to remove the copper salts, and the residue was washed with 10 mL of ether (Et_2O). The filtrate was extracted 3 times with 10 mL of Et_2O. The combined organic layers were washed 2 times with 10 mL of 2 N HCl and once with brine. After drying over $MgSO_4$, the organic layer was concentrated in vacuo to afford the conjugate addition product which was purified by medium-pressure liquid chromatography (MPLC) (pentane/5–25% ether, v/v).

Conjugate Addition of Higher Order Organocuprates to α,β-Unsaturated Enones. The formation and subsequent reaction of the higher order organocuprates was identical with the above procedure except that copper(I) thiocyanate (0.1273 g, 1.14 mmol) was used instead of copper(I) bromide.

Conjugate Addition of Chiral Organocuprate 11 to α,β-Enones. Prolinol (0.1173 g, 1.16 mmol) was dissolved in 5 mL of ether (Et_2O) in a septum sealed 50-mL, two-necked, round-bottomed flask under N_2. The solution was cooled to −25 °C. Methyllithium (2 equiv, 1.66 mL, 2.32 mmol) was added dropwise. After 30 min, copper(I) bromide (1.663 g, 1.16 mmol) was added via a solid addition funnel followed immediately by the addition of 1 more equiv of methyllithium (0.83 mL, 1.16 mmol). The tan mixture was stirred at −25 °C for 30 min. Upon warming to 0 °C over 15 min the mixture turned dark brown. The cuprate was cooled to −78 °C, and 2-cyclohexen-1-one (0.0993 g, 1.00 mmol) was added in 2 mL of ether. After 3 h, the reaction was warmed to −50 °C where stirring was continued for 1 more h. Saturated aqueous ammonium chloride (5 mL) was added to quench the reaction. The reaction mixture was warmed to room temperature and filtered through Celite. The filtrate was extracted 3 times with 15 mL of Et_2O. The combined organic layers were washed 2 times with 10 mL of 2 N HCl and once with 5 mL of brine, dried over $MgSO_4$, and concentrated in vacuo to yield 3-methylcyclohexan-1-one. The product was purified by MPLC.

Conjugate Addition of Halide Free Organocuprates to α,β-Enones. Methyl copper free of LiBr was prepared according to Lipshultz's[28] procedure. A 10-mL centrifuge tube containing copper(I) bromide (0.0998 g, 0.69 mmol) and 2 mL of THF under N_2 was cooled to −78 °C. Methyllithium (0.46 mL, 0.69 mmol) was added dropwise. A yellow precipitate formed as the mixture was warmed to 0 °C. The tube was spun in a centrifuge, and the clear yellow supernant liquid was removed via a syringe. The methyl copper was washed 3 more times with 2 mL of THF, respectively. After the final washing, 1 mL of Et_2O was added, and the slurry was cooled to −78 °C. The lithium anion of L-(+)-2-[(phenylthio)methyl]pyrrolidine which was formed by the addition of methyllithium (0.46 mL, 0.69 mmol) to the (phenylthio)amine (0.1357 g, 0.70 mmol) at 0 °C was added by cannula. The yellow solution was warmed to 0 °C and then recooled to −78 °C. 2-Cyclohexen-1-one (0.0605 g, 0.63 mmol) in 1 mL of Et_2O was added, the stirring was continued for 90 min. Saturated aqueous ammonium chloride (5 mL) was added to quench the reaction. After filtering through Celite, the filtrate was extracted 3 times with 10 mL of Et_2O. The combined organic layers were washed twice with 5 mL of 2 N HCl and once with 5 mL of brine. Drying over $MgSO_4$ and concentration in vacuo afforded 3-methylcyclohexanone which was purified by MPLC.

Recovery of Chiral Ligands. The procedure[45] of Mukaiyama was employed. The acidic solution from the organocuprate conjugate addition workup was neutralized with solid $NaHCO_3$ and concentrated in vacuo. The residue was diluted with 5 mL of 10% NaOH and then extracted 4 times with 10 mL of ether. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo to yield the chiral amines in 75% yield with no detectable racemization occurring.

