4]

In addition to the ability of the formamidinate anions to stabilize the V_2^{4+} core, they (and the closely related triazenides, $ArNNNAr^-$) have been the key to obtaining the first Co_2^{4+} and Ir_2^{4+} compounds. Furthermore, because of their own electronic properties, such as high basicities and π-orbital energies, they have made available dimetal compounds with unprecedented electronic properties.

It did not take long until formamidinate ligands, mainly those with Ar = phenyl or *p*-tolyl, had been employed to make compounds of virtually every M_2^{n+} core, whether known to exist with other ligands or not. We thought we had the "perfect" ligand for this field of chemistry, and we optimistically started to tackle the toughest of the previously unrealized M_2^{n+} species, especially Nb_2^{4+} and Ta_2^{4+}. It was here that formamidinate ligands met their Waterloo. The enormously strong reducing power of these species and/or the strong reductants needed to prepare them chewed up the formamidinate ligands.[5,6] An overview of all of the observed types of dismemberment and mayhem is presented in Figure 3.

In the face of these frustrations, we looked for a ligand that retained the $N{=}C{=}N^-$ feature of the formamidinates but was buttressed to be more resistant to fragmentation. Fortunately, such a ligand not only exists but, better yet, is commercially available at a reasonable price. The compound, **7**, whose formal name is almost too horrible to contemplate, fills the bill. We designate it only by the acronym Hhpp, and the anionic ligand obtainable therefrom by deprotonation is hpp^-. This ligand rather easily gave some compounds[7] analogous to those already obtainable with formamidinates, such as $V_2(hpp)_4$, $Cr_2(hpp)_4$, and $Mo_2(hpp)_4$. Once it had passed this entry-level test, we proceeded to give it the real test: would it survive under excruciating reducing conditions?



1,3,4,6,7,8-hexahydro-2H-
pyrimido[1,2-a]pyrimidine
(Hhpp)

7

It came through the first such test with flying colors.[8] We were able to prepare the first paddlewheel-type compound containing a Nb≡Nb triple bond, Figure 4. In addition, we have found that the triply-bonded $Mo_2(hpp)_4^{2+}$ ion, the first Mo_2^{6+} species of this general type, can be prepared.

So, have we now got the perfect ligand? Not quite, but I think we are close. The hpp ligand has the problem of giving complexes that are sometimes not quite as soluble as one would like. We are now trying to make one or more derivatives of Hhpp with aliphatic side chains that should enhance solubility without altering the stability.

2. New Isomers and New Reactions Galore

As a necessary preface to this topic (and the next one) we remind (or inform) the reader of the numbering scheme for the ligands in an (idealized) square prismatic $Re_2X_nL_{8-n}$ molecule. This is shown in Figure 5 together with five illustrations of its employment.

Back in 1976 R. A. Walton discovered that under a certain set of circumstances (i.e., time of reaction, temperature, choice of solvent and the R group(s) involved) reaction III occurs rather

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[4] These reactions lead, apparently, to V=O and V(μ-O)$_2$V products with loss of all V−V bonding.

[5] Cotton, F. A.; Daniels, L. M.; Matonic, J. H.; Murillo, C. A.; Wang, X. *Polyhedron* **1997**, *16*, 1177.

[6] Cotton, F. A.; Daniels, L. M.; Murillo, C. A.; Wang, X. *Inorg. Chem.* **1997**, *36*, 896.

[7] Cotton, F. A.; Timmons, D. J. *Polyhedron* **1998**, *17*, 179.

[8] Cotton, F. A.; Matonic, J. H.; Murillo, C. A. *J. Am. Chem. Soc.* **1997**, *119*, 7889.

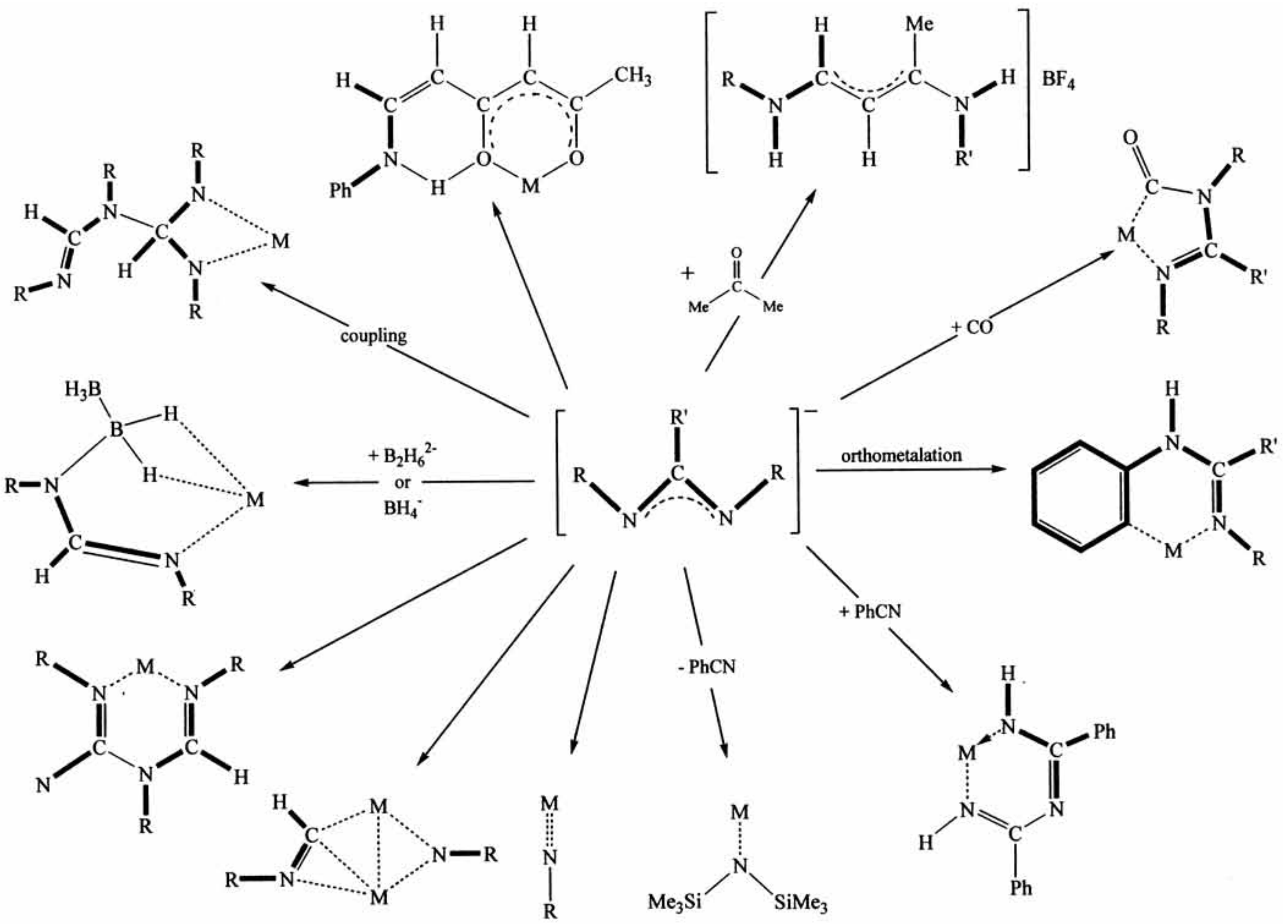

Figure 3. Dismemberment reactions of formamidinate ligands.

