

Conclusion

The XPS of the three classes of platinum blues examined in this study clearly demonstrate that they have similar electronic structures. An independent investigation²⁸ of *cis*-diammineplatinum uridine blue by EXAFS spectroscopy showed it to have a geometry consistent with that found for the α -pyridone blue. It therefore appears that, as stated previously,¹⁰ the features embodied in *cis*-diammineplatinum α -pyridone blue, namely, a mixed oxidation state, amidate bridged, oligomeric structure, are reflective of the entire class of "Platinblau" compounds.

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References and Notes

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Molecular and Electronic Structure of Tetraallyldirhenium

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Abstract: The title compound, whose preparation was recently reported by Wilkinson and co-workers, has been investigated to determine its molecular structure and to clarify the nature of the multiple Re-Re bond. The structure is quite different from that of the Cr and Mo compounds of the same stoichiometry. The $Re_2(C_3H_5)_4$ molecule has virtual D_{2h} symmetry and no bridging allyl groups. The mean Re-Re distance in the two crystallographically independent molecules is 2.225 (7) Å. The four chemically equivalent $Re(\eta^3-C_3H_5)$ bonds are typical of metal to η^3 -allyl bonds in general. The electronic structure has been treated using the Hartree-Fock-Roothaan SCF method in the Fenske-Hall approximation. The highest filled orbital is of a_1 symmetry and has δ -antibonding character. However, electrons occupying it do not appear to destabilize the molecule very much. There are strong π and σ M-M bonds. The Re-Re bond can be considered effectively triple. The crystallographic data are: space group $C2$ with $a = 12.218$ (3), $b = 8.692$ (2), $c = 18.763$ (4) Å, $\beta = 97.28$ (2)°, $Z = 6$. There are four molecules on the general position and two on the special positions of type $(0, y, 0; 1/2, 1/2 + y, 0)$ having C_2 symmetry. The structures of the two crystallographic types of molecule are essentially identical.

Introduction

A number of recent observations have combined to focus attention on the question of how sensitive M-M bond lengths are to the gain or loss of δ or δ^* electrons. The cleanest case available involving metal atoms in the second transition series is provided by the $Mo_2(SO_4)_4^{4-}$ and $Mo_2(SO_4)_4^{3-}$ ions, where the first one has a $\sigma^2\pi^4\delta^2$ configuration and the second a $\sigma^2\pi^4\delta$ configuration.¹ The corresponding Mo-Mo distances are 2.111 (1) and 2.164 (2) Å. This increase of ca. 0.05 Å upon the loss of one δ electron takes place with retention of essentially

identical structural constraints.² Consistent with this is the fact that Mo-Mo triple bonds, where there are no δ electrons, have lengths in the range 2.16-2.22 Å.^{3,4} Thus, each addition of a one-half δ component seems to shorten an Mo-Mo bond by roughly 0.05 Å.

In the third transition series, however, the evidence available at present, though limited, tends to imply that δ bonding has less of an effect on the bond length. Thus, in the $W_2(CH_3)_8^{4-}$ and $[W_2(CH_3)_{8-x}Cl_x]^{4-}$ ions⁵ which have quadruple bonds, the W-W distances are about 2.26 Å while in the triply bonded

W_2X_6 compounds⁶ the W-W distances are in the range 2.26–2.30 Å. In the case of $Re_2Cl_4(PEt_3)_4$, an SCF- $X\alpha$ -SW calculation of the ground state⁷ shows that the configuration is $\sigma^2\pi^4\delta^2\delta^*2$, but the Re-Re distance, 2.232 (5) Å,⁸ is not significantly greater than those in $Re_2Cl_8^{4-}$ (2.222 (2) Å⁹) and $Re_2Cl_6(PEt_3)_2$ (2.222 (3) Å¹⁰) where there are $\sigma^2\pi^4\delta^2$ configurations.

In this context the compound $Re_2(allyl)_4$, recently reported by Masters, Mertis, Gibson, and Wilkinson,¹¹ aroused our interest. It has the same stoichiometry as the chromium and molybdenum tetraallyls, in which quadruple bonds are presumed to exist¹² but there are two more metal electrons present. Professor G. Wilkinson and Mr. C. Mertis kindly offered to supply a sample and we used this to carry out a crystal structure determination. When the result of this was seen, we considered it worthwhile to do an approximate MO calculation. All of this work is reported here.