General Procedure for the Preparation of Diastereomeric Ketals.[26] The 3-substituted cycloalkanones were dissolved in benzene and treated with 2 equiv of (*R*,*R*)-(−)-2,3-butanediol and a catalytic amount of *p*-toluenesulfonic acid in a one-necked, 25-mL, round-bottomed flask equipped with a Dean-Stark trap, condenser, and N_2 inlet. The solution was refluxed for 24 h, cooled, and concentrated in vacuo. The residue, dissolved in 10 mL of pentane, was washed with 5 mL of saturated $NaHCO_3$ and then 5 mL of 5% $NaHSO_3$. The two aqueous layers were each back-extracted with 5 mL of pentane. The combined organic layers were dried over K_2CO_3, concentrated in vacuo, and purified by MPLC. The optical purity of the ketals was determined by ^{13}C NMR.

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Registry No. 1, 23356-96-9; **2**, 63126-47-6; **3**, 51207-66-0; **5**, 106865-55-8; **6**, 106865-52-5; *N*-benzoyl-L-(+)-2-pyrrolidinemethanol, 65950-13-2; *N*-benzoyl-L-(+)-2-[(phenylthio)methyl]pyrrolidine, 106865-53-6; phenyl disulfide, 882-33-7; *N*-benzoyl-L-2-[(methylthio)-methyl]pyrrolidine, 106865-54-7; *trans*-3-penten-2-one, 3102-33-8; copper(I) bromide, 7887-70-4; (*S*)-3-methylcyclopentanone, 6672-24-8; (*R*)-3-methylcyclopentanone, 6672-30-6; (*S*)-3-*tert*-butylcyclopentanone, 66007-65-6; (*S*)-4-methyl-2-octanone, 106865-56-9; (*R*)-4-methyl-2-octanone, 106865-57-0; tributylphosphine, 998-40-3; methyl disulfide, 624-92-0; 2-cyclohexen-1-one, 930-68-7; 2-cyclopentenone, 930-30-3; *trans*-3-octen-2-one, 18402-82-9; methyllithium, 917-54-4; butyllithium, 109-72-8; *tert*-butyllithium, 594-19-4; copper(I) thiocyanate, 1111-67-7; (*S*)-3-methylcyclohexanone, 24965-87-5; (*R*)-3-methylcyclohexanone, 13368-65-5; (*S*)-3-butylcyclohexanone, 72746-41-9; (*S*)-3-*tert*-butylcyclohexanone, 57287-85-1; (2*R*,3*R*)-(−)-2,3-butanediol, 24347-58-8.

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An ab Initio Study on $(C_5H_5V)_2C_8H_8$

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Abstract: The bonding in the organometallic compound μ-(η^5:η^5-cyclooctatetraene)bis[(η^2-cyclopentadienyl)vanadium] involves a complex mixture of metal–metal and metal–ligand contributions. Although there is a direct V–V 3d interaction, it is not as strong as a double bond with some triple bond character as has been suggested based upon experiment. The balance between metal–metal and metal–ligand bonding results in the appearance of a low-lying triplet state which retains the V–V 3d bonding. A small singlet–triplet separation is consistent with the change in magnetic properties with temperature.

I. Introduction

The organometallic compound $(C_5H_5V)_2C_8H_8$ has been synthesized and its structure determined,[1] see Figure 1. The two V atoms are bonded to a common C_8H_8, group, and this constrains the V–V distance to be relatively short. The measured V–V bond length of 2.44 Å (compared to 2.62 Å in bulk V[2]) is sufficiently

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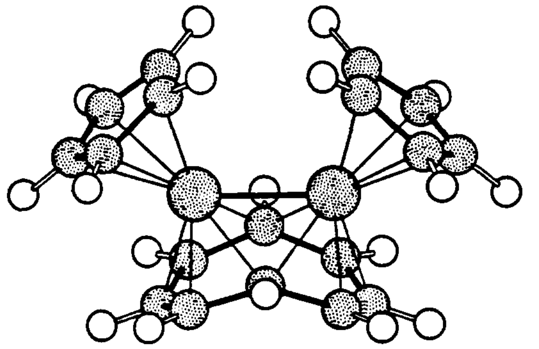

Figure 1. The geometry of the $(C_5H_5V)_2C_8H_8$ molecule.

short to have been interpreted as a V–V double bond with some triple bond character. An interesting feature of this molecule is that the magnetic properties indicate a singlet ground state, with a very low-lying triplet state, which becomes populated as the temperature is increased.[3] However, this low-lying triplet state would seem to imply weak V–V bonding since one of the V–V bonds is so easily broken. Weak V–V bonding would suggest that the short V–V distance is a result of the ligand ring holding the vanadium atoms in place. The fact that the bond length in the diatomic molecule V_2 is 1.76 Å[4] and that the 3d–3d overlap drops off rapidly with distance, also suggests that the V–V bond might be even weaker than a double bond. To resolve the questions about the metal–metal bonding, we have investigated the 3d–3d bonding in the $(C_5H_5V)_2C_8H_8$ system by using ab initio self-consistent-field (SCF) wave functions.

