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# AN ACCOUNT OF STUDIES INTO HYDRIDO-METAL COMPLEXES AND CLUSTER COMPOUNDS

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The path which led my co-workers and me into studies of the title compounds began with our investigations into the synthesis and chemical properties of technetium carbonyl [1].

In my initial year at UCLA starting in the summer of 1960, I was fortunate to be approached by Jack Hileman who was on sabbatical leave from El Camino College, Torrance, California. Jack was interested in carrying out some inorganic syntheses and I recommended to him the metal carbonyls. After he had completed some trial runs we learned that weighable quantities of technetium had become available at an affordable cost from the Oak Ridge National Laboratories [2]; the cost which was near $ 17,000/gram before March 1959 [3] and something like $ 1600 to $ 2800/gram after March 1959, had just dropped to $ 100/gram (as $NH_4TcO_4$).

This provided Jack an opportunity to apply his newly won skills to a problem in research since the carbonyl of technetium had as yet not been reported. Twenty years earlier, $Re_2(CO)_{10}$ had been obtained by Professor W. Hieber and H. Fuchs in Munich [4] through the fetchingly simple reaction of $Re_2O_7$ with CO under pressure and elevated temperature. By contrast, the carbonyl of the lighter congener, $Mn_2(CO)_{10}$, was much more difficult to prepare. Its synthesis had been achieved in quantities sufficient for characterization (in about 1% yield in the reaction of $MnI_2$ with Mg under CO pressure) only a few years earlier [5].

Although technetium-99 is a beta emitter (0.29 meV, $t_{1/2} = 2.12 \times 10^5$ y) its radioactivity is safely contained by the walls of normal pyrex laboratory ware. Direct contamination was still a danger, however, because of the general toxicity of the metal carbonyls we were already working under conditions where they were rigorously confined within the chemical apparatus. Radioactivity in the laboratory was monitored by a Geiger counter equipped with very thin (2 mg) windows made available to us by Professor C.S. Garner of UCLA.

The chemistry of technetium is more like that of rhenium than that of manganese [3]. The ammonium pertechnetate obtained from Oak Ridge was thus pyrolyzed at 400°C and under an atmosphere of dry oxygen at 600°C converted into the pale yellow heptoxide. This proved to be easily convertible into the carbonyl, $Tc_2(CO)_{10}$, at 220°C under 5,000 PSI CO pressure. Our first char-

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acterization was by infrared spectra in the carbonyl stretching region; cyclohexane solution showed a three band pattern [1a], analogous to but not superimposable with the three principal absorptions evidenced each for $Re_2(CO)_{10}$ [4] and $Mn_2(CO)_{10}$ [5].

Recognizing our debt to Professor Hieber for his pioneering work on $Re_2(CO)_{10}$ we wrote to him of our results in June 1961 sending a preprint of the manuscript we had submitted to the Journal of the American Chemical Society. Not surprisingly it turned out that Professor Hieber had also been pursuing the synthesis of $Tc_2(CO)_{10}$ but because of the unavailability to him of weighable quantities of this element he had followed its synthesis by radioactive tracer techniques. He and Herget, like we, found that it followed closely the preparative conditions suitable for $Re_2(CO)_{10}$. Shortly after the arrival of my letter a rapid communication emanated from Munich which cordially acknowledged our parallel studies [1b]. Through these exchanged courtesies an amicable relationship developed between our two laboratories. Many capable postdoctoral fellows * came to Los Angeles from Munich in the years following, including students of Professor E.O. Fischer who also shared an interest in the organometallic chemistry of technetium [6].

Among various aspects of the chemistry of $Tc_2(CO)_{10}$ which we investigated [7] those pertinent to this account were our attempts to make the hydrido complex $HTc(CO)_5$. The synthesis of this derivative could be anticipated through a reduction of the carbonyl with sodium followed by acidification, parallel to the synthesis of $HRe(CO)_5$ [8]. Our earliest experiments along these lines proved disappointing because only the merest traces of a volatile carbonyl, identifiable as $HTc(CO)_5$ through its carbonyl stretching absorptions, could be obtained after acidification. Further down I will discuss our assignment of molecular geometry of the pentacarbonyl hydrides of this sub-group based on their terminal carbonyl infrared absorptions. For the moment however, we wondered whether other carbonyl products had been formed in the two step sequence. We examined the residues by extraction with cyclohexane and in these solutions found a substance giving four absorptions in the carbonyl stretching region not unlike those of the *cis*-tetracarbonyl halides we had been examining for technetium and its congeners [7,9]. We wondered whether this material could be a tetracarbonyl hydroxy-dimer but further experiments established a trimeric molecular weight with analytical data for no heavy atoms other than $Tc_3(CO)_{12}$. We reported these results in preliminary fashion in September 1962 at a Symposium on Organometallic Compounds which was organized by H.C. Clark in Vancouver, Canada ** [10].

In the tetracarbonyl trimer we had a difficult problem. Through the Evans method using $^1H$ NMR [11] we knew the compound was diamagnetic. Thus it had to contain other atom(s) which were undetectable by the standard gravimetric methods of analysis. The principal candidate of course was hydrogen; one hydrogen in the technetium tetracarbonyl trimer would account for only

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* In this group were G. Bürger, B. Deubzer, W. Fellmann, H. Brunner, A. Maasböl, C.G. Kreiter and R. Aumann. The latter three were co-sponsored by my eminent colleague at UCLA the late S. Winstein.

** Many recognize this meeting to be the direct precursor for the series of International Conferences on Organometallic Chemistry which in September 1979 at Dijon, France celebrated its IXth biannual gathering.

0.16% by weight. We needed larger quantities of this material to attempt its complete characterization, which, for technetium, would be hampered by its radioactivity and its cost. Thus we set out to synthesize the analogous rhenium and manganese compounds and happened upon a polynuclear chemistry that was rich beyond our expectations.

I shall describe our research into the polynuclear derivatives presently. I believe, however, it would first be appropriate to give an account of our spectroscopic studies of the pentacarbonyl halides and hydrides of this sub-group and their structural implications. The principal belief for the structure of the hydrido-metal carbonyls held at that time was that their coordination geometry was determined by the carbonyl groups and that the hydrogen atom(s) occupied an interstitial position, either face or edge bridging in the complex. Earlier electron diffraction studies for $HCo(CO)_4$ and $H_2Fe(CO)_4$ had indicated complexes of tetrahedral geometry [12a] but these were pre-electronic computer analyses in which the observed radial distribution curves could be tested against only a limited number of models.

Structures for $HMn(CO)_5$ with carbonyl groups occupying trigonal bipyramidal [13a] or possibly square pyramidal [13b] positions around the manganese atom were assigned on the basis of infrared studies. Further developments, however challenged and eventually dismissed the ideas that terminally bound hydrogen must be relegated to an "interstitial" position on the coordination sphere of a mononuclear complex. The first of these developments were X-ray structure determinations for newly discovered hydrido-metal complexes $HPt(Br)(PEt_3)_2$ [14a] and $HOs(Br)(CO)(PPh_3)_2$ [14b]. The hydrogen atom was not located in these studies, however, its position could be inferred from that of the other ligands bonded to the metal atom. These clearly indicated a "vacant" coordination site which was correctly * assumed to be occupied by hydrogen. The surrounding ligands were bent slightly towards the "vacant" site which was understood to result from the greater steric interaction of these ligands with each other than with the hydrogen atom **.