Experimental Section

Samples of $Re_2(allyl)_4$ were supplied by Professor G. Wilkinson and Mr. K. Mertis of Imperial College, London. The compound was recrystallized from pentane at $-20^\circ C$. This process and all other operations on the compound were carried out under N_2 .

Crystals of $Re_2(allyl)_4$ were immersed in mineral oil and examined under a microscope. Unfortunately $Re_2(allyl)_4$ persistently crystallizes as plates. A crystal measuring ca. $0.03 \times 0.10 \times 0.25$ mm was separated from a larger plate and mounted, immersed in epoxy cement, in a 0.2-mm i.d. glass capillary. The crystal was mounted with its longest dimension nearly coincident with the ϕ axis of the x-ray goniometer. This crystal was shown to be of good quality by scans of several intense low-angle reflections which had peak widths at half-height of ca. 0.25° . Cell constants and axial photographs indicated that the crystal belonged to the monoclinic system with $a = 12.218$ (3), $b = 8.692$ (2), $c = 18.763$ (4) Å, $\beta = 97.28$ (2)°, $V = 1976.5$ (7) Å³. The observed volume is consistent with that expected for $Z = 6$.

Data were collected at $23^\circ C$ on a Syntex P $\bar{1}$ autodiffractometer equipped with a graphite crystal monochromator and using Mo $K\alpha$ ($\lambda = 0.710730$ Å) radiation. The θ - 2θ scan technique was used with scans ranging between 1.0° above and 1.0° below the calculated $K\alpha_1$, $K\alpha_2$ doublet, variable scan speeds of from 4.0 to 24.0° /min, and a scan to background time ratio of 2.0. The intensities of three standard reflections were monitored frequently throughout data collection and remained constant. The intensities of 2436 unique reflections having $0^\circ < 2\theta < 55^\circ$ were recorded.

It was recognized that, even with such a small crystal, the linear absorption coefficient ($\mu = 193.6$ cm⁻¹) was large enough to require application of an absorption correction to the data. Since the crystal was mounted embedded in epoxy cement, accurate measurements using an optical goniometer were not possible. We therefore elected to apply an empirical absorption correction to the data. Psi scans of several reflections having $\chi = 90 \pm 10^\circ$ were obtained. Since the crystal was a flattened needle oriented nearly along φ , the intensities of these reflections showed a smooth, sinusoidal dependence upon φ . ψ scans of four reflections were taken by varying ψ from 0.0 to 180.0° in steps of 10° . Transmission coefficients as a function of ψ were in good agreement and the four curves were averaged. Relative transmission coefficients ranged from 0.34 to 1.00. The empirical absorption correction was based upon this curve. The minimum, maximum, and average transmission coefficients were 0.34, 1.00, and 0.801, respectively.

The corrected intensities were then reduced to a set of relative $|F_o|^2$ values.¹³ Of the 2436 unique reflections, 1755 had $|F_o|^2 > 3\sigma(|F_o|^2)$ and were used in subsequent structure solution and refinement.¹³

The only systematic absences observed during data collection were on hkl for $h + k = 2n + 1$ indicating three possible space groups: $C2/m$ (no. 12), Cm (no. 8), or $C2$ (no. 5). Statistical tests suggested that the space group was acentric. The three-dimensional Patterson map, which was quite complicated, suggested that the correct space group was $C2$. This was confirmed by the subsequent structure solution and refinement using space group $C2$. The positions of two of the three crystallographically independent rhenium atoms were found in a direct methods solution employing the MULTAN program. The third independent Re atom was found in the first difference Fourier

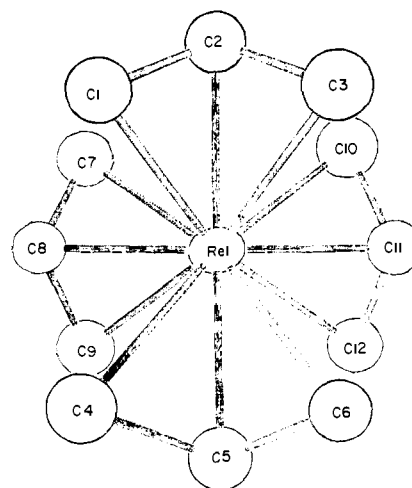


Figure 1. An ORTEP view of molecule I looking directly down the Re(1)–Re(2) bond, with atoms represented by 40% probability ellipsoids and showing the atom labeling scheme. Re(2) is “hidden” by Re(1) and atoms C(7) to C(12) are bonded to Re(2).

map. The carbon atoms were located, with some difficulty, following refinement of the positional and anisotropic temperature parameters of the three rhenium atoms.