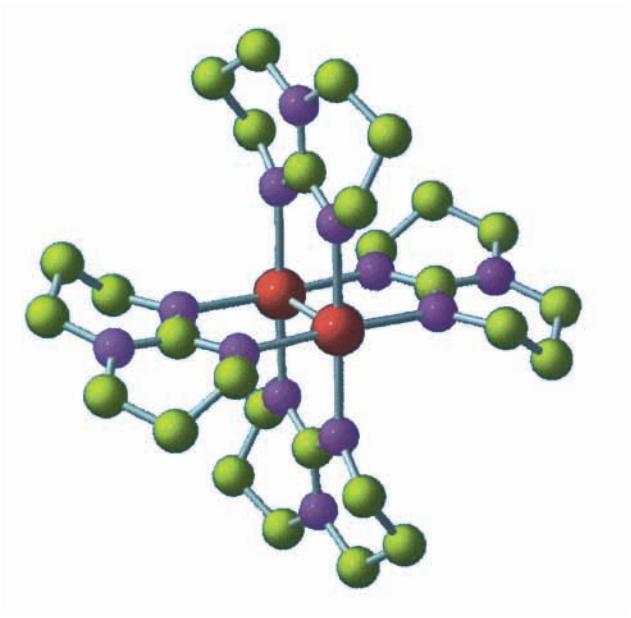

Figure 4. The $Nb_2(hpp)_4$ molecule.

than the simple, nonreductive substitution reaction IV, which was already known. X-ray study showed that the $Re_2Cl_4(PEt_3)_4$ compound first produced had the 1,3,6,8 arrangement of the PEt_3 ligands.[9] Moreover, the mean torsion angle was 0°, despite the fact that there is no δ bond present.[10] It was proposed that “the staggering of the large PEt_3 groups with respect to one another results in eclipsing of the ligand set as a whole.”

$$[Re_2Cl_8]^{2-} \xrightarrow{\text{excess } PR_3} Re_2Cl_4(PR_3)_4 \qquad (III)$$

$$[Re_2Cl_8]^{2-} + 4PR_3 \longrightarrow Re_2Cl_6(PR_3)_2 + 2Cl^- \qquad (IV)$$

Subsequently, several other $Re_2X_4(PR_3)_4$ compounds were shown to have the 1,3,6,8 structure and the idea that this was going to be the only one accessible took hold. When the first $Re_2Cl_5L_3$ compound (with L = PMe_3) was made, by reaction V, we were unsurprised to find that it was the 1,3,6 isomer.[11] However, when we attempted to carry out reaction VI, we failed; instead, to our very great surprise, it was reaction VII that actually occurred.[11]

After recovering from surprise that the 1,2,7 isomer had been made, we decided that it was likely to be a metastable, kinetic product, which could, therefore, be thermally transformed into the 1,3,6 isomer. However, we were unable to do this; no conversion took place up to temperatures at which decomposition occurred. We considered the possibility that the stability

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(9) Cotton, F. A.; Frenz, B. A.; Ebner, J. R.; Walton, R. A. *Inorg. Chem.* **1976**, *15*, 1630.

(10) In ref 9, it was not recognized that this was so, based on a $\sigma^2\pi^2\delta^2\delta^{*2}$ configuration, since there was no increase in the Re−Re bond length relative to that in $Re_2Cl_6(PEt_3)_2$ where the electron configuration is $\sigma^2\pi^4\delta^2$. It was not realized until later that the tendency of the abolition of the δ bond to increase the Re−Re bond length is offset by the tendency of the reduction in valence state of the Re_2^{n+} unit from n = 6 to n = 4 to shorten the Re−Re bond because of better σ and π overlaps.

(11) Cotton, F. A.; Price, A. R.; Vidyasagar, K. *Inorg. Chem.* **1990**, *29*, 5143.

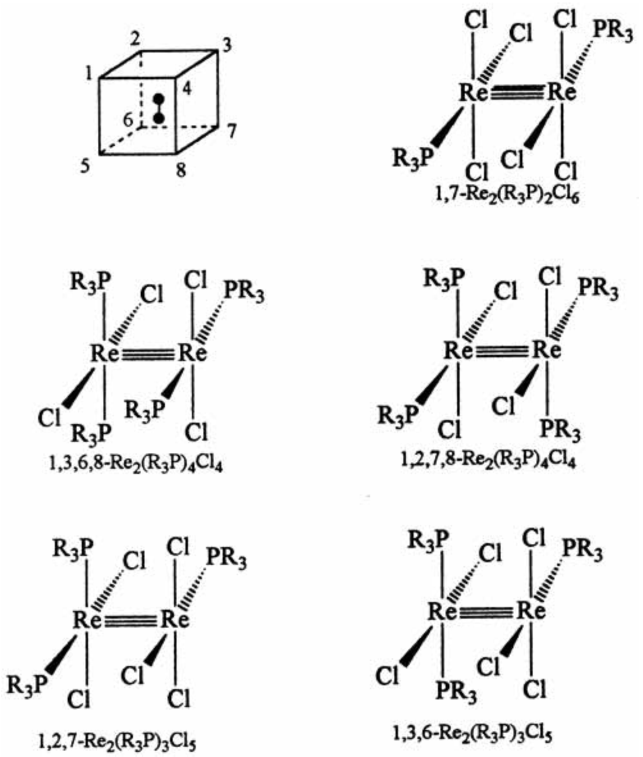


Figure 5. The numbering scheme for prismatic $M_2X_nL_{8-n}$ compounds and five illustrations of its application.

$$\text{1,3,6,8-}Re_2Cl_4(PMe_3)_4 \xrightarrow{Cl_2} \text{1,3,6-}Re_2Cl_5(PMe_3)_3 \qquad (V)$$

$$\text{1,3,6,8-}Re_2Cl_4(PMe_3)_4 \xrightarrow{Cl_2 + PMe_3} Re_2Cl_6(PMe_3)_4 \qquad (VI)$$

$$\text{1,3,6,8-}Re_2Cl_4(PMe_3)_4 \xrightarrow{Cl_2 + PMe_3} \text{1,2,7-}Re_2Cl_5(PMe_3)_3 \qquad (VII)$$

order could be the reverse of what we had been expecting and tried to convert thermally the 1,3,6 isomer to the 1,2,7 isomer, but this, too, failed.