II. Method of Calculation

The V basis set is derived from the (12s6p4d) primitive set of Roos, Veillard, and Vinot[5] and is contracted to [8s4p2d]. To this, the two diffuse p functions of Wachters[6] are added; these p functions as well as the two most diffuse s functions are multiplied by 1.5 to make them more suitable for describing the molecular system. The diffuse 3d function of Hay[7] is also added. This produces a V basis of the form (12s8p5d)/[8s6p3d]. The C basis set is a [4s2p] contraction of the (7s3p) primitive set of van Duijneveldt.[8] For H a (3s)/[2s] basis set is used.[8] Even though these basis sets are only slightly better than double-ζ for each atom, for a system with 38 atoms the total number (304) of contracted functions is rather large. The problems with integral storage are avoided by using the DISCO direct SCF approach,[9] where the integrals are computed as needed to construct the Fock matrix on each interaction. Presently this approach is limited to the SCF level. Since an accurate description of transition-metal–transition-metal 3d–3d bonding requires extensive electron correlation, we restrict ourselves to qualitative questions concerning the nature of the bonding. The structure is fixed at the experimental[1] geometry, see Figure 1.

The SCF approach used here is expected to be more accurate than less expensive empirical methods such as extended Hückel. Although semiempirical approaches can yield insight into the bonding, they may also miss effects that can be observed in ab initio SCF calculations. For example, Hoffmann and co-workers[10] were able to show that there was no direct Fe–Fe bond in $Fe_2(CO)_9$ and to identify the bridging CO π interaction as the bonding mechanism. However, subsequent SCF calculations[11] have also found a bridging CO 5σ effect. Hence the ab initio SCF approach applied to $(C_5H_5V)_2C_8H_8$ is expected to delineate the important contributions to the bonding.

Table I. Symmetry Properties of the V 3d Orbitals with Respect to the V–V Bonding in $(C_5H_5V)_2C_8H_8$[a]

	a_1 Symmetry	
$3d\sigma^b(2x^2-y^2-z^2)$	$3d\delta(y^2-z^2)$	$3d\pi(xz)$
	a_2 Symmetry	
$3d\delta^*(yz)$	$3d\pi^*(xy)$	
	b_1 Symmetry	
$3d\sigma^*(2x^2-y^2-z^2)$	$3d\delta^*(y^2-z^2)$	$3d\pi^*(xz)$
	b_2 Symmetry	
$3d\delta(yz)$	$3d\pi(xy)$	

[a] The V atoms are on the x axis. The z axis is the C_2 axis in the C_{2v} point group. [b] We use $C_{\infty v}$ notation about the V–V axis for the 3d orbitals; however, in the molecule all 3d orbitals in the same symmetry are allowed to mix.

The usual view[12] of the bonding in these sandwich compounds is that the metal atom becomes charged, donating the valence 4s electrons to the ligand π system. Then, there is an interaction between the ligand π orbitals and the empty d orbitals of the metal. In this view, there is no 4s or 4p involvement in the bonding, thus basis functions would not be needed to describe the 4s and 4p orbitals. Because the 4s and 4p orbitals are diffuse, they can lead to basis set superposition errors. They also lead to a large overlap contribution, which is hard to definitively assign in the Mulliken population analysis. Thus, elimination of these basis functions would simplify the analysis of the bonding in these systems. However, an SCF calculation on ferrocene[13] shows a 4s population of 0.23 electrons, which persists at the CI level, see Table III in ref 14. (Also note that in ref 13 the exponents to describe the 4p orbitals were not included in the basis). Other organometallic systems[11,15,16] also show reasonably large valence 4s/4p populations. It has been shown[16] that these metal valence populations are not necessarily an artifact of the SCF approximation. While the contribution of these diffuse 4s and 4p functions is small, on the order of 0.3 eV, they are not zero. Therefore, in this work, we consider basis sets with and without the valence 4s and 4p functions. The basis set without the 4s/4p valence functions, denoted no4s4p, should accurately portray the bonding if there were no 4s and 4p involvement in the bonding, while the full basis set, in spite of the problems described above, describes the system if the metal retains any valence charge. In this work we find that the difference between the two descriptions is reasonably small, especially for the 3d populations, which greatly facilitates the analysis of the bonding.