The structure was refined to convergence using anisotropic thermal parameters for the Re atoms and isotropic thermal parameters for the carbon atoms. Final residuals were

$$R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} = 0.051$$

$$R_2 = \left[\frac{\sum w(|F_o| - |F_c|)^2}{\sum w|F_o|^2} \right]^{1/2} = 0.0638$$

The estimated standard deviation of an observation of unit weight was 1.277. The other enantiomorph was also refined to convergence and yielded a slightly larger ($R_2 = 0.0640$) residual. Although the differences in residuals are not statistically significant, we chose the former enantiomorph over the latter because the Re-C and C-C bond distances varied less widely. There were a number of peaks in the final difference Fourier map—all within ca. 1 Å of the rhenium atoms. We ascribe these peaks to inadequacies in our absorption correction. We could find no peaks of chemical significance. A table of observed and calculated structure factors is available as supplementary material.

MO Calculation. The Fenske-Hall simplification of the Hartree-Fock-Roothaan type of calculation was used. Programs were supplied by Professor M. B. Hall, who also provided guidance in their use.

The atomic orbital coefficients of Richardson and co-workers were used,¹⁴ with double ζ functions for the metal d orbitals. Coefficients of 1.0 and exponents of 2.2 were chosen for the metal 5s and 5p orbitals, respectively, and these orbitals were orthonormalized with respect to the inner shell s and p orbitals. Calculations were carried out using Tc(+1) and Tc(+2) coefficients. The former yielded a final net metal charge (d orbitals only) more consistent with the chosen “oxidation state”, and these results are the ones reported here.

Results

Crystal and Molecular Structure. The atomic positional and thermal parameters are given in Table I and the bond distances and angles are given in Table II. Figures 1 and 2 are ORTEP drawings of the two independent molecules, showing the numbering scheme used in the tables.

The unit cell, which is monoclinic with space group $C2$, contains six molecules. Four of these occupy the fourfold general position and thus have no imposed crystallographic symmetry. The representative molecule of this set is composed of Re(1), Re(2) and C(1), C(2), . . . , C(12). The other two molecules are at the pair of twofold special positions $0, y, 0$ and $1/2, 1/2 + y, 0$, and have C_2 symmetry axes crystallographically imposed. The independent atoms comprising this pair of molecules are Re(3) and C(13)–C(18). These two crystallographically independent molecules are designated I and II, respectively.

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations^a

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re(1)	-0.15334 (8)	0.0000 (0)	-0.38066 (6)	0.00580 (5)	0.0108 (1)	0.00157 (3)	-0.0043 (2)	0.00091 (6)	0.0000 (1)
Re(2)	-0.11113 (8)	-0.1565 (2)	-0.28692 (6)	0.00529 (5)	0.0102 (1)	0.00223 (3)	-0.0018 (2)	0.00134 (6)	0.0005 (2)
Re(3)	-0.04009 (9)	-0.6600 (2)	0.04979 (6)	0.00814 (7)	0.0115 (1)	0.00192 (3)	-0.0018 (3)	0.00157 (7)	-0.0002 (2)
C(1)	-0.175 (3)	0.235 (4)	-0.343 (2)	5.2 (7)					
C(2)	-0.063 (2)	0.203 (4)	-0.336 (2)	3.9 (6)					
C(3)	-0.018 (2)	0.149 (4)	-0.394 (2)	4.4 (6)					
C(4)	-0.322 (2)	-0.033 (3)	-0.435 (2)	3.9 (6)					
C(5)	-0.256 (2)	-0.166 (5)	-0.449 (2)	4.4 (6)					
C(6)	-0.148 (3)	-0.123 (4)	-0.486 (2)	5.0 (7)					
C(7)	-0.147 (3)	-0.052 (5)	-0.179 (2)	6.4 (9)					
C(8)	-0.251 (3)	-0.104 (4)	-0.226 (2)	4.9 (7)					
C(9)	-0.266 (3)	-0.258 (4)	-0.249 (2)	5.0 (7)					
C(10)	0.067 (3)	-0.171 (5)	-0.256 (2)	5.2 (7)					
C(11)	0.041 (2)	-0.249 (4)	-0.320 (2)	4.4 (7)					
C(12)	-0.040 (3)	-0.374 (4)	-0.322 (2)	5.6 (8)					
C(13)	-0.048 (3)	-0.430 (4)	0.091 (2)	5.1 (7)					
C(14)	0.059 (3)	-0.482 (6)	0.109 (2)	6.2 (8)					
C(15)	0.089 (3)	-0.622 (5)	0.144 (2)	6.6 (9)					
C(16)	-0.088 (2)	-0.893 (4)	0.076 (2)	4.0 (6)					
C(17)	-0.160 (3)	-0.836 (5)	0.019 (2)	5.3 (7)					
C(18)	-0.220 (3)	-0.691 (5)	0.025 (2)	6.2 (9)					