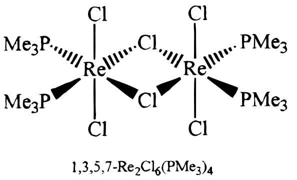
Matters rested there until 1996 when I decided to have a further look at this problem and, in the hands of Evgeny Dikarev and Marina Petrukhina, two outstanding Russian visitors, exciting new results were obtained. Our synthetic strategy was based on the assumption that unknown and entirely unanticipated compounds might be made by (i) the use of new reaction conditions (solvent, time, temperature) for "old" processes and (ii) the employment of unusual starting materials in well-known reactions.

First, a quantitative method to produce 1,2,7 isomers by the reduction of the $Re^{III}-Re^{III}$ complexes was found. It was shown that $[Re_2Cl_8]^{2-}$ reacts with small basic phosphines ($PR_3 = PMe_3$,[12] PMe_2Ph[13]) at room temperature in alcohols to produce 1,2,7-$Re_2Cl_5(PR_3)_3$, shown in reaction VIII. However, the

$$[Re_2Cl_8]^{2-} \xrightarrow{PR_3} \text{1,2,7-}Re_2Cl_5(PR_3)_3 \qquad (VIII)$$

ability of phosphine groups to occupy cis positions is certainly limited by their size. Thus, some other phosphines with larger cone angles also cause a one-electron reduction of octachlorodirhenate,[14] but the reaction proceeds only as far as the disubstituted anionic species, $[Re_2Cl_6(PR_3)_2]^-$ ($PR_3 = PEt_3$, PEt_2Ph).

A possible explanation for why small phosphines prefer to give initially a 1,2,7 geometry was suggested when we examined[15] a reaction of $[Re_2Cl_8]^{2-}$ with PMe_3 in an inert, nonpolar solvent, benzene, with the hope of eliminating (or slowing down) the reduction processes so as to obtain $Re^{III}-Re^{III}$-type products. Indeed, the dirhenium(III) complex of stoichiometry $Re_2Cl_6(PMe_3)_4$ is first precipitated from solution within 4−6 h but is then gradually converted to 1,2,7-$Re_2Cl_5(PMe_3)_3$. The remarkable compound $Re_2Cl_6(PMe_3)_4$, the first stage of the reaction between octachlorodirhenate and PMe_3, consists of a chlorine-bridged, edge-sharing, bioctahedral dirhenium molecule, **8**. The Re−Re distance is 3.8486(4) Å, indicating the absence of metal−metal bonding. All phosphine groups are located in the same plane as the metal centers and the bridging chloride ligands. According to the numbering scheme for edge-sharing complexes,[16] **9**, we can define the latter as the 1,3,5,7 isomer. The P−Re−P angles for trimethylphosphine ligands are 93.91(5)°. Thus we have a cis disposition of PMe_3 ligands on each Re atom already in the intermediate on the route to the 1,2,7 isomer of $Re_2Cl_5(PMe_3)_3$.



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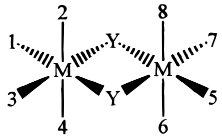

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At this point it became clear that we have an opportunity for stereochemical control of the reaction (preserving a cis arrangement) at ambient or low temperatures. The 1,2,7-$Re_2Cl_5(PR_3)_3$ isomers ($PR_3 = PMe_3$, PMe_2Ph) provided us with stereochemically interesting starting materials exhibiting very accessible potentials for one-electron reduction and one-electron oxidation reactions. These two processes were then accomplished[13,15] chemically, Figure 6, using well-known techniques.

One-electron reduction of the 1,2,7 isomer by cobaltocene at room temperature followed by nonredox substitution of Cl^- by phosphine in the resulting anionic species leads exclusively to the formation of the 1,2,7,8 isomer of $Re_2Cl_4(PR_3)_4$, Figure 6, presumably because substitution at any other position is unfavorable for steric reasons ($PR_3\cdots PR_3$ contacts across the Re−Re bond). The reaction product has the phosphine ligands in a cis arrangement at each metal center and, in fact, is the first example of this type of isomer in the entire class of $M_2X_4(PR_3)_4$ compounds (M = Tc, Re, Mo, W; X = Cl, Br, I; PR_3 = monodentate phosphine).

On the other hand, one-electron oxidation of a 1,2,7 isomer by $NOBF_4$ at ambient temperature in the presence of $Bu^n{}_4NCl$[13,15] as a chloride source (Figure 6) gave a 1,7-$Re_2Cl_6(PR_3)_2$ product. For $PR_3 = PMe_3$ that synthesis was of unusual interest since all previous attempts to prepare $Re_2Cl_6(PMe_3)_2$ by different reactions and starting materials had failed, owing to the intervention of the reduction. An equimolar amount of the chloride intended to replace phosphine is absolutely critical for

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[12] Cotton, F. A.; Dikarev, E. V. *Inorg. Chem.* **1996**, *35*, 4738.

[13] Cotton, F. A.; Dikarev, E. V.; Petrukhina, M. A. *Inorg. Chem.* **1998**, *37*, 1949.

[14] Petrukhina, M. A.; Cotton, F. A.; Dikarev, E. V. Presented at the 215th National Meeting of the American Chemical Society, Dallas, TX, March 29 to April 2, 1998.

[15] Cotton, F. A.; Dikarev, E. V.; Petrukhina, M. A. *J. Am. Chem. Soc.* **1997**, *119*, 12541.

[16] For the numbering scheme for edge-sharing complexes, see: Cotton, F. A.; Eglin, J. L.; James, C. A. *Inorg. Chem.* **1993**, *32*, 687.