At the same time, infrared studies on the pentacarbonyl halides, whose geometry was unquestionably octahedral or near-octahedral, revealed a most interesting feature in their carbonyl stretching absorptions. Reports varied in the number of principal bands: some containing three while others contained only two. Analysis of the spectra of this group of complexes by M.A. El-Sayed at UCLA [15a] and concurrently by L.E. Orgel at Cambridge [15b] pointed out that in octahedral geometry co-planarity of the four radial carbonyl groups leads to cancellation in the $A_1$ (radial) mode of their oscillating dipoles and therefore cancellation in its intensity. Through mixing of $A_1$ (radial) mode with the $A_1$ (axial) mode and/or through departure of the four radial groups from co-planarity, the $A_1$ (radial) absorption could gain intensity. In the pentacarbonyl iodides, for instance, the high energy $A_1$ (radial) band is quite prominent but in the pentacarbonyl halides it is vanishingly weak [15a]. Armed with this insight and with the knowledge from the above-mentioned X-ray structure

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* Future developments in which hydrogen was located by difference X-ray methods and/or by neutron diffraction studies in other if not in these two specific examples have fully justified these conclusions [14c].

** The same state of affairs prevails in the complexes $HCo(CO)_4$ and $H_2Fe(CO)_4$, as indicated in a rece redetermination by electron diffraction of their structures [12b].

determinations [14a,b] that hydrogen could occupy a coordination position in its own right around a transition metal atom, Dale Huggins (my first graduate student) suggested in his Dissertation in 1963 [16] that the carbonyl stretching absorptions of the pentacarbonyl hydrides, consisting of one medium, one strong and one vanishingly weak absorption at high energy (at 2118 $cm^{-1}$ for instance in $HMn(CO)_5$), are perfectly consistent with octahedral geometry ($C_{4v}$ symmetry) for these derivatives. Not long thereafter the X-ray structure determination of $HMn(CO)_5$ was reported [17a,b], confirming this geometry. The radial groups in $HMn(CO)_5$ are not co-planar but bent some 6 or 7° away from the normal towards the inferred position of the hydrogen atom (which was located in a later study [17c]).

With our attentions thus directed towards the infrared absorptions in the carbonyl stretching region we were inevitably drawn to a more complete study to assign the minor peaks attributed to $^{13}CO$ absorptions and to examine the relative intensities of the bands for insight into geometry of these derivatives [18,19,20]. For $HMn(CO)_5$ for instance we obtained a surprisingly good agreement for a calculated angle of 96° between the axial and radial CO groups compared to the average of 97° found in the structure determination [17]. For other derivatives such as $Mn_2(CO)_{10}$ and the pentacarbonyl halides the agreement is not as good indicating some caution should be exercised in regard to the underlying assumptions [21]. Despite these limitations such methods have found usefulness for first approximation determinations of the geometry of carbonyl species which can be formed and studied only under matrix isolation [22].

Another interesting feature noted in our studies of the hydrido- and deuterio-pentacarbonyls [19] and in concurrent studies of other hydrido- and deuterio-metal complexes by Vaska [23] is the shift of certain carbonyl absorptions upon deuteration, arising from the coupling of metal—hydrogen and carbonyl stretching modes. In the pentacarbonyl hydrides $\nu(M{-}H)$ is found below the carbonyl stretching region ($cm^{-1}$): $\nu(Mn{-}H)$ 1775 ($\nu(Mn{-}D)$ 1285), $\nu(Re{-}H)$ 1882 ($\nu(Re{-}D)$ 1313) [18,19]. Deuteration in these derivatives produces a shift to lower energy in the $A_1$ (axial) carbonyl absorption and its $^{13}C$ satellite [19]. The explanation for this is shown schematically in Fig. 1. When the metal—hydrogen mode is lower in energy than the carbonyl stretching mode, mixing between these two species leads to a higher energy position of the absorption which is principally the carbonyl stretch. Correspondingly, the mode which is principally the metal—hydrogen stretch is shifted to lower energy. In the deuterated derivative the carbonyl and the metal—deuterium stretching modes are separated further in energy and their interaction is thus reduced. This causes the absorption representing principally the carbonyl stretch to appear at lower energy than in the hydrido derivative. The effect is larger on rhenium ($\Delta\nu(CO) \simeq -5$ $cm^{-1}$) than on manganese ($\Delta\nu(CO) \simeq -1$ $cm^{-1}$), in part because $\nu(Re{-}H)$ is closer to the carbonyl region than is $\nu(Mn{-}H)$ (see above). A much larger effect was observed by Vaska ($\Delta\nu(CO) = -32$ $cm^{-1}$) in deuteration of *cis*-$H_2Os(CO)$*mer*-$(PPh_3)_3$ [23] even though $\nu(CO) = 1950$ and $\nu(MH)$ (*trans* to CO) = 1852 $cm^{-1}$ are comparable to the separation of the corresponding modes in $HRe(CO)_5$; a greater electron density on the metal atom due to the presence of phosphine ligands in the osmium

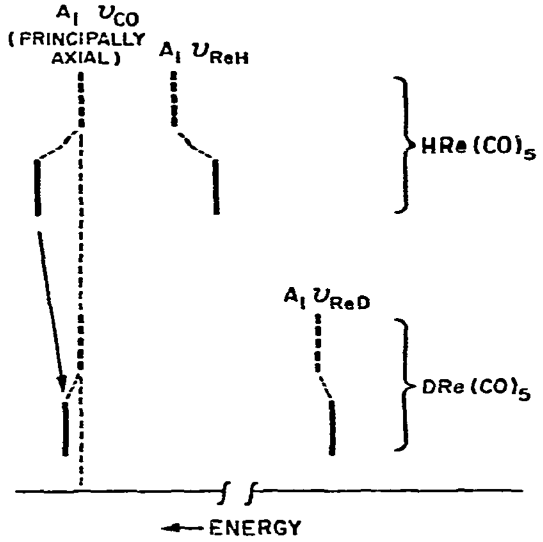


Fig. 1. Representation of observed shift of $A_1$ (principally axial) carbonyl stretching absorption in deuteration of HRe(CO)$_5$. Taken from ref. 19; reproduced with permission.

derivative might account for the greater coupling. By similar arguments it may be seen that deuterium substitution will cause carbonyl absorptions to shift to higher energy if $\nu$(M—H) is higher in energy than $\nu$(CO). This is seen in *trans*-HRh(CO)(PPh$_3$)$_3$ where $\nu$(Rh—H) = 2041, $\nu$(CO) = 1923 cm$^{-1}$ and $\Delta\nu$(CO) = +32 cm$^{-1}$ going to the deuterated derivative [23]. Further examples of this resonance effect are given in reference 24d, pp, 273—274. Paul Braterman, who was a postdoctoral fellow at UCLA jointly with M.A. El-Sayed and myself and who collaborated in our infrared studies, went on to write a most useful monograph in this field [25].