III. Results and Discussion

Upon the basis of the bonding in other organometallic ring systems,[12] we consider the zeroth order description of the bonding to be the donation of the 4s valence electrons to the ring π orbitals. This would lead to a charged system with two V^{2+}, two $(C_5H_5)^-$, and a $(C_8H_8)^{2-}$ subunit. The ligand π systems would have $4n + 2$ electrons. The ligand σ electrons are not expected to be involved in the metal–ligand bonding, and V 1s–3p electrons are not expected to be involved in either the V–V or vanadium–ligand bonding. Combining the ligand occupation and the vanadium cores (i.e., all but the six V 3d electrons) leads to an occupation of

$$...28a_1^2 14a_2^2 25b_1^2 16b_2^2 \qquad (1)$$

The occupation of the 3d electrons depends upon both the V–V

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Table II. The Computed Separations between the Low-Lying States[a]

Full Basis Set	
${}^1A_1 \ldots 29a_1^2 14a_2^2 26b_1^2 17b_2^2$	*b*
${}^1A_1 \ldots 30a_1^2 14a_2^2 25b_1^2 17b_2^2 (26b_1^2 \rightarrow 30a_1^2)$	3.61 eV
${}^1A_1 \ldots 30a_1^2 13a_2^2 26b_1^2 17b_2^2 (14a_2^2 \rightarrow 30a_1^2)$	6.05 eV
No 4s4p Basis Set	
${}^1A_1 \ldots 29a_1^2 14a_2^2 26b_1^2 17b_2^2$	*c*
${}^1A_1 \ldots 30a_1^2 14a_2^2 25b_1^2 17b_2^2 (26b_1^2 \rightarrow 30a_1^2)$	3.75 eV
${}^1A_1 \ldots 30a_1^2 13a_2^2 26b_1^2 17b_2^2 (14a_2^2 \rightarrow 30a_1^2)$	6.53 eV
${}^3A_2 \ldots 30a_1^1 14a_2^1 26b_1^2 17b_2^2 (14a_2^1 \rightarrow 30a_1^1)$	1.85 eV
${}^3B_1 \ldots 30a_1^1 14a_2^2 26b_1^1 17b_2^2 (26b_1^1 \rightarrow 30a_1^1)$	−1.09 eV

[a] The total occupation and excitation relative to the lowest closed-shell occupation are given. [b] Total energy −2576.1823 Hartree. [c] 0.96 eV above the same occupation using the full basis set.

bonding and the metal–ligand bonding. As noted above, the ionic model is only the zeroth order description; there is also ligand π to empty 3d donation. Thus it becomes advantageous to doubly occupy the 3d orbitals, both to form V–V bonds and make empty orbitals suitable for ligand-to-metal donation. Therefore six high spin coupled atomiclike 3d orbitals are very unfavorable. Since the experimental bond distance has been interpreted as showing a double bond with some triple bond character, it appears that the V–V bonding may be more important than the metal–ligand bonding in determining the ground-state occupation, so we first considered only the V–V bonding aspect. Since the 3dδ–3dδ overlap is much smaller than either the 3dσ–3dσ or 3dπ–3dπ overlaps, if a triple bond forms, it must be a σ and two π bonds. From the symmetry properties of the V 3d orbitals with respect to V–V bonding (see Table I), the six V 3d bonding electrons would occupy two a_1 orbitals and a b_2 orbital, yielding an overall occupation of

$$\ldots 30a_1^2 14a_2^2 25b_1^2 17b_2^2 \tag{2}$$

However, the orbital energies of the SCF wave function clearly show that this is not the lowest closed shell singlet state, but rather that the occupation (3)

$$\ldots 29a_1^2 14a_2^2 26b_1^2 17b_2^2 \tag{3}$$

should yield a lower singlet state. In the SCF approximation, occupation (3) is indeed favored by 3.61 eV relative to (2), see Table II, even though occupation (3) has a 3d–3d anti-bonding orbital occupied, instead of a metal–metal bonding orbital. The reason that (3) is favored over (2) is the ligand–metal interaction. The $17b_2$(3dπ) and $29a_1$(3dσ) orbitals are approximately parallel to the plane of the ligands, and as such should be less strongly affected by metal–ligand interactions than the $30a_1$(3dπ) orbital. The ground state of the ligand negative ions have a total of four occupied π orbitals of a_1 symmetry so it becomes unfavorable to occupy two V 3d orbitals of a_1 symmetry. This leads to the favoring of (3) over (2).