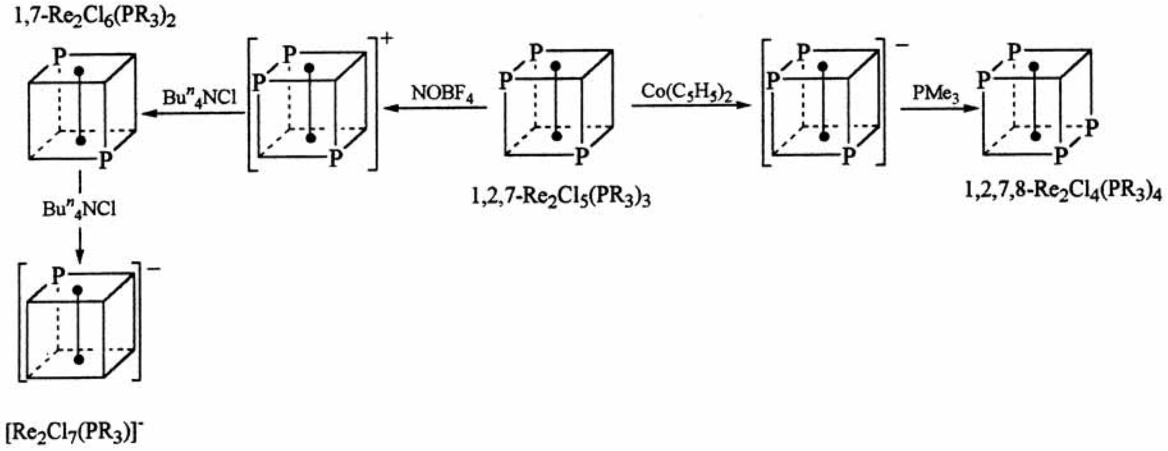
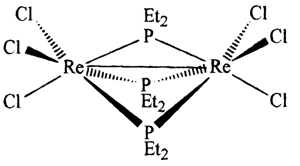


Figure 6. Systematic, controlled stereochemistry starting from 1,2,7-$Re_2Cl_5(PR_3)_3$.

the desired process, as the use of excess results in other products, such as $[Re_2Cl_7(PR_3)]^-$ and even $[Re_2Cl_8]^{2-}$.

Another small phosphine which we thought might be employed in reactions of these kinds is diethylphosphine, PEt_2H. It is known that not only can secondary phosphines react in the same manner as tertiary phosphines but, also, a deprotonation may occur giving a dialkylphosphido group capable of bonding as either a terminal or bridging anionic ligand. We have found[17] that for the interaction of $[Re_2Cl_8]^{2-}$ with PEt_2H the reaction conditions (especially the solvent and amount of phosphine) have a great influence on reaction pathway even when working at room temperature only.

In CH_2Cl_2 and with an excess of phosphine, reaction IX occurs to produce a Re_2^{8+} complex, **10**. In the solid state this diamagnetic compound has a structure consisting of a face-sharing bioctahedral anion with three bridging phosphide groups and six terminal chloride ions.



$[Re_2(\mu\text{-}PEt_2)_3Cl_6]^-$

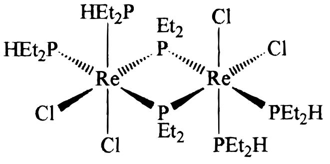
10

$$[Re_2Cl_8]^{2-} \xrightarrow{PEt_2H} [Re_2(\mu\text{-}PEt_2)_3Cl_6]^- \quad (IX)$$

$$[Re_2Cl_8]^{2-} \xrightarrow{PEt_2H} Re_2(\mu\text{-}PEt_2)_2Cl_4(PEt_2H)_4 \quad (X)$$

When the reaction is carried out in C_3H_7OH or C_6H_6, plus HCl and with an excess of phosphine, a dirhenium(III) complex is obtained according to reaction X. The structure is that of an edge-sharing bioctahedral dirhenium molecule with two bridging phosphide groups and four terminal phosphine ligands. The arrangement of the neutral terminal ligands with centrosymmetric occupation of two axial and two equatorial positions is an example of the rare type of 1,2,5,6 isomer, **11**.

Finally, reaction in C_2H_5OH and in the absence of an excess of phosphine leads to a disproportionation to dirhenium(IV) and dirhenium(II) compounds shown in reaction XI. The Re^{II}−Re^{II} complex is the third example of a 1,2,7,8 isomer.

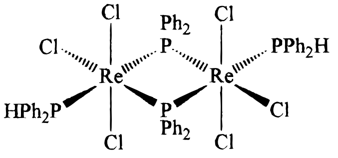


1,2,5,6-$Re_2(PEt_2)_2Cl_4(PEt_2H)_4$

11

$$2[Re_2Cl_8]^{2-} + 10PEt_2H \longrightarrow [Re_2(\mu\text{-}PEt_2)_3Cl_6]^- + Re_2Cl_4(PEt_2H)_4 + 3PEt_2H_2^+ + 6Cl^- \quad (XI)$$

The variety of complexes that have been obtained with diethylphosphine can be explained not only by its ability to form a dialkyl phosphide group but also by its ability to bind to metal atoms with small P−Re−P angles. On the contrary, the bigger secondary phosphine, PPh_2H, was found[18] to produce only one product, $[Re_2(\mu\text{-}PPh_2)_2Cl_6(PPh_2H)_2]^{2-}$, the edge-sharing bioctahedral dianion having two bridging phosphide groups and only two terminal phosphine ligands, **12**.



$[Re_2(\mu\text{-}PPh_2)Cl_6(PPh_2H)_4]^{2-}$

12

3. Some Intriguing Ditungsten Compounds

We have recently concluded a lengthy study of a class of compounds first reported by D. C. Bradley in 1989. Bradley reported[19] the processes summarized in reaction XII. We have here simply a replacement of the two amine ligands, Me_3CNH_2, by phosphines, PR_3, but there are, in general, two products,

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[17] Cotton, F. A.; Dikarev, E. V.; Petrukhina, M. A. *Inorg. Chem.*, in press.

[18] Dikarev, E. V.; Cotton, F. A.; Herrero, S.; Petrukhina, M. A. Presented at the 215th National Meeting of the American Chemical Society, Dallas, TX, March 29 to April 2, 1998.

[19] Bradley, D. C.; Hursthouse, M. B.; Powell, H. R. *J. Chem. Soc., Dalton Trans*. **1989**, 1537.

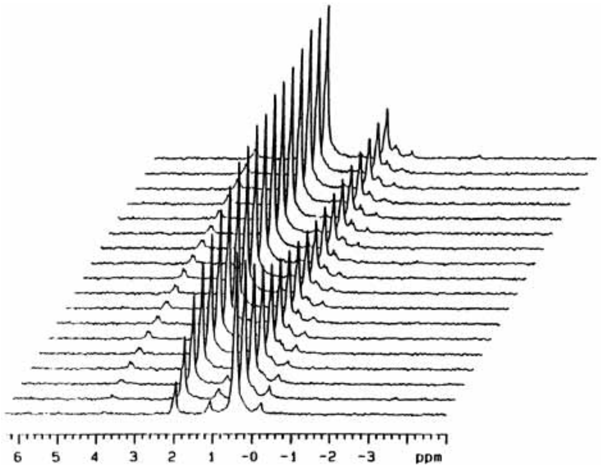
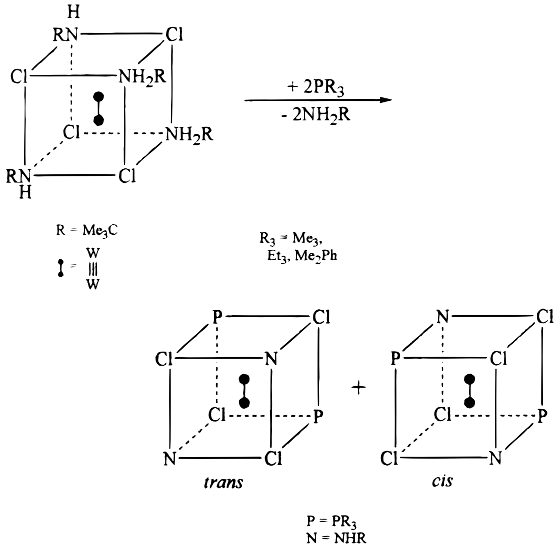