Returning to our work on the polynuclear derivatives, we were interested as explained above to obtain derivatives of rhenium and manganese analogous to the trimer of technetium which we had isolated as a by-product of our synthesis of HTc(CO)$_5$. The first attempts began with the reduction of Re$_2$(CO)$_{10}$ by sodium amalgam in tetrahydrofuran under reflux (to assist the formation of tetracarbonyl derivatives); the yields however were low. Since there had been reports of the action of NaBH$_4$ on Mn$_2$(CO)$_{10}$ [26a] or Fe(CO)$_5$ [26b], we were prompted to try NaBH$_4$ as the reducing agent in place of Na/Hg. After suitable work-up we obtained the desired product, first reported as Re$_3$(CO)$_{12}$H$_n$, in 46% yield based on Re$_2$(CO)$_{10}$ [27]. We confirmed its molecular weight as a trimer by careful osmometric measurements and its diamagnetism by bulk susceptibility studies [27b] but due to its low solubility we were unable on our existing 60 MHz spectrometer to observe its $^1$H NMR. This was later accomplished by B. Fontal using a 100 MHz instrument equipped with variable temperature probe for a sample dissolved in acetonitrile saturated at 70°C: $\tau$ = 27.1 ppm [28]. The presence of three hydrogen atoms per molecule was determined by high resolution mass spectrometry [29]. We were not then nor have we been able since to obtain suitable single crystals of the rhenium trimer for an X-ray study. B. Fontal, however, isolated single crystals of the salts of two conjugate base anions $[Ph_4As][H_2Re_3(CO)_{12}]$ and $[Ph_4As]_2[HRe_3(CO)_{12}]$ [28]. The structure of each of these two salts were determined [30 and 31, respectively] but the hydrogen atoms were not located directly. The position of these, each bridging along respective edges of the metal triangles, was inferred through indirect evidence: hydrogen-bridged edges appear lengthened by about 0.15 Å and carbonyl groups adjacent to such edges in the plane containing the metal triangle are bent away from the hydrogen-bridged edge by some ten of fifteen degrees [30,31]. Spectroscopic studies of these and related derivatives [24d,31b,32] revealed hydrogen absorptions more prominently in the Raman than in the infrared which were considerably broadened ($\Delta\nu_{1/2} \sim 110\ cm^{-1}$) and shifted to lower energy ($\Delta\nu \sim 1000\ cm^{-1}$) from their appearance and position in hydrido-metal complexes where the hydrogen atoms were terminally bounded. This provided important corroborating evidence for the assignment of cluster-bonded hydrogen to edge-bridging positions which could only be inferred indirectly in the early X-ray studies. Thus the "interstitial" position for hydrogen had returned in the hydrido-metal clusters after having first been assigned and then discarded for the mono-nuclear hydrido-metal complexes as recounted above. Later structure studies showed that when another atom or group of atoms bridge the two metal atoms also bridged by hydrogen, the effect on the metal—metal separation is dominated by the stereochemical requirements of the bridging unit other than hydrogen [33]. In such cases bond angles might still indicate the position of hydrogen. Modern studies using low temperature X-ray data and difference methods however now lead to almost routine location of hydrogen [14c].

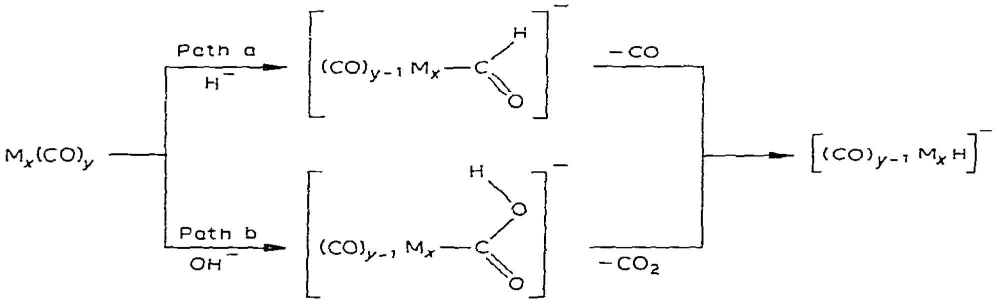
Fontal's studies [23] led to other discoveries. In the first place he showed that the monoanion $[H_2Re_3(CO)_{12}]^-$ could be obtained from the neutral derivative by deprotonation with mild bases [28]; $pK_a$ of $H_3Re_3(CO)_{12} \simeq 3.5 \pm 0.5$ while that of $[H_2Re_3(CO)_{12}]^-$ was estimated to be between 10 and 18. Thus bases strong enough to deprotonate the monoanion would also be strong enough to cause further degradation. A suitable salt of the dianion $[HRe_3(CO)_{12}]^{2-}$ could only be obtained by precipitation from the solution obtained in the reduction step [28]. Fontal's studies showed that these solutions were quite complex; after acidification, $^1H$ NMR contains some fifteen high-field resonances attributable to hydrido-metal species. By varying the conditions of the reduction and also the nature of the added cation, Fontal selectively precipitated other species such as $[n\text{-}Bu_4N]_2[Re_4(CO)_{16}]$ and $[Ph_4As]_2$-$[H_6Re_4(CO)_{12}]$ [28]. The structures of these were determined [34,31b,35]. The hydrogen atoms in the $[H_6Re_4(CO)_{12}]^{2-}$ dianion were not located. Six in number were determined by internal calibration against the $^1H$ NMR signal of the cation. A bridging position of the hydrogen atoms was inferred (one each on the six edges of the tetrahedron) from the elongation of the metal—metal separations: these average to 3.160(7) Å compared to 3.02 Å in $Re_2(CO)_{10}$. The bridging positions for the hydrogen atoms is confirmed by the broadness ($\Delta\nu_{1/2} \sim 110\ cm^{-1}$) and shift to lower energy ($\Delta\nu_{1/2} \sim 110\ cm^{-1}$) of the hydrogen absorptions in the Raman [31b,35]. The structure of the dianion is to play an important role in contrasting with another hydrido-tetrarhenium cluster in which face-bridging hydrogen was found, see below.

