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Electronic Structure of Piano Stool Dimers. 4. Electronically Induced Changes in the Electrophilic and Nucleophilic Reactions and the Conformations of a Series of Isovalent Hydrocarbyl-Bridged Complexes[1]

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Abstract: The electronic structures of a series of piano stool dimer complexes of formulation $Cp_2M_2(EO)_m(\mu\text{-}L)$ (M = Mn, Fe, Co; E = C, N; m = 2–4; L = CH_2, CH^+) have been investigated via nonempirical Fenske–Hall molecular orbital calculations. The very different reactivities of two of these complexes, $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ and $[CpRh(CO)]_2(\mu\text{-}CH_2)$, toward acids is explained through the available charge and/or orbital-controlled pathways that are allowed. Thus, each of these is predicted to undergo charge-controlled protonation at the methylene carbon, but only the Rh system has a sterically available