Figure 7. ^{31}P{^{1}H} NMR spectra showing conversion of *trans*-$W_2Cl_4(NHBu^t)_2(PMe_2Ph)_2$ to *cis*-$W_2Cl_4(NHBu^t)_2(PMe_2Ph)_2$ as a function of time at 50 °C in toluene. (Reprinted with permission from ref 21. Copyright 1994 American Chemical Society.)

which are cis and trans isomers, with reference to the positions of the chlorine atoms on each tungsten atom.



(XII)

In our first two studies we dealt with some preparative and crystallographic questions[20] but also, *much* more significantly, with the equilibration of the cis and trans isomers in solution,[21] which was conveniently observed by ^{31}P NMR spectroscopy. It was found that a solution prepared from the pure cis (or pure trans) crystalline solid would equilibrate thermally (with only slight decomposition) to an equilibrium mixture of the two, as shown, for example, in Figure 7, taken from ref 21. It may be noted that in some cases[22] the cis isomer is so much more stable than the trans that trans → cis isomerization proceeds to completion.

It was hypothesized that such interconversions would require the traversal of an intermediate formed by the loss of one ligand. In the solvent toluene, the only likely candidate for ligand dissociation is the neutral ligand PR_3, and, therefore, to test this hypothesis, the rates of isomerization were studied as a function of added phosphine. As shown in Figure 8, there was, indeed, an initial decrease in rate, but thereafter the reaction continued but at a rate independent of phosphine concentration. The inescapable conclusion is that while there is a process that depends on PR_3 dissociation, there is also one that does not. We have recently employed density functional theory (DFT) to search configuration space for pathways that could account for such a unimolecular rearrangement. We have now found a plausible intramolecular process that permits this trans−cis rearrangement, as well as that to the other cis isomer, to be discussed shortly. Our calculated activation energies for these processes (which will be published soon) are about 25 kcal mol^{-1}, which is in nice agreement with experimental estimates. Stay tuned.

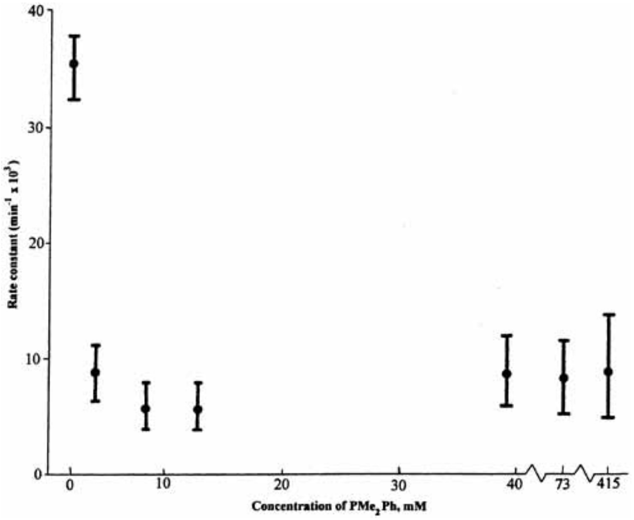


Figure 8. The dependence of the rate constant for the trans → cis isomerization of $W_2Cl_4(NHCMe_3)_2(PMe_2Ph)_2$ on the amount of added PMe_2Ph.

In several additional papers we showed that this sort of chemistry could be generalized to allow the preparation of compounds containing NR_2 (R = Et, Bu^n, and hex) groups[23] as well as still other phosphines. Among the other phosphines employed were the bidentate phosphines $Me_2P(CH_2)_{1,2}PMe_2$ and $Ph_2P(CH_2)_{1,2}PPh_2$.[24] One particularly interesting result was the formation of a compound with a cis arrangement of Cl atoms on one W atom and a trans arrangement on the other[25] as well as the already known cis,cis- and trans,trans-type molecules. This occurs as shown in reaction XIII, where N represents NEt_2 or $Nhex_2$ and L-L is dppe, dmpe, or dmpm. In a follow-up study of this phenomenon, the formation of all three isomers (cis,cis, cis,trans, and trans,trans) of $W_2Cl_4(Net_2)_2$(dppm) was followed as a function of time, while the temperature rose from −50 °C when the reactants were mixed to +20 °C. It was found that the trans,trans isomer formed first and cis,trans appeared shortly thereafter, but both finally disappeared in favor of the cis,cis isomer.[26]

Another, even greater, surprise was encountered[27] with the use of the bidentate phosphine $Ph_2P(CH_2)_3PPh_2$. In this case we obtained, in addition to the expected W_2^{6+} product, one in

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(20) Cotton; F. A.; Yao, Z. *J. Cluster Sci.* **1994**, *5*, 11.

(21) Chen, H.; Cotton, F. A.; Yao, Z. *Inorg. Chem.* **1994**, 33, 4255.

(22) Cotton, F. A.; Dikarev, E. V.; Wong, W.-Y. *Inorg. Chem.* **1997**, *36*, 3268.

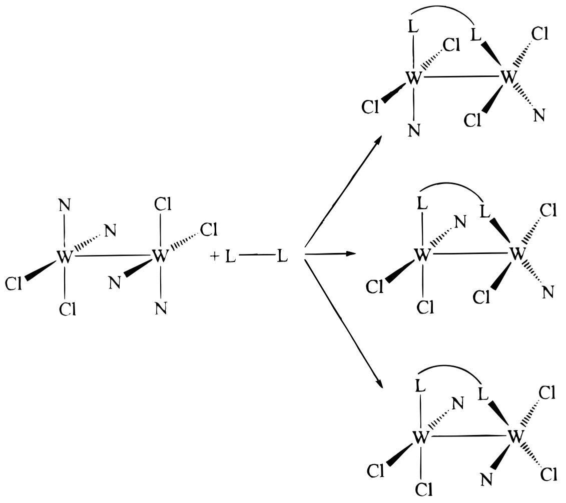
(23) Cotton, F. A.; Dikarev, E. V.; Wong, W.-Y. *Inorg. Chem.* **1997**, *36*, 559.