Open chain rather than triangular or polyhedral complexes were obtained by us when salts of pentacarbonyl anions $[Re(CO)_5]^-$ or $[Mn(CO)_5]^-$ were combined into the "tetracarbonyl" anion mix before acidification. Thus W. Fellmann isolated $HRe_3(CO)_{14}$ [36] and $HRe_2Mn(CO)_{14}$, whose structure was determined [37]. Later, the structure of the trirhenium complex was also completed [38]. These and the $[HM_2(CO)_{10}]^{2-}$, M = Cr, Mo or W, dianions [39] were the first examples of complexes containing metal moieties linked solely through a hydrogen-bridged metal—metal bond; the hydrogen position was first inferred and then located by neutron diffraction (see account in ref. 39c). The trinuclear species was shown easily to react with carbon monoxide at ambient pressure and temperature according to equation 1 [40].

$$HRe_3(CO)_{14} + CO \rightarrow HRe(CO)_5 + Re_2(CO)_{10} \qquad (1)$$

With $^{13}CO$, stereospecific radially $^{13}CO$-labelled $Re_2(CO)_{10}$ is the product. The microscopic reverse of this reaction was later achieved by Shapley and co-workers [41] in the reaction of $HRe(CO)_5$ with osmium carbonyl clusters containing easily displaceable ligands i.e. $Os_3(CO)_{12-x}S_x$ ($x = 1$ or 2, S = cyclooctene or acetonitrile) to give complexes of the overall formula $HReOs_3(CO)_{16}$ or $H_2Re_2Os_3(CO)_{20}$. The $Re(CO)_5$ groups in these compounds are coplanar with the $Os_3$ and attached to it by metal—metal bonds; the hydrogen atoms are believed to be edge-bridging on the $Os_3$ triangle.

Parallel to our studies on rhenium were some with di-manganese decacarbonyl; reduction of the latter with $NaBH_4$ under refluxing THF followed by acidification leads to $H_3Mn_3(CO)_{12}$ [42a] and the novel $HMn_3(B_2H_6)(CO)_{10}$ [42a,43]. The latter is the principal product while $H_3Mn_3(CO)_{12}$ is obtained in only very low yields. This trimer however is accessible by two other routes: E.O. Fischer and R. Aumann obtained it in the reduction of $CH_3Mn(CO)_5$ with $NaBH_4$ followed by acidification [42b] while the Cambridge group obtained it by treatment of $Mn_2(CO)_{10}$ with alcoholic KOH also followed by acidification [42c]. The latter method gives very good yields. The degradation of carbonyls by hydride and by hydroxide paths may well share common mechanistic paths and thus lead to the same products. If nucleophilic attack at carbon of coordinated CO is a common starting point, the hydridic path may lead to CO evolution by hydride migration, path (a), reaction 2. The hydroxylic path, with an intermediate containing hydrogen in a $\beta$ position to the metal, may involve elimination of $CO_2$ leading to the same lower carbonyl species, path (b).



(2)

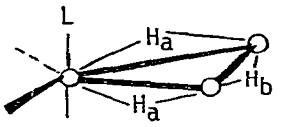
Single crystals of $H_3Mn_3(CO)_{12}$ were elusive, but unlike those of $H_3Re_3$-

$(CO)_{12}$ which remain so, were finally obtained through a collaborative effort by two of my former students [42d]; the hydrogen atoms were located using difference Fourier techniques based on a low angle data. The hydrogen atoms are coplanar with the manganese triangle, each hydrogen symmetrically bridging an edge of that triangle. The metal—metal separations average to 3.111(2) Å, lengthened by some 0.19 Å over that found in $Mn_2(CO)_{10}$ [42d].

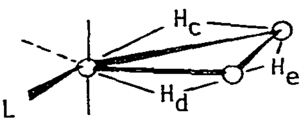
Our interests have temporarily led us away from the carbonyl anion mixtures but as indicated in the work of B. Fontal [28] discussed above, these must contain many interesting species other than those isolated thus far. Starting from the reduction of $Re_2(CO)_{10}$ by alcoholic base, M. Freni and co-workers in Milan have isolated still different polynuclear derivatives [44a,b] as well as new salts of two anions previously isolated by us $[NEt_4]_2[HRe_3(CO)_{12}]$ and $[NEt_4]_2$-$[Re_4(CO)_{16}]$; the structures of these have been determined [44c] resulting in molecular parameters not varying significantly from those determined earlier for our analogous derivatives.

We briefly extended the chemistry of the trinuclear dianion $[HRe_3(CO)_{12}]^{2-}$ by combining a suitable salt of it with $Me_2SnCl_2$; the heterometal complex $HRe_2(SnMe_2)(CO)_{12}$ was obtained [31b] and its structure determined [45]. The $Me_2Sn$ group is asymmetrically attached to one edge of the $Re_3$ triangle (Re—Sn = 2.68 and 2.87 Å) with the longer separation to the rhenium atom of the edge to which the hydrogen atom is presumed to be bridging (Re—(H)—Re = 3.23 Å) [45]. Such mixed metal cluster complexes may have importance not only in their own right but also as precursors for alloy catalysts [46a,b] using methods by which cluster compounds have been converted into metal crystallites on catalyst supports [46c,d].

Our work next took a dramatic turn in what began as a straightforward investigation into phosphine substituted derivatives of $H_3Re_3(CO)_{12}$. We were interested to investigate these to see whether chemical shift differences for hydrogen and its coupling to $^{31}P$ could be of assistance in assigning stereochemistry. This in fact proved to be the case [45b,47] as we could separate axially and radially mono-substituted derivatives and assign these on the basis of the high-field $^1H$ NMR [45b,47].

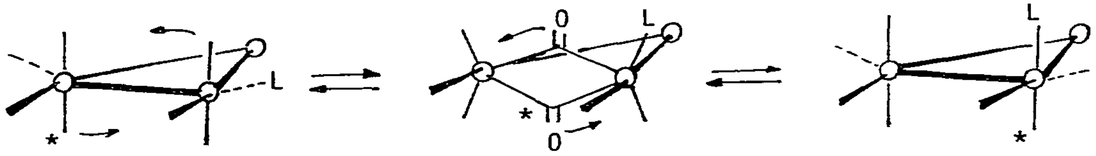


$H_3Re_3(CO)_{11}L$(axial)



$H_3Re_3(CO)_{11}L$(radial)

The isomeric mixture does not equilibrate on the NMR time scale. Kinetics for interconversion however could be followed by growth of the signals for the radial isomer in an isolated sample of the axial isomer. Activation parameters for the interconversion of $H_3Re_3(CO)_{11}L$ axial to radial were on the order of $25 \pm 1$ kcal $mol^{-1}$ for L = $PPh_3$, $PEt_3$ or $P(OMe)_3$ [47]. These barriers are considerably higher than observed for rearrangements in the isoelectronic $M_3(CO)_{12}$ clusters of the iron sub-group; for M = Fe, $\Delta G^{\ddagger} < 5$ kcal $mol^{-1}$ [48a] while for M = Os, $\Delta G^{\ddagger} \sim 13$ kcal $mol^{-1}$ [48b,c]. These differences indicate either that isomerization follows different pathways or, if a common path is followed, structures of the type postulated for the interconversion of the $M_3(CO)_{12}$ isomers which involve double-edge bridging carbonyl groups are



much less accessible in the hydrogen-bridged tri-rhenium complexes. The trend in activation energies follows the trend of inter-metal separations: Fe—Fe in $Fe_3(CO)_{12}$ = 2.6 Å [49a]; Os—Os in $Os_3(CO)_{12}$ = 2.8 Å [49b] while Re—H—Re in $H_3Re_3(CO)_{12}$ = 3.2 Å as might be expected from distances observed in the structures of the conjugate base anions (see above).