^a The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

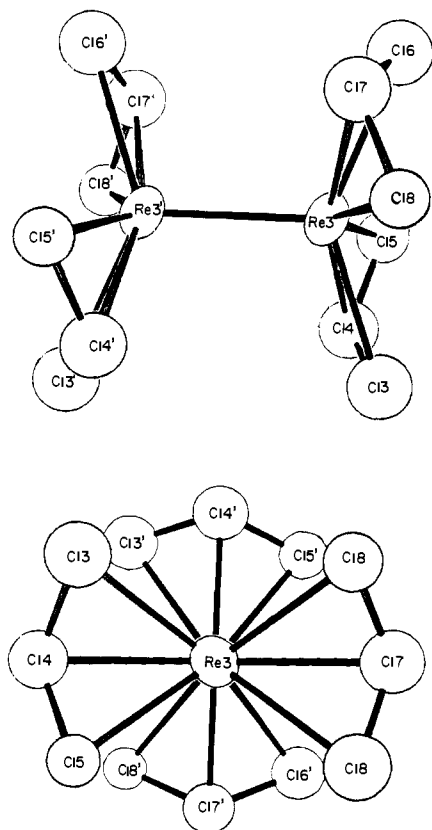


Figure 2. Two ORTEP views of molecule II. Above is a view perpendicular to the Re(3)-Re(3') bond and below is a view directly down the Re(3)-Re(3') bond. Atoms are represented by 40% probability ellipsoids and the labeling scheme is shown. Molecule II has crystallographic C₂ symmetry.

Molecules I and II are essentially identical and both have dimensions conforming very closely to D_{2d} symmetry, as is emphasized by the views down the Re-Re axes in Figures 1 and 2. The six crystallographically independent but chemically identical allyl groups are indistinguishable within experimental error. The mean C-C distance is 1.44 ± 0.05 Å, the mean C-C-C angle is 120 ± 3°, and the mean Re-C distance is 2.21

Table II. Bond Distances (Å) and Angles (deg) in Re₂(allyl)₄

Atoms	Distance	Atoms	Distance
Re(1)-Re(2)	2.232 (1)	C(17)-C(16)	1.40 (4)
Re(3)-Re(3')	2.217 (2)	-C(18)	1.46 (5)
Re(1)-C(1)	2.19 (4)	Atoms Angle	
-C(2)	2.19 (3)	Re(2)-Re(1)-C(1)	110 (1)
-C(3)	2.14 (3)	-C(2)	98 (1)
-C(4)	2.20 (3)	-C(3)	111 (1)
-C(5)	2.21 (3)	-C(4)	113 (1)
-C(6)	2.26 (3)	-C(5)	97 (1)
Re(2)-C(7)	2.31 (4)	-C(6)	112 (1)
-C(8)	2.22 (3)	Re(1)-Re(2)-C(7)	114 (1)
-C(9)	2.29 (3)	-C(8)	100 (1)
-C(10)	2.19 (3)	-C(9)	111 (1)
-C(11)	2.19 (3)	-C(10)	112 (1)
-C(12)	2.22 (3)	-C(11)	97 (1)
Re(3)-C(13)	2.16 (4)	-C(12)	110 (1)
-C(14)	2.18 (4)	Re(3)-Re(3')-C(13)	111 (1)
-C(15)	2.24 (4)	-C(14)	99 (1)
-C(16)	2.18 (3)	-C(15)	109 (1)
-C(17)	2.15 (4)	-C(16)	110 (1)
-C(18)	2.20 (3)	-C(17)	98 (1)
C(2)-C(1)	1.38 (4)	-C(18)	111 (1)
-C(3)	1.37 (4)	C(1)-C(2)-C(3)	119 (3)
C(5)-C(4)	1.45 (4)	C(4)-C(5)-C(6)	113 (3)
-C(6)	1.61 (4)	C(7)-C(8)-C(9)	122 (3)
C(8)-C(7)	1.51 (5)	C(10)-C(11)-C(12)	118 (3)
-C(9)	1.41 (5)	C(13)-C(14)-C(15)	126 (4)
C(11)-C(10)	1.37 (5)	C(16)-C(17)-C(18)	121 (3)
-C(12)	1.47 (4)	C(2)-Re(1)-C(5)	166 (1)
C(14)-C(13)	1.39 (5)	C(8)-Re(2)-C(11)	163 (1)
-C(15)	1.41 (6)	C(14)-Re(3)-C(17)	163 (1)