(24) Cotton, F. A.; Dikarev, E. V.; Wong, W.-Y. *Inorg. Chem.* **1997**, *36*, 80.

(25) Cotton, F. A.; Dikarev, E. V.; Wong, W.-Y. *Inorg. Chem.* **1997**, *36*, 902.

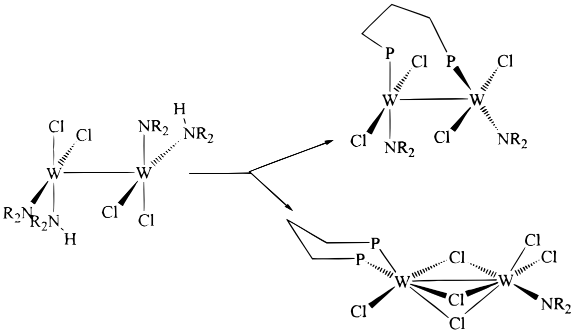
(26) Cotton, F. A.; Dikarev, E. V.; Nawar, N.; Wong, W.-Y. *Inorg. Chim. Acta* **1997**, *262*, 21.

(27) Cotton, F. A.; Dikarev, E. V.; Wong, W.-Y. *Polyhedron* **1997**, *16*, 3893.



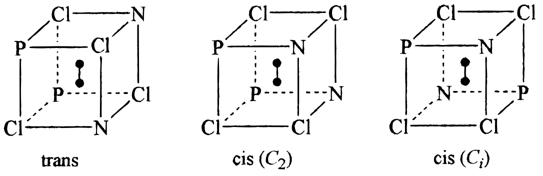
(XIII)

which oxidation had occurred to give a W_2^{7+} product with a face-sharing bioctahedral structure, as shown in reaction XIV. We have not been able to account for this oxidation.



(XIV)

Finally, in concluding our work in this area, we dealt further with the isomer interconversion process as well as with another question that has not yet been expressly raised. We have so far discussed only "the cis" and trans isomers, but in fact there are *two* possible cis isomers, as shown in **13**. The second cis isomer has C_i symmetry, and to distinguish the two cis isomers, we designate them cis(C_2) and cis(C_i). The big question was, why had the cis(C_i) isomer never been observed, even in solution. We carried out several MO and molecular mechanics calculations, none of which gave any reason to believe that this "missing" isomer should be markedly less stable than the other two. On the other hand, it must be recognized that even if disfavored by only a few kilocalories per mole (say 3−6) it might elude detection. We kept looking, however, and became more and more frustrated by not being able to find even one example. Finally, by dint of trying many new combinations of NR_2 and PR_3 ligands we succeeded with the compound $W_2Cl_4(NHEt)_2(PMe_3)_2$, chosen so as to have sterically undemanding ligands.[28] We were now able to see the cis(C_i) isomer as well as the cis(C_2) isomer as they arose from the trans isomer in solution at room temperature.



trans cis (C_2) cis (C_i)

13

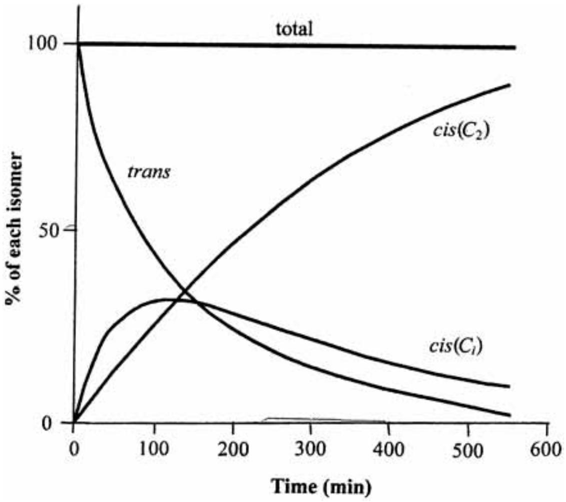


Figure 9. Plot of the percentages of the three isomers of $W_2Cl_4(NHEt)_2(PMe_3)_2$ versus time at room temperature in C_6D_6/THF.

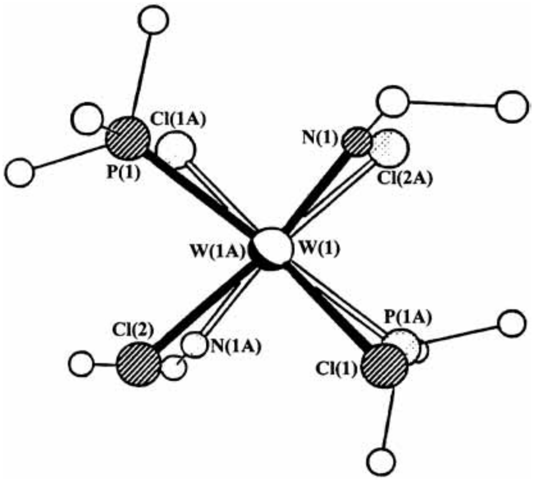


Figure 10. The cis(C_i) isomer of the $W_2Cl_4(NHEt)_2(PMe_3)_2$ molecule as observed crystallographically.

As shown in Figure 9, the cis(C_i) isomer reaches a maximum of only ∼25% and then declines, along with the trans isomer, while the cis(C_2) isomer steadily increases to become, asymptotically, the sole thermodynamic product. The isolation of the crystalline cis(C_i) isomer was accomplished by quickly removing in a vacuum the solvent from the reaction mixture at about the time the concentration of the isomer was maximal. The solid mixture of isomers was then extracted with toluene, and from this solution, at −20 °C overnight, a small quantity of crystals was obtained. An end-on view of the molecule is shown in Figure 10, where it is clear that this is, indeed, the heretofore missing centrosymmetric, cis(C_i) isomer. The cis(C_i) isomers of the $W_2Cl_4(NHPr^n)_2(PMe_3)_2$ and $W_2Cl_4(NHBu^n)_2(PMe_3)_2$ molecules were also observed by ^{31}P NMR in solution, but they were not isolated. Perhaps they are too soluble to survive during a lengthy crystallization process.

4. Is Three a Crowd? Bond Stretch Isomerism Redux?

Prior to 1994 several compounds of the type shown in Figure 11 had been reported,[29] in all of which the two M−M distances

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(28) Cotton, F. A.; Dikarev, E. V.; Wong, W.-Y. *Inorg. Chem.* **1997**, *36*, 2670.