While these results were interesting in their own right they were not the dramatic turn of events which I mentioned above. This came about during our very first attempts to make the substituted derivatives of $H_3Re_3(CO)_{12}$. We chose to follow the reaction by monitoring the carbonyl stretching region in the infrared, a common practice. A reaction mixture was supposedly put together in hydrocarbon solution and heating begun. Hours passed and there were no apparent changes in the carbonyl stretching region over temperature regions up to 110° C. This was surprising but nevertheless solvent was exchanged for a higher boiling material and heating was continued. To our surprise it was necessary to reach a temperature of 190° C (in decalin) before we noticed a change in the infrared accompanied by a deep red coloration of the solution. Upon cooling and work-up a red product was isolated whose full-length IR showed no traces of $PPh_3$! A retrospective analysis indicated that the $PPh_3$ had been omitted from the reaction mixture and that we had inadvertently carried out the pyrolysis of $H_3Re_3(CO)_{12}$ in hydrocarbon solution. This was a most happy accident since the product isolated proved to be $H_4Re_4(CO)_{12}$, a most interesting material [50]. The molecular formula including the presence of four hydrogen atoms was determined by high resolution mass spectrometry. By count of 56 valence electrons we realized we had an electronically unsaturated cluster since the count for a saturated (electron precise) * tetrahedral cluster would be 60 [51].

A two band pattern in the carbonyl stretching region indicated $T_d$ symmetry for $H_4Re_4(CO)_{12}$ like that observed for the $[H_6Re_4(CO)_{12}]^{2-}$ dianion mentioned above. The four hydrogen atoms in $H_4Re_4(CO)_{12}$ were thus required to be in positions where they would maintain the molecular symmetry, either terminally bonded one on each metal on an axis of symmetry or face-bridging. A sample of $D_4Re_4(CO)_{12}$ was prepared and its infrared spectrum scanned in comparison with that of $H_4Re_4(CO)_{12}$; it would have been better to be able to obtain a Raman scan however due to the red color of the compound, this was not possible on the spectrophotometer available to us. In the infrared no bands characteristic of a terminal Re—H (or Re—D) could be observed and the

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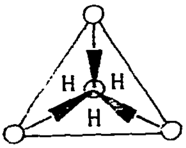
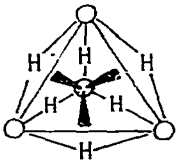
* Electron precise is a term used to designate a polyhedral cluster where an electron-pair bond may be associated with each polyhedral edge joining the atoms in the cluster.

bridging modes (if any) were too weak to be seen. This behavior strongly suggested a bridging position for each of the hydrogen atoms. This was later confirmed by a structure study using a clever signal-averaging technique for Fourier difference maps related by symmetry [52]. A further interesting feature of this structure was found in the configuration of the carbonyl groups. These proved to be eclipsed with the edges of the tetrahedron while in $[H_6Re_4(CO)_{12}]^{2-}$ a 60 electron species with hydrogen atoms bridging the edges, the carbonyl groups were staggered with respect to these edges. These structural features were successfully related to the different electron count in these species by Hoffmann and Schilling [53]. In this treatment, the frontier orbitals of the cluster are constructed by overlap of the appropriate lobes of the $M(CO)_3$ fragments. There are three lobes on each fragment that are available for cluster bonding. These are disposed in a staggered conformation with respect to the three terminally-bonded CO groups, reminiscent of the parent octahedral $M(CO)_6$ complex from which the $M(CO)_3$ fragments are taken to be derived. In the cluster in which the carbonyl groups are staggered with respect to the edges, the metal—metal bonding takes place over the edges giving rise to an ordering of $t_2$, $e$, and $a_1$ orbitals (in increasing energy) for the six bonding cluster orbitals. In a tetrahedron where the carbonyl groups are eclipsed with the edges, metal—metal bonding takes place over the faces. In these the energy ordering is found to be $t_2$, $a_1$ and $e$ (in increasing energy). In this configuration the $t_2$ orbitals are more deeply stabilized but the $e$ set descending from the anti-bonding $e$ orbitals of the localized three-center interactions on each face are found to be higher lying than the $a_1$ orbital of the staggered conformation [53]. Thus one can see why a 56 electron cluster like $H_4Re_4(CO)_{12}$ would prefer the eclipsed configuration leaving empty the higher lying $e$ orbitals. Another difference between these species is seen in the $^1H$ NMR; the chemical shift of the bridging hydrogens in $[H_6Re_4(CO)_{12}]^{2-}$ is at $\tau = 27.4$ ppm while that for $H_4Re_4(CO)_{12}$ is at $\tau = 15.1$ ppm, anomalously low for a cluster-bonded hydrogen [24d]. Undoubtedly the unsaturated nature of the latter reflected by the empty $e$ orbitals near the occupied levels plays a role in this observation.



$H_4Re_4(CO)_{12}$ (eclipsed)



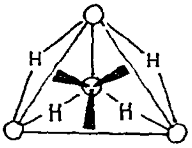
$[H_6Re_4(CO)_{12}]^{2-}$ (staggered)

Treatment of $H_4Re_4(CO)_{12}$ with $NaBH_4$ leads to $[H_6Re_4(CO)_{12}]^{2-}$ [50]. This reaction must be carried out heterogeneously with the cluster in a hydrocarbon solvent; solvents with donor power as also donor ligands lead to fragmentation of the cluster [50]. The reaction of $H_4Re_4(CO)_{12}$ with CO is particularly significant. This is summarized in equation 3. As in the case of $HRe_3(CO)_{14}$ (reaction 1, above) this occurs at ambient conditions; $H_3Re_3(CO)_{12}$ and

$$\begin{array}{llr} H_4Re_4(CO)_{12} + 5\ CO \xrightarrow[\text{room temp}]{\text{1 atm}} H_3Re_3(CO)_{12} + & HRe(CO)_5 & (3) \\ & \downarrow & \\ & 1/2\ H_2 + 1/2\ Re_2(CO)_{10} & \end{array}$$

$HRe(CO)_5$ are the initial products [50]. With heating the latter is converted into hydrogen gas and $Re_2(CO)_{10}$. We had thus found a path connecting $Re_2(CO)_{10}$ to hydrido-metal clusters and we wondered whether we could find conditions for its reverse: this would give us a facile route to the hydrido-metal clusters starting from $Re_2(CO)_{10}$. Indeed this proved to be the case as we observed formation first of $H_3Re_3(CO)_{12}$ and then $H_4Re_4(CO)_{12}$ by bubbling $H_2$ gas through a solution of $Re_2(CO)_{10}$ in refluxing hydrocarbon [54]. Investigation of other metal carbonyls in rapid succession showed this reaction to be extremely useful in high yield syntheses of $H_4Ru_4(CO)_{12}$ starting from $Ru_3(CO)_{12}$ starting from $Ru_3(CO)_{12}$ and $H_2Os_3(CO)_{10}$ and $H_4Os_4(CO)_{12}$ starting from $Os_3(CO)_{12}$ [54].