± 0.03 Å. In each of these figures the error interval gives the mean deviation from the average. There is no significant difference between the distances from Re atoms to outer carbon atoms (2.22 ± 0.03 Å) and from Re atoms to inner carbon atoms (2.19 ± 0.02 Å). In view of the relatively large uncertainties arising here from the extreme heaviness of the metal atoms and probably also from some significant error in the absorption corrections, the average dimensions of the Re-C₃ moieties are in quite satisfactory accord with the usual values for M(η³-allyl) groups.

The two independent values of the Re-Re distance, 2.232

Table III. The Provenance and Bonding Role of the Lowest Empty and Highest Filled MOs^a

Orbital	Energy, eV	% character											Principal role in bonding ^a
		2M 4d				2M 5s	2M 5p		4 C ₃ H ₅				
		z ²	x ² - y ²	xy	{xz/yz}		z	{x/y}	π	π _n	π*		
4b ₂	6.31	2	13	0	0	4	8	0	1	0	71	L*	
5a ₁	4.96	2	15	0	0	0	0	0	1	0	80	L*	
5e	3.18	0	0	0	5	0	0	0	0	0	94	L*	
2b ₁	-0.44	0	0	51	0	0	0	0	0	46	0	(M-L _n)*	
2a ₂	-1.41	0	0	47	0	0	0	0	0	50	0	(M-L _n)*	
4a ₁	-1.80	10	0	0	0	10	64	0	0	0	16	M-M σ	
4e	-5.02	0	0	0	86	0	0	2	0	6	3	M-M π*	
3b ₂	-6.18	58	2	0	0	1	24	0	8	0	5	M-M σ*	
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3a ₁	-10.39	0	70	0	0	14	0	0	2	0	11	M-M δ*	
3e	-11.32	0	0	0	12	0	0	11	0	76	1	L _n	
2b ₂	-12.09	11	70	0	0	5	0	0	0	0	11	M-M δ	
2e	-13.90	0	0	0	86	0	0	2	0	7	1	M-M π	
1b ₁	-14.26	0	0	40	0	0	0	0	0	54	0	M-L _n	
1a ₂	-14.71	0	0	43	0	0	0	0	0	50	0	M-L _n	
2a ₁	-15.18	52	6	0	0	15	2	0	24	0	0	M-M σ	
1e	-16.84	0	0	0	1	0	0	5	94	0	0	L	
1b ₂	-18.05	6	4	0	0	6	0	0	80	0	0	L	
1a ₁	-18.33	28	1	0	0	0	2	0	62	0	0	M-L	

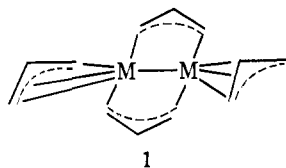
^a L, L_n, and L* designate allyl π, π_n, and π* orbitals, respectively. M-M π means π bonding between metal atoms, and so forth. Those orbitals below the horizontal line are filled.

(1) and 2.217 (2) Å, differ by an amount that is statistically significant by the usual criterion (>3σ) but there does not appear to be any chemical significance in this. For purposes of discussion the mean value, 2.225 (11) Å, will be used.

Electronic Structure. The more important numerical results of the calculation are collected in Table III, and the energy levels which will be the subject of discussion are shown diagrammatically in Figure 3. The highest occupied MO is the 3a₁ orbital distinguished by the pair of arrows; all those of lower energy are occupied, though the arrows have been omitted for simplicity.