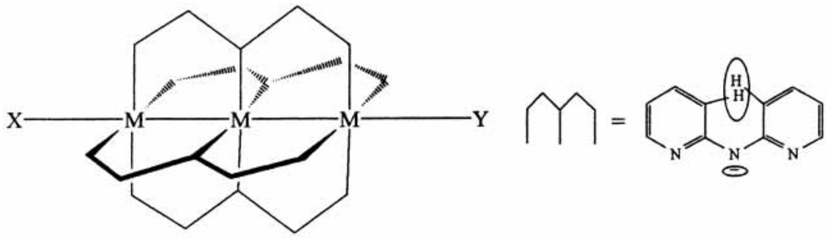

Figure 11. Trinuclear complexes formed with the anion of di-2-pyridylamine (dpa$^-$). Note that the ligand cannot actually be planar because of the H···H repulsion circled, and thus the complexes are helical. There is a total twist of ca. 45° from one end to the other.

were short and equal. Delocalized M−M bonding over the M_3 chains was indicated. In 1994 S. Peng and co-workers[30] made the startling report that for M = Co and X = Y = Cl the Co_3 chain was highly *unsymmetrical*, with distances of 2.09 and 2.47 Å. My first reaction to this was one of skepticism, since it was so at odds with previous results. Subsequently, Peng reported two more compounds of the same type, with M = Ru and Rh, that were again symmetrical.[31] This made me decide to re-examine the cobalt compound to see if perhaps there was an error in the structural work.

Since the reported preparative procedure left much to be desired, we made the compound by a better one and obtained it in a different crystal form. We then found[32] that our crystals were isotypic to those of all the previously reported symmetrical compounds and were, as would be expected, composed of symmetrical molecules with Co−Co distances of 2.32 Å, close to the average of those reported by Peng. Needless to say, we were now even more inclined to think that Peng's structure was incorrect, but nonetheless, we playfully suggested that perhaps the late and mostly unlamented idea of "bond stretch isomers" had unexpectedly been reincarnated. Little did we really believe that, in fact, *it had*.

No sooner had our paper[32] appeared, with its ironical allusion to bond stretch isomers, when we obtained the cobalt compound in another crystalline form (not Peng's either) where,[33] *mirabile dictu*, it was unsymmetrical, with Co−Co distances of 2.29 and 2.46 Å—practically identical to those reported by Peng.[30] What we had previously suggested, tongue in cheek, was now reality, i.e., "the unusual phenomenon whereby molecules differ only in the length of one or more bonds."[33] Much remains to be learned about these Co_3 species. The symmetrical isomer can be seen on the cover, where it will be noted that it, and all its homologues with other metals, are helical. This is a result of the requirement to avoid a too-close contact between hydrogen atoms, as shown in Figure 11.

Not only does the story not end here, it gets better. Our own major thrust in this area has, so far, been to look at trichromium compounds,[34] $Cr_3(dpa)_4XY$. Once again, it is found that both symmetrical and unsymmetrical isomers occur. With X = Y = Cl or PhC≡C− the compounds are symmetrical (Cr−Cr ≈ 2.36 Å), but in all cases where X ≠ Y (e.g., X = Cl or F, Y = PF_6 or BF_4) the compound is completely unsymmetrical, to the extent that there are one extremely short (quadruple) bond, 1.9−2.00 Å, and one nonbonded contact, 2.58−2.64 Å. Of course, this cannot be called (seriously or in jest) bond stretch isomerism, because the unsymmetrical Cr_3 chains are in unsymmetrical environments in terms of the axial ligands.

True bond stretch isomerism reappears in molecules obtained by one-electron oxidation of the central Cr_3^{6+} unit to Cr_3^{7+}. The results[35c] so far are summarized in Figure 12. Here we see a truly remarkable phenomenon: the gradual evolution from the symmetrical structure to the most extreme unsymmetrical structure. In the first three cases, it is only the uncoordinated counterions that change.

Clearly, there is a huge list of further studies that need to be made before we fully define the behavior of these systems, and then there will be the challenge of explaining why.

5. Mythical Metal−Metal Bonds

As an important part of our work on M−M bonds we naturally keep track of what others do: there are some 50−80 papers per year, apart from our own. Occasionally, something that turns up seems hard to believe, and we then try to see if there is an error. Sometimes the error is minor (though not insignificant), as, for example, a miscalculation of a bond length.[35] In several cases, however, it has turned out that there was a major error, usually based on seriously mishandled crystallography.

One case concerned the report of a compound "containing a Ta−Ta bond without bridging ligands".[36] Since the making of such a compound had been the goal of much work in my laboratory, and we had failed, I read this report very carefully. When I noted that there were hair-raisingly incredible features of the reported structure, we repeated the work.[37] The preparative work was easy to repeat, but the crystallography was seriously in error. The correct structure was found to have entirely believable internuclear distances and two hydrogen atoms bridging between the tantalum atoms. The presence of these hydrogen atoms was then confirmed by proton NMR.

From this and other occurrences, I think that we are into a period where the exponential growth in published crystal structures is being accompanied by a superexponential growth of bad (when not outright wrong) crystal structures. Even what

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(29) (a) Wu, L.; Field, P.; Murphy, C.; Nagle, P.; Hathaway, B.; Simmons, C.; Thornton, P. *J. Chem. Soc., Dalton Trans.* **1990**, 3835. (b) Aduldecha, S.; Hathaway, B. *J. Chem. Soc., Dalton Trans.* **1991**, 993. (c) Pyrka, G. J.; El-Mekki, M.; Pinkerton, A. A. *J. Chem. Soc., Chem. Commun.* **1991**, 84.

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(32) Cotton, F. A.; Daniels, L. M.; Jordan, G. T., IV. *Chem. Commun.* **1997**, 421.

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(37) Cotton, F. A.; Murillo, C. A.; Daniels, L. M.; Wang, X. *J. Am. Chem. Soc.* **1996**, *118*, 12449.