The high yield synthesis of $H_4Ru_4(CO)_{12}$ permitted us to purify a sample through crystallization from the reaction mixture. We confirmed its molecular formula through high-resolution mass spectrometry. Its infrared absorptions in the carbonyl region showed five maxima, indicating a structure of $D_{2d}$ symmetry. Such a symmetry requires the hydrogen atoms to be bridging four of the six edges [54]. This was confirmed by X-ray study [55]. In this study the carbonyl groups were found to be staggered with respect to the tetrahedral edges as in $[H_6Re_4(CO)_{12}]^{2-}$, both 60 electron cluster species.



$H_4Ru_4(CO)_{12}$ $D_{2d}$

The existence of isomeric structures for $H_4M_4$ polyhedra naturally led us to wonder whether there could be facile exchange among such isomers. In such an exchange, we could envisage that the ground state structure observed for one would serve as the transition state for intramolecular tautomerism in the other, much the same as the roles that all-terminal and edge doubly-bridged structures are believed to play in the rapid intramolecular tautomerism observed for the irongroup trimetal dodecacarbonyls (discussed above). We thus synthesized $P(OMe)_3$ substituted derivatives of $H_4Ru_4(CO)_{12}$ and $H_2Ru_4(CO)_{13}$ and showed through $^1H$ NMR that the hydrogen atoms were engaged in rapid intramolecular tautomerism [56]. The activation energies were found to be in the range of 3 t to 8 kcal $mol^{-1}$, with signals of the limiting structures frozen out at around −80°C for all but the symmetric $H_4Ru_4(CO)_8L_4$. These studies did not permit us to specify a pathway for the interchange, i.e. whether face-bridging species played a part, however, the theoretical studies by Hoffmann and Schilling indicate there is very little energy difference between face- or edge-bridging in the 60 electron tetrahedral structure [53].

A similar facile tautomerism is observed for the anion $[H_3Ru_4(CO)_{12}]^-$ obtained by deprotonation of the neutral parent compound [57]. For this anion, two interconverting structures one of $C_{3v}$ and one of $C_2$ symmetry were indicated by the low temperature limiting spectra [57]. The anion $[H_3Ru_4(CO)_{12}]^-$ has recently been identified as a principal constituent of a water-gas shift catalyst-system obtained from $Ru_3(CO)_{12}$ in alkaline aqueous media [58].

Yet another placement of the hydrogens on a neutral 60 electron cluster has recently been observed by Shapley and Churchill in $H_4Ru_4(CO)_{10}(Ph_2PCH_2CH_2PPh_2)$ [59]. The phosphine is chelated to one metal and presumably the increase in the basicity of this metal as a result of this has drawn three of the hydrogen atoms (as protons): one each to the three edges by which the substituted metal is attached to the other metal atoms. The remaining hydrogen atom is found bridging an edge on the triangle composed of these three metal atoms [59]. In this derivative the resonances of three of the hydrogen atoms are observed to coalesce while the resonance of the fourth hydrogen remains unchanged; an exchange path traversing structures containing terminally bonded hydrogen atoms is proposed [59].

The Schilling Hoffmann treatment [53] indicates a higher energy difference between face and edge bridging in the 56 electron clusters. Indeed this is observed in $H_4Re_4(CO)_{11}PPh_3$ [60]. This derivative could not be obtained in the treatment of $H_4Re_4(CO)_{12}$ with $PPh_3$ as fragmentation of the cluster is observed under these conditions [50]. The substituted derivative could, however, be obtained by treatment of $Re_2(CO)_9L$ with $H_2$ [60]. Some $H_4Re_4(CO)_{12}$ is also produced but owing to the delicate nature of these tetrahedral clusters the usual chromatographic separations could not be undertaken. Nevertheless, the $^1H$ NMR of the mixture clearly shows limiting signals for $H_4Re_4(CO)_{11}PPh_3$ at —29° C with coalescence of the peaks of three of the hydrogen atoms at 80° C with the resonance of the fourth hydrogen remaining unchanged [60]. A much higher barrier for rearrangement is thus indicated in keeping with the theoretical treatment [53].

Our desire to investigate tautomerism in other hydrido-metal clusters led us to phosphite substituted derivatives of the mixed metal complex $HFeCo_3(CO)_{12-x}L_x$, $L = P(OMe)_3$, $x = 1, 2, 3$ and 4 [61]. We were unable to see the hydrogen resonance in any of these and thus embarked on a structure determination for the trisubstituted derivative making use of the low-temperature capability which my colleague C.E. Strouse had built for the diffractometer at UCLA [62]. The hydrogen atom was located by Fourier difference maps using a low angle portion of the data set. The hydrogen atoms is found to be bridging the tri-cobalt face some 0.75 Å away from the plane containing the metal atoms and outside the cluster [61]. In a parallel and independent neutron diffraction study [63] these results were confirmed yielding an average Co—H distance of 1.734(7) Å, slightly longer than the average distance of 1.63(15) Å obtained in the X-ray study. This is of course as expected since the neutron diffraction data locates the nucleus while the X-ray data locates the (valence) electrons for hydrogen which are drawn towards the atoms to which it is bonded.

In desires to pursue other mixed metal hydrido-cluster complexes Mark Andrews was led to a study of the reaction between salts of the nucleophilic anion $[Fe_2(CO)_8]^{2-}$ with $[W(CO)_5I]^-$. The latter is known in acetonitrile to produce the complex $W(CO)_5(N{\equiv}CCH_3)$ on which nucleophilic substitution by $[Fe_2(CO)_8]^{2-}$, was expected. We did not isolate any mixed metal complexes in this work. Instead we obtained a series of tri-iron complexes containing triply bridging groups derived from the reduction of acetonitrile: $HFe_3(CH_3C{=}NH)(CO)_9$ and $HFe_3(N{=}CHCH_3)(CO)_9$ [65a,b]. These were shown in turn to be convertible on the one hand to $Fe_3(N{\equiv}CCH_3)(CO)_9$ and on the other to $H_2Fe_3(NCH_2CH_3)(CO)_9$ [64c,d] illustrating the stepwise reduction of acetonitrile on the face of a tri-iron cluster complex. Our attentions have now been drawn into studies of the modification of organic substrates by metal cluster complexes of potential significance both in homogeneous and heterogeneous catalysis [65]. This account has thus led us into current interests and a point at which it is appropriate to bring it to a close.

## Acknowledgments

I would like to express my deepest thanks for the talented collaboration of the co-workers I have mentioned here and for the uninterrupted financial support of the National Science Foundation over the course of this work. I would like also to acknowledge my debt to colleagues in this field whose studies influenced our work as recounted above. I could not in this account discuss our studies of the cyclometalation reaction in which I and other capable students have been involved over a number of years. This is an interesting story which I intend to tell in its own right in a separate account.