Discussion

Molecular Structure. The most prominent point of interest is that the structure of Re₂(C₃H₅)₄ is different from that found in Cr₂(C₃H₅)₄¹⁵ and Mo₂(C₃H₅)₄,¹⁶ which are isostructural to each other. In these molecules there are two bridging allyl groups and two conventional "π-allyl" or η³-allyl types. As shown schematically in **1**, these are so arranged that the mol-



ecules possess only a plane of symmetry, perpendicular to the M-M axis. Re₂(C₃H₅)₄, in contrast, possesses a highly symmetrical D_{2d} structure, as shown in Figures 1 and 2.

We cannot answer the question of why Re₂(allyl)₄ has a different structure from Mo₂(allyl)₄ without knowing first why Mo₂(allyl)₄ does have the very unsymmetrical structure that it has. The literature does not record any explanation of this, and we do not at present have any to propose. Instead, we concern ourselves with formulating the electronic structure of Re₂(C₃H₅)₄ in as much detail as possible on the basis of the structure we have found. Before doing this, however, we shall discuss the evidence concerning the structure of the molecule in solution.

The ¹H NMR spectrum, kindly supplied by Professor Wilkinson, is consistent with the idea that the structure found in the crystal persists in solution. The spectrum can be satisfactorily assigned to a molecule with only one type of allyl

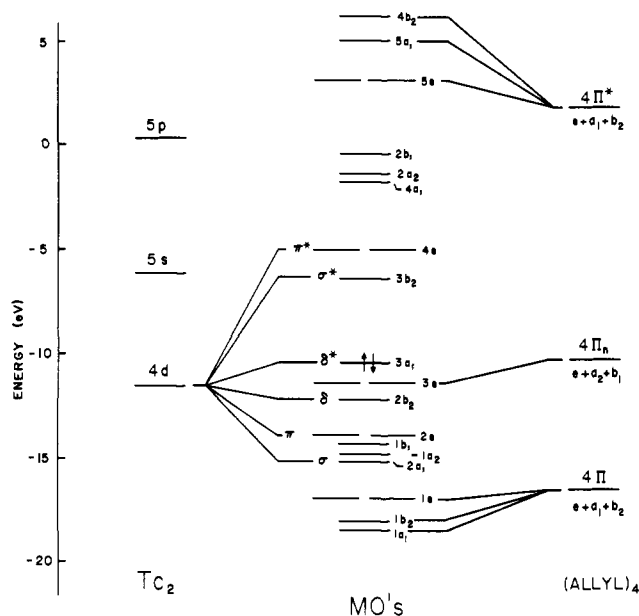


Figure 3. A molecular orbital diagram for Tc₂(allyl)₄ showing the orbitals pertinent to metal-metal and metal-ligand bonding. The highest occupied MO is marked with arrows. Connecting lines indicate those MOs predominantly metal or ligand in character. MOs without such connecting lines are of fairly evenly mixed provenance.

group. The first detailed observation and interpretation of a rigid (η³-C₃H₅)M system was presented some years ago for the (η³-C₃H₅)Mn(CO)₄ molecule,¹⁷ where fine structure due to the three major types of H-H coupling was resolved. In the present case, the spectrum can be analyzed in an analogous way with values of the coupling constants that are similar but, of course, not identical. A multiplet centered at τ 4.23 can be assigned to the unique proton, C, and its structure is fully explained assuming J_{AC} ≈ 9 Hz and J_{BC} ≈ 5 Hz, where A and B refer to the anti and syn protons, respectively. A triplet at τ 5.88 can be assigned to the syn (B) protons and has the appearance of a triplet because J_{AB} ≈ J_{BC} ≈ 5 Hz. Actually these two J's are not exactly equal and the central peak is slightly broader than the outer ones, because there are actually two

doublets with almost overlapping peaks rather than one true triplet. Finally, the "quartet" at τ 10.53, in which the first and third lines are narrower than the second and fourth, is assigned to the anti (A) protons and its structure is accounted for as the result of the coupling constants already mentioned. It would be possible to reverse the assignments (and coupling constants) of the syn and anti protons, but those just suggested are consistent in their relative magnitudes with those proposed earlier in the allylmanganese carbonyl.