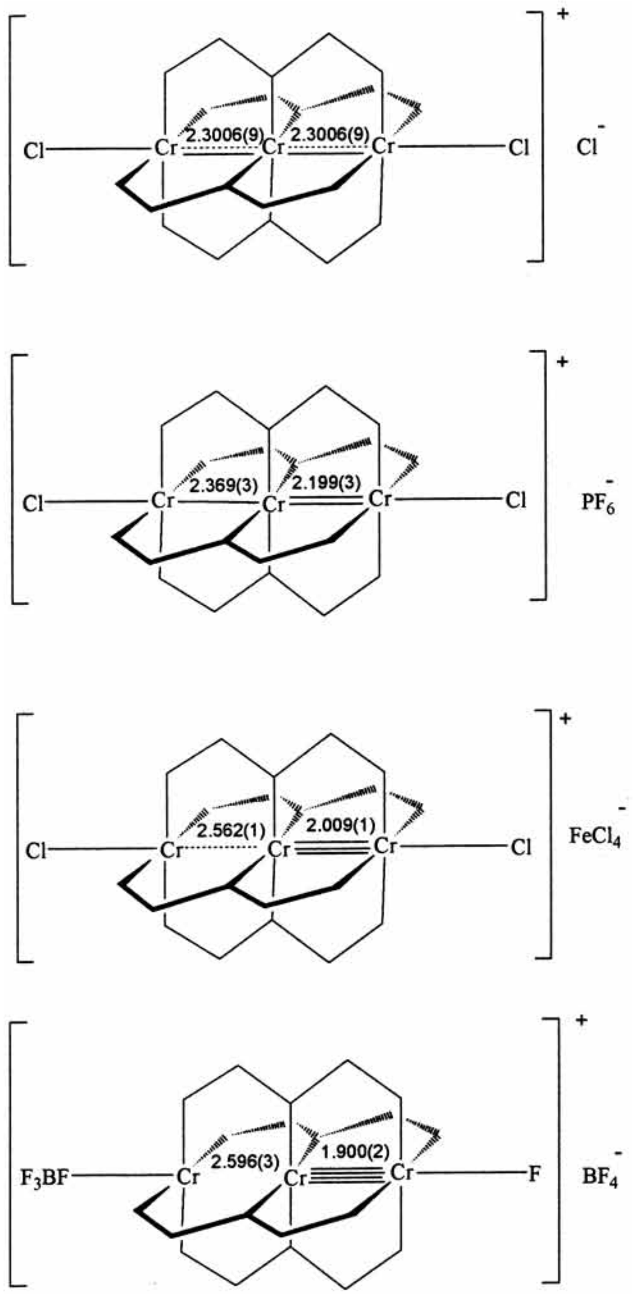

Figure 12. Three examples of the $[Cr_3(dpa)_4Cl_2]^+$ ion in which the Cr_3 chain changes from perfectly symmetrical to highly unsymmetrical. At bottom is a related cation where an end-group difference leads to the extreme of unsymmetricality.

ought to be straightforward structures (let alone those with unusual problems, such as the one I shall describe next) can be mishandled. Ironically, however, in all the cases I am aware of, erroneous structures almost always show features that would warn a good chemist that something must be wrong. My advice to chemists is: If a reported structure surprises you a little too much, regard it with suspicion and consult a qualified crystallographer about it.

Another case that was particularly interesting to us has as its prime subject the mythical compound "$Cp^*Tc_2O_3$".[38] This was reported to have infinite linear chains, $(TcO_3TcCp^*)_\infty$, with the planes of Cp* and triangular O_3 units perpendicular to the chain direction. The tip-off even for a chemist who knows absolutely nothing at all about crystallography was the claim that there were Tc−Tc distances of 1.86 Å. This is absolutely unbelievable. For one who knows practically nothing but at least a little about crystallography, an even more compelling feature of the report was that the quotient of the unit cell volume divided by the number of (non-hydrogen) atoms therein was 9 Å.[3] This is about half the normal value and is flat-out impossible. For these and several other none-too-subtle reasons, it was (or should have been) obvious that the structure was erroneous. My own immediate hypothesis was that the crystals were either twinned or disordered. To sort out the problem, fresh crystals were required, but it turned out that all efforts by several masterly preparative chemists over several years failed to reproduce the synthesis.

I then recalled that there was a rhenium compound, Cp^*ReO_3, that had been reported to form "twinned crystals"[39] the structure of which had never been solved. I had a hunch that "$Cp^*Tc_2O_3$" was really Cp^*TcO_3 and that the same twinning problem occurred in both the technetium and rhenium cases. Indeed, the two compounds were seen to crystallize isomorphously when the literature data were compared. It therefore seemed that by figuring out what the problem was with the crystal structure of Cp^*ReO_3 we would also solve the problem of the mythical compound "$Cp^*Tc_2O_3$". I engaged some accomplices and we proceeded to do just that.[40] However, not everything turned out exactly as expected.

We did solve the structure of Cp^*ReO_3. Interestingly, the crystals were *both* twinned *and* disordered—a double whammy that threw the original crystallographer for a loop. This compound does, of course, consist of Cp^*ReO_3 molecules, and in the twinned/disordered arrangement it looks superficially as though $(Cp^*ReO_3Re)_\infty$ chains exist, corresponding to a composition of $Cp^*Re_2O_3$. However, because the latter formula requires twice as many Re atoms as are actually there, each Re site had to be refined at half occupancy.

It then occurred to us to go back and make sure that this was also the case for the Tc atoms. We were flabbergasted to find that it *was not*. The Tc atoms had been refined perfectly well at full occupancy.

So, here is the O'Henry ending to the story. The fact that Tc atoms could refine quite well as full atoms, even though each Tc site had only half an atom, could mean only one thing: *The "Tc" atoms were not Tc atoms*. We then noted that the unit cell dimensions for "$Cp^*Re_2O_3$" and "$Cp^*Tc_2O_3$" were not merely similar, as expected for isomorphous Re and Tc compounds. They were identical! Moreover, the infrared bands assigned to M−O stretching vibrations in the "two" compounds were identical to within ±1 cm^{-1}, which could not possibly be true for MO_3 and $M'O_3$ groups with metal atoms differing by a factor of ca. 2 in mass. Finally, we took note of the fact that the Re atom has very nearly twice the X-ray scattering power of the Tc atom.

It then became inescapable that not only does the compound "$Cp^*Tc_2O_3$" not exist, neither does a Tc analogue to Cp^*ReO_3 exist. That would explain why even skilled preparative chemists could not repeat the reported preparation of "$Cp^*Tc_2O_3$", and could not make Cp^*TcO_3 either. The latter had, presumably never been made in the first place, at least not in crystalline

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(38) Kanellakopulos, B.; Nuber, B.; Raptis, K.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1055.

(39) Klahn-Olwa, H.; Sutton, D. *Organometallics* **1984**, *3*, 1313. Herrmann, W. A.; Serrano, R.; Bock, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 383.

(40) Burrell, A. K.; Cotton, F. A.; Daniels, L. M.; Petricek, V. *Inorg. Chem.* **1995**, *34*, 4253.

form. Very likely it had never been made at all, in any form. Rather, some unfortunate (or careless) person began the entire synthetic sequence with $Re_2(CO)_{10}$ rather than $Tc_2(CO)_{10}$. With regard to Tc−Tc bonds, the shortest one yet reported[41] to exist is still the one in $K_2Tc_2Cl_6$, 2.045 Å.

Acknowledgment. The work described here was supported by the National Science Foundation, The Robert A. Welch Foundation, and Texas A&M University. I am grateful to several colleagues, in particular Prof. Carlos A. Murillo and Drs. Isabel Pascual and Evgeny Dikarev for help with the preparation of this article.

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