## References

1 (a) J.C. Hileman, D.K. Huggins and H.D. Kaesz, J. Amer. Chem. Soc., 83 (1961) 2953; (b) W. Hieber and C. Herget, Angew. Chem., 73 (1961) 579.
3 E. Anders, Ann. Rev. Nuclear Sci., 9 (1959) 203.
4 W. Hieber and H. Fuchs, Z. Anorg. Allgem. Chemie, 248 (1941) 256.
5 E.O. Brimm, M.A. Lynch, Jr. and W.J. Sesny, J. Amer. Chem. Soc., 76 (1954) 3831.
6 (a) F. Baumgärtner, E.O. Fischer and U. Zahn, Chem. Ber., 94 (1961) 2198; (b) Chr. Palm, E.O. Fischer and F. Baumgärtner, Naturwiss., 49 (1962) 279.
7 J.C. Hileman, D.K. Huggins and H.D. Kaesz, Inorg. Chem., 1 (1962) 933.
8 W. Beck, W. Hieber and G. Braun, Z. Anorg. Allgem. Chem., 308 (1961) 23.
9 M.A. El-Sayed and H.D. Kaesz, Inorg. Chem., 2 (1963) 158.
10 Proceedings of the Symposium on Organometallic Compounds, Sept. 4—6, 1962, Vancouver Canada: Can. J. Chem., 41 (1963) 1250.
11 D.F. Evans, J. Chem. Soc., (1959) 2003.
12 (a) R.V.G. Ewens and M.W. Lister, Trans. Faraday Soc., 35 (1939) 681; (b) E.A. McNeill and F.R. Scholer, J. Amer. Chem. Soc., 99 (1977) 6243.
13 (a) W.E. Wilson, Z. Naturforsch., 13b (1958) 349; (b) F.A. Cotton, J.L. Down and G. Wilkinson, J. Chem. Soc., (1959) 833.
14 (a) P.G. Owston, J.M. Partridge and J.M. Rowe, Acta Cryst., 13 (1960) 246; (b) P.L. Orioli and L. Vaska, Proc. Chem. Soc. (London), (1962) 333; (c) R. Bau (Ed.), Transition Metal Hydrides, Adv. Chem. Ser., (1978) 167.
15 (a) M.A. El-Sayed and H.D. Kaesz, J. Molec. Spectr., 9 (1962) 310; (b) L.E. Orgel, Inorg. Chem., 1 (1962) 25.
16 (a) D.K. Huggins, Dissertation, UCLA (1963) pp. 48—68; (b) D.K. Huggins and H.D. Kaesz, J. Amer. Chem. Soc., 86 (1964) 2734.
17 (a) J.A. Ibers, Abstracts of Papers Presented at the 147th National meeting of the A.C.S., Philadelphia, Pa., April 5—10, 1964; Div. Inorg. Chem., paper no. 50; (b) S.J. La Placa, J.A. Ibers and W.C. Hamilton, Inorg. Chem., 3 (1964) 1491; (c) S.J. La Placa, W.C. Hamilton, J.A. Ibers and A. Davison, Inorg. Chem., 8 (1969) 1928.
18 H.D. Kaesz, R. Bau, D. Hendrickson and J.M. Smith, J. Amer. Chem. Soc., 89 (1967) 2851.
19 P.S. Braterman, R.W. Harrill and H.D. Kaesz, J. Amer. Chem. Soc., 89 (1967) 2851.
20 P.S. Braterman, R. Bau and H.D. Kaesz, Inorg. Chem., 6 (1967) 2097.
21 (a) L.H. Jones, R.S. McDowell and M. Goldblatt, Inorg. Chem., 8 (1969) 2349; (b) L.H. Jones, Inorg. Chem., 7 (1968) 1681.
22 R.N. Perutz and J.J. Turner, (a) Inorg. Chem., 14 (1975) 262; (b) J. Amer. Chem. Soc., 97 (1975) 4791.
23 L. Vaska, J. Amer. Chem. Soc., 88 (1966) 4100.