We turn now to the electronic structure of the $\text{Re}_2(\text{C}_3\text{H}_5)_4$ molecule. If each C_3H_5 group is treated as a sort of bidentate, uninegative ligand, the compound may be considered to contain Re(II) and to be isoelectronic with $\text{Re}_2\text{Cl}_4(\text{PET}_3)_4$. It thus has two essentially metal-based electrons beyond the eight required to form a quadruple Re-Re bond. In order to determine, as reliably as possible without as yet undertaking an SCF-X α -SW calculation,¹⁸ the pattern of occupied orbitals we have done a Fenske-Hall calculation, the results of which are presented in Table III and Figure 3. The calculation was carried out on "Tc₂(allyl)₄" using average bond distances and angles taken from the $\text{Re}_2(\text{allyl})_4$ structure, this being necessitated by the unavailability of atomic wave functions for metals in the third transition series.

The results of the calculation suggest that the Re-Re bond in this compound is best regarded as essentially a triple one. The σ and π components, provided essentially by the $2a_1$ and $2e$ orbitals, respectively, are strong. The $2b_2$ and $3a_1$ orbitals are of M-M δ and δ^* character, respectively. However, neither seems to make a major contribution to the M-M bond energy since they lie only about 0.9 eV above and below the energy of the metal d orbitals from which they are formed, and the δ and δ^* components seem to cancel each other quite effectively.

It is reasonable to suppose that here, and in other cases involving bonds between metal atoms of the third transition series, the δ interactions, both bonding and antibonding, are sufficiently weak that they cannot appreciably affect the M-M distance. In the third transition series the metal atoms possess dense cores because of the 14 4f electrons and it seems likely that the M-M distance resulting from the relatively strong σ and π bonding interactions cannot be significantly shortened by the addition of the relatively weak δ bond, nor is the length of an M-M quadrupole bond appreciably increased upon the loss of the δ component, either by its actual abolition (loss of δ bonding electrons) or its cancellation (addition of δ antibonding electrons). Presumably, in the second transition series, where the metal atom valence shell orbitals are similar in size (i.e., have similar radial wave functions) to their congeners in the third transition series but lack the filled 4f shell, the cores are more compressible and hence the M-M distances are somewhat more susceptible to the presence or absence of δ bonding.

It should be noted that under D_{2d} symmetry there are actually two d orbitals on each metal atom that are of δ type, namely, d_{xy} and $d_{x^2-y^2}$. In the above discussion of the M-M δ bonding and antibonding MOs, $2b_2$ and $3a_1$, we were dealing with MOs whose provenance is in the $d_{x^2-y^2}$ orbitals. These are oriented obliquely with respect to the allyl groups, and do not overlap very well with them. Hence, the $2b_2$ and $3a_1$ orbitals have relatively pure metal character. The d_{xy} orbitals, however, are directed toward the midpoints of the allyl groups and

overlap well with allyl π orbitals. The $1a_2$ and $1b_1$ MOs, therefore, have approximately equal metal and ligand character and are, in fact, the most effective MOs for metal-ligand bonding.

The photoelectron spectrum of $\text{Re}_2(\text{C}_3\text{H}_5)_4$ has been measured by Cowley and co-workers, who will report the results in detail elsewhere. They find the first few peaks at the following positions (eV): 6.73 (narrow), 7.77 (broad), 7.98 (narrow), 8.94 (shoulder), \sim 9.50 (very broad with several shoulders). These energies clearly do not agree well with the calculated values, although the general pattern, that is, three peaks at low energies which are narrow, broad, and again narrow, followed by a gap of about 1.5 eV, and then a broad, unresolved region of absorption, is qualitatively in agreement with the calculated pattern. The poor numerical agreement is disturbing but not entirely surprising in view of several considerations. First, the effect of using $\text{Tc}_2(\text{C}_3\text{H}_5)_4$ rather than $\text{Re}_2(\text{C}_3\text{H}_5)_4$ in the calculation is unknown, though we had not expected any drastic error to result. Second, a previous study of a metal η^3 -allyl system, $\text{Ni}(\eta^3\text{-C}_3\text{H}_5)_2$, revealed gross inadequacy of Koopman's theorem,¹⁹ with both individual ionization energies and their order changing considerably compared to the results for the un-ionized ground state.

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Supplementary Material Available: A table of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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