Upon the basis of the orbital energies of (2) and (3), the only other candidate for the ground state is

$$\ldots 30a_1^2 13a_2^2 26b_1^2 17b_2^2 \tag{4}$$

This occupation arises as a double excitation (relative to occupation (2) from $14a_2$, a ligand orbital, to a 3d–3d bonding orbital. However, this occupation still has a 3d–3d anti-bonding orbital occupied as in occupation (3). The SCF energy for occupation (4) is in fact higher than for the states arising from occupations (2) and (3), which is again consistent with the orbital energies.

Table III. Populations for an Individual Vanadium Atom in the $(C_5H_5V)_2C_8H_8$ Complex Decomposed by Symmetry

	Full Basis Set ${}^1A_1$ State	
a_1	3dπ(xz) = 0.64	3dδ + 3dσ^a = 0.32
b_1	3dπ^*(xz) = 0.47	3dδ^* + 3dσ^* = 0.20
bond order[b]	3dπ(xz) = 0.17	net 3dδ + 3dσ = 0.12
a_2	3dπ^*(xy) = 0.04	3dδ^*(yz) = 0.19
b_2	3dπ(xy) = 0.45	3dδ(yz) = 0.18
bond order	3dπ(xy) = 0.41	3dδ(xy) = −0.01
	Total Populations	
4s[a] = 0.01 net[c] = 1.87	4p = 0.61	3d = 2.50
	no4s4p Basis Set ${}^1A_1$ State	
a_1	3dπ(xz) = 0.68	3dδ + 3dσ^a = 0.40
b_1	3dπ^*(xz) = 0.58	3dδ^* + 3dσ^* = 0.33
bond order	3dπ(xz) = 0.10	3dδ + 3dσ = 0.07
a_2	3dπ^*(xy) = 0.14	3dδ^*(yz) = 0.23
b_2	3dπ(xy) = 0.48	3dδ(yz) = 0.30
bond order	3dπ(xy) = 0.34	3dδ(yz) = 0.07
	Total Populations	
4s[a] = 0.15 net[c] = 1.75	4p[d] = −0.03	3d = 3.13
	no4s4p Basis Set ${}^3B_1$ State	
a_1	3dπ(xz) = 0.52	3dδ + 3dσ^a = 0.98
b_1	3dπ^*(xz) = 0.13	3dδ^* + 3dσ^* = 0.34
bond order	3dπ(xz) = 0.39	3dδ + 3dσ = 0.64
a_2	3dπ^*(xy) = 0.11	3dδ^*(yz) = 0.24
b_2	3dπ(xy) = 0.43	3dδ(yz) = 0.31
bond order	3dπ(xy) = 0.32	3dδ(yz) = 0.07
	Total Populations	
4s[a] = 0.24 net[c] = 1.73	4p[d] = −0.02	3d = 3.05

[a] The 3s component of the 3d basis functions is included in the calculation; however, the totally symmetric component is projected out, and its contribution is added to the s population. [b] The bond order is computed as the difference in the total occupation of the bonding orbital minus the anti-bonding population divided by two. Note that since the occupations are given per V, the bond order appears as the difference between bonding and anti-bonding orbitals. [c] The net charge on V. [d] Contribution from the remaining p functions other than those used to describe the 4p orbital.

Mulliken populations for the two basis sets with and without 4s and 4p functions are summarized in Table III. Since the lowest closed-shell state has an occupation which involves occupying a 3d–3d anti-bonding orbital instead of a 3d–3d bonding orbital, we analyze the bonding in more detail. The relative order and separations between the three states arising from occupations (2), (3), and (4) are the same in both basis sets. Thus we can compare the populations in the two basis sets for the lowest ${}^1A_1$ state arising from closed shell occupation, (3). The net charge on the V atoms is close to 2+ for both basis sets. The elimination of the 4s and 4p basis functions naturally results in the elimination of the 0.61 electron 4p population, although the 4s population increases to 0.15 by making use of the 3s component of the 3d basis functions. However, this 0.50 electron reduction of the 4s–4p population does not result in an increased charge on the metal atom as in other systems,[11,15,16] since the 3d populations are increased by more than is lost in the 4s–4p. The change in the 3d population is not collected into one orbital but rather spread over all ten orbitals. Thus, the relatively small changes in the individual 3d and in the net populations between the two different basis sets suggests that, while it is difficult to determine the true contribution of either the 4s or 4p orbitals, the 3d bonding can be analyzed based on the populations.