24 (a) J. Chatt, Science, 160 (1968) 723; (b) A.P. Ginsberg, Transition Metal Chem., 1 (1965) 112; (c) M.L. Green and D.J. Jones, Adv. Inorg. Chem. Radiochem., 7 (1965) 115; (d) H.D. Kaesz and R.B. Saillant, Chem. Rev., 72 (1972) 231.
25 P.S. Braterman, Metal Carbonyl Spectra, Academic Press, New York, 1975.
26 (a) W. Hieber, W. Beck and G. Zeitler, Angew. Chemie, 73 (1961) 364; (b) D.T. Haworth and J.R. Ruff, J. Inorg. Nucl. Chem., 17 (1961) 184.
27 H.D. Kaesz, W. Fellmann, D.K. Huggins and J.M. Smith, (a) Abstracts of Papers Presented to the 147th National Meeting of the A.C.S., Philadelphia, Pa., April 5—10 1964; Div. Inorg. Chem., paper no. 28; (b) J. Amer. Chem. Soc., 86 (1964) 4841; (c) M.A. Andrews, S.W. Kirtley and H.D. Kaesz, Inorg. Syntheses, XVII (1977) 66.
28 B. Fontal, Dissertation, UCLA, 1969.
29 J.M. Smith, K. Mehner and H.D. Kaesz, J. Amer. Chem. Soc., 89 (1967) 1759.
30 M.R. Churchill, P.H. Bird, H.D. Kaesz, R. Bau and B. Fontal, J. Amer. Chem. Soc., 90 (1968) 7135.
31 (a) S.W. Kirtley, C.B. Knobler and H.D. Kaesz, cited in H.D. Kaesz, Chem. Ber., 9 (1973) 347; (b) S.W. Kirtley, Dissertation, UCLA, 1972.
32 H.D. Kaesz and S.W. Kirtley, Abstracts of Papers Presented at the 163rd National Meeting of the A.C.S., April 9—14, 1962; Div. Inorg. Chem., paper no. 129.
33 (a) R. Bau, B. Don, R. Greatrex, R.J. Haines, R.A. Love and R.D. Wilson, Inorg. Chem., 14 (1975) 3021; (b) M.R. Churchill, B.G. de Boer and F.J. Rotella, Inorg. Chem., 15 (1976) 1843.
34 (a) R. Bau, B. Fontal, H.D. Kaesz and M.R. Churchill, J. Amer. Chem. Soc., 89 (1967) 6374; (b) M.R. Churchill and R. Bau, Inorg. Chem., 7 (1968) 2606.
35 H.D. Kaesz, B. Fontal, R. Bau, S.W. Kirtley and M.R. Churchill, J. Amer. Chem. Soc., 91 (1969) 1021.
36 W. Fellmann and H.D. Kaesz, Inorg. Nucl. Chem. Lett., 2 (1966) 63.
37 H.D. Kaesz, R. Bau and M.R. Churchill, J. Amer. Chem. Soc., 89 (1967) 2775.
38 R.P. White Jr., T.E. Block and L.F. Dahl, private communication.
39 (a) H. Behrens and W. Klek, Z. Anorg. Allgem. Chemie, 292 (1957) 151; (b) L.B. Handy, P.M. Treichel, L.F. Dahl and R.G. Hayter, J. Amer. Chem. Soc., 88 (1966) 366; (c) R. Bau, R.G. Teller, S.W. Kirtley and T.F. Koetzle, Accts. Chem. Res., 12 (1979) 176.
40 R.W. Harrill and H.D. Kaesz, Inorg. Nucl. Chem. Lett., 2 (1966) 69.
41 J.R. Shapley, G.A. Pearson, M. Tachikawa, G.E. Schmidt, M.R. Churchill and F.J. Hollander, J. Amer Chem. Soc., 99 (1977) 8064.
42 (a) W. Fellmann, D.K. Huggins and H.D. Kaesz, Proc. VIIIth Int. Conf. Coord. Chem., Vienna, Aust., 1964, 255; (b) E.O. Fischer and R. Aumann, J. Organometal. Chem., 8 (1967) P1; (c) B.F.G. Johnson, R.D. Johnson, J. Lewis and B.H. Robinson, Inorg. Synth., 12 (1970) 43; (d) S.W. Kirtley, J.P. Olsen and R. Bau, J. Amer. Chem. Soc., 95 (1973) 4532.
43 (a) H.D. Kaesz, W. Fellmann, G.R. Wilkes and L.F. Dahl, J. Amer. Chem. Soc., 87 (1965) 2753; (b) H.D. Kaesz and S.W. Kirtley, Inorg. Synth., XX (1980) in press.
44 (a) V.G. Albano, G. Ciani, M. Freni and P. Romiti, J. Organometal. Chem., 96 (1975) 259; (b) A. Bertolucci, M. Freni, P. Romiti, G. Ciani, A. Sironi and V.G. Albano, J. Organometal. Chem., 113 (1976) C61; (c) G. Ciani, G. D'Alfonso, M. Freni, P. Romiti and A. Sironi, J. Organometal. Chem., 157 (1978) 199.
45 (a) B.T. Huie, Dissertation, UCLA, 1975; (b) B.T. Huie, C.B. Knobler and H.D. Kaesz, manuscript in preparation; (c) H.D. Kaesz in Y. Ishiii and M. Tsutsui, (Eds.), Organotransition-Metal Chemistry, Plenum Press, New York, 1975, pp. 302—303.
46 (a) J.K.A. Clarke, Chem. Rev., 75 (1975) 291; (b) V. Ponec, Catal. Rev. Sci. Eng., 11 (1975) 1; (c) H.D. Kaesz, R.A. Love, B.A. Matrana, A.P. Humphries and S. Siegel, Abstracts of Papers Presented to the National Meeting of the A.C.S., Aug. 28—Sept. 2, Chicago, Ill., 1977; paper no. PETR 044; (d) J.R. Anderson, P.S. Elmes, R.F. Howe and D.E. Mainwaring, J. Catal., 50 (1977) 508; (e) M. Ichikawa, J. Catal., 56 (1979) 127.
47 (a) R.B. Saillant, J.R. Blickensderfer and H.D. Kaesz, manuscript in preparation; (b) J.R. Blickensderfer, Dissertation, UCLA, 1974.
48 (a) F.A. Cotton and D.L. Hunter, Inorg. Chim. Acta, 11 (1974) L9; (b) S. Aime, O. Gambino, L. Milone, E. Sappa and E. Rosenberg, Inorg. Chim. Acta, 15 (1975) 53; (c) B.F.G. Johnson, J. Lewis, B.E. Reichert and K.T. Schorpp, J. Chem. Soc. (Dalton), (1976) 1403.
49 (a) F.A. Cotton and J.M. Troup, J. Amer. Chem. Soc., 96 (1974) 4155; (b) E.R. Corey and L.F. Dahl, Inorg. Chem., 1 (1962) 521.
50 (a) R. Saillant, G. Barcelo and H.D. Kaesz, J. Amer. Chem. Soc., 92 (1970) 5739; (b) J.R. Johnson and H.D. Kaesz, Inorganic Syntheses, XVIII (1978) 60.
51 (a) P. Chini, Inorg. Chim. Acta Rev., 2 (1968) 31; (b) R. Mason and D.M.P. Mingos, J. Organometal. Chem., 50 (1973) 53.
52 R.D. Wilson and R. Bau, J. Amer. Chem. Soc., 98 (1976) 4687.
53 R. Hoffmann, B.E.R. Schilling, R. Bau, H.D. Kaesz and D.M.P. Mingos, J. Amer. Chem. Soc., 100 (1978) 6088.

54 (a) H.D. Kaesz, S.A.R. Knox, J.W. Koepke and R.B. Saillant, Chem. Commun., (1971) 477; (b) S.A.R. Knox, J.W. Koepke, M.A. Andrews and H.D. Kaesz, J. Amer. Chem. Soc., 97 (1975) 3942.

55 R.D. Wilson, S.M. Wu, R.A. Love and R. Bau, Inorg. Chem., 17 (1978) 1271.

56 (a) S.A.R. Knox and H.D. Kaesz, J. Amer. Chem. Soc., 93 (1971) 4594; (b) J.W. Koepke, Dissertation, UCLA, 1974.

57 J.W. Koepke, J.R. Johnson, S.A.R. Knox and H.D. Kaesz, J. Amer. Chem. Soc., 97 (1975) 3947.

58 C. Ungermann, V. Landis, S.A. Moya, H. Cohen, H. Walker, R.G. Pearson, R.G. Rinker and P.C. Ford, J. Amer. Chem. Soc., 101 (1979) 5922.

59 J.R. Shapley, S.I. Richter, M.R. Churchill and R.A. Lashewycz, J. Amer. Chem. Soc., 99 (1977) 7385.

60 (a) M.A. Andrews and H.D. Kaesz, unpublished; (b) M.A. Andrews, Senior Dissertation, New College, Sarasota, Fla., 1973.

61 B.T. Huie, C.B. Knobler and H.D. Kaesz, J. Amer. Chem. Soc., 100 (1978) 3059.

62 C.E. Strouse, Rev. Sci. Instrum., 47 (1976) 871.

63 R.G. Teller, R.D. Wilson, R.K. McMullan, T.F. Koetzle and R. Bau, J. Amer. Chem. Soc., 100 (1978) 3071.

64 (a) M.A. Andrews and H.D. Kaesz, J. Amer. Chem. Soc., 101 (1979) 7328; (b) M.A. Andrews, G. van Buskirk, C.B. Knobler and H.D. Kaesz, J. Amer. Chem. Soc., 101 (1979) 7245; (c) M.A. Andrews and H.D. Kaesz, J. Amer. Chem. Soc., 101 (1970) 7255; (d) M.A. Andrews, C.B. Knobler and H.D. Kaesz, J. Amer. Chem. Soc., 101 (1979) 7260.

66 (a) H.D. Kaesz, Chemistry in Britain, 9 (1973) 344; (b) R. Ugo, Catal. Rev. Sci. Eng., 11 (1975) 225; (c) E.L. Muetterties, Bull. Soc. Chim. Belg., 84 (1975) 397.