The total metal–metal bonding population minus the total anti-bonding population divided by two is one way to estimate the bond order. The bond order varies from 0.58 in the no4s4p basis set to 0.69 in the full basis set. These populations indicate that the V–V bonding is complex, since the V–V interaction and the metal–ligand interaction both involved the V 3d orbitals, with the 3d occupations determined as a compromise between the metal–metal and metal–ligand interaction. Thus it is possible to lower the energy of the system by exciting from a V–V bonding orbital into a V–V anti-bonding orbital, if the V–V anti-bonding orbital has metal–ligand bonding character. The V 3d(xy) orbitals are approximately parallel to the planes of the ligands and might therefore be expected to have the smallest metal–ligand interaction. Thus it would be best to analyze the bonding in this orbital only in terms of metal–metal bonding. In fact, the 3dπ(xy) bond order of 0.41 in the full basis or 0.34 in the no4s4p basis is the largest of any of the 3d orbitals. If one assumes that all the bonding orbital occupations contribute to metal–ligand bonding, the V–V bond order would be between 1.59 and 1.86. Thus our minimum estimate of the V–V bond order comes from the difference between bonding and anti-bonding populations and is 0.58, while our upper estimate, based only on the bonding populations, is 1.86 V–V bonds. Thus the calculations support the interpretation of the experiment that direct V–V bonding exists but suggest that it is not as strong as a V–V double bond with some triple bond character.

Since the experiments show the presence of a low-lying triplet state, we have also considered two triplet states arising from single excitations into the $30a_1$ V–V bonding orbital, by using only the no4s4p basis set. The $^3B_1$ state arising from the single excitation $26b_1 \rightarrow 30a_1$ is considerably lower than the $^3A_2$ state arising from $14a_2 \rightarrow 30a_1$. The $^3B_1$ state arises from moving a V–V anti-bonding electron into a V–V bonding orbital, while the $^3A_2$ state arises from moving a ligand electron into a V–V bonding orbital. As in the case of the closed-shell occupations, exciting from the ligand orbital is less favorable. The $26b_1^1 \rightarrow 30a_1^1$ excitation leads to a state lower in energy than the lowest closed-shell occupation (3). SCF wave functions do not describe closed-shell singlet and triplet states equally well. This is a result of the singlet state having one more doubly occupied orbital than the triplet. A rule of thumb is that each electron pair has about one eV more correlation energy than a pair of high spin coupled-open shell electrons. Therefore, the one extra bonding pair of electrons in the singlet state will lead to about one eV more correlation in the singlet state. Thus with the inclusion of correlation, it is expected that the $^1A_1$ and $^3B_1$ states would be very close in energy. By comparing these calculations with experiment[1,3] it is highly likely that the $^1A_1$ state from occupation (3) is the ground state and the $^3B_1$ state is the triplet state that causes a change in the magnetic properties with increased temperature. The $26b_1^1 \rightarrow 30a_1^1$ excitation moves an electron from an orbital which is metal–metal anti-bonding and metal–ligand bonding, into an orbital which is metal–metal bonding. This suggests a similar magnitude for the energetics for the two bonding mechanisms. Thus, the presence of a low-lying triplet state does not suggest that the V–V bonding is weak and that a V–V bond is breaking. In fact the V–V bonding character is probably increasing, (compare the bond orders for the two states in Table III) and the bonding in this system is rather a complex balance between V–V and vanadium–ligand bonding.

IV. Conclusions

The calculations show that there is a direct V–V 3d bond. However, the interaction is complex because of the 3d involvement in both the metal–metal and metal–ligand bonding. Therefore, 3d orbitals which are V–V anti-bonding can be occupied if at the same time they are vanadium ligand bonding. This leads to the lowest closed-shell occupation, while the occupation which arises by only considering V–V 3d interactions is 3.6 eV higher. The low-lying triplet state does not arise by breaking a weak metal–metal bond but rather by promoting an electron from a metal–ligand bonding orbital into a metal–metal orbital.

Reactions of Carbon Monoxide with Trimethylsilyl and Tris(trimethylsilyl)silyl Derivatives of Group 4 Metals. Synthesis, Characterization, and Reactivity of Silaacyl Complexes

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Abstract: The new silyl derivatives $Cp_2M[Si(SiMe_3)_3]Cl$ ($Cp = \eta^5\text{-}C_5H_5$; **3**, M = Zr; **4**, M = Hf), $Cp_2ClZr(\mu\text{-}O)ZrCp_2[Si(SiMe_3)_3]$ (**5**), and $Cp_2Zr[Si(SiMe_3)_3]SiMe_3$ (**6**) are prepared by reaction of $(THF)_3LiSi(SiMe_3)_3$ with the appropriate metal halide. The compounds $Cp_2Zr[Si(SiMe_3)_3]BH_4$ (**7**) and $Cp_2Zr[Si(SiMe_3)_3]Me$ (**8**) are obtained from reaction of **3** with $LiBH_4$ and MeMgBr, respectively. Reaction of $Cp_2Zr(SiMe_3)Cl$ (**1**) with carbon monoxide provides the silaacyl $Cp_2Zr(\eta^2\text{-}COSiMe_3)Cl$ (**9**) and the first observation of carbon monoxide insertion into a transition-metal–silicon bond. Complex **9** is isolated in 90% yield and has been characterized by its spectral properties and crystal structure, which establishes bidentate ligation of the silaacyl group. Crystals of **9** belong to space group $P2_1/n$, with $a = 9.7608$ (12) Å, $b = 12.8694$ (16) Å, $c = 12.6837$ (15) Å, $\beta = 91.074$ (10)°, $V = 1593.0$ (6) Å^3, and $Z = 4$. In contrast, carbonylation of **3** does not yield an isolable silaacyl complex. Carbonylation of **6** and **8** produce the acyl derivatives $Cp_2Zr(\eta^2\text{-}COSiMe_3)[Si(SiMe_3)_3]$ (**11**) and $Cp_2Zr(\eta^2\text{-}COMe)[Si(SiMe_3)_3]$ (**12**), respectively. The titanium silyl $Cp_2Ti(SiMe_3)Cl$ reacts cleanly with carbon monoxide by an apparent ligand-induced reductive elimination to produce $Cp_2Ti(CO)_2$ and Me_3SiCl. Compound **9** does not react with pyridine but with $2,6\text{-}Me_2C_6H_3NC$; the ketenimine complex $Cp_2Zr[OC(SiMe_3)(CN\text{-}2,6\text{-}Me_2C_6H_3)]Cl$ (**14**), characterized in solution, is formed. Complex **9** reacts with $LiOCMe_3$ via decarbonylation to give $Cp_2Zr(SiMe_3)(OCMe_3)$. Electrophiles $Me_3SiOSO_2CF_3$ or $MeOSO_2CF_3$ react with **9** to afford $Cp_2Zr(\eta^2\text{-}COSiMe_3)(OSO_2CF_3)$ and Me_3SiCl or MeCl, respectively. Protonation of **11** with benzoic acid produces the benzoate complex $Cp_2Zr[Si(SiMe_3)_3](\eta^2\text{-}O_2CPh)$ (**16**). Insertion of the isocyanide $2,6\text{-}Me_2C_6H_3NC$ into the Zr–Si bonds of **1** and **3** occurs readily to give $Cp_2Zr[\eta^2\text{-}C(N\text{-}2,6\text{-}Me_2C_6H_3)SiMe_3]Cl$ (**17**) and $Cp_2Zr[\eta^2\text{-}C(N\text{-}2,6\text{-}Me_2C_6H_3)Si(SiMe_3)_3]Cl$ (**18**), respectively. The Zr–Si bond of **1** is cleaved rapidly by H_2 to give $[Cp_2ZrHCl]_n$ and $HSiMe_3$. Compound **6** reacts similarly with H_2 to afford $HSiMe_3$ and $HSi(SiMe_3)_3$ quantitatively. No reactions were observed between **1** and ethylene, phenylacetylene, benzonitrile, carbon dioxide, or carbon disulfide nor between **3** and phenylacetylene, 4-methoxybenzonitrile, or phenyl isocyanate.

Numerous unsaturated molecules are catalytically or stoichiometrically reduced by transition-metal–silane systems.[1-4] The degree to which insertions into M–Si bonds contribute to this reactivity is unclear, since few insertions involving metal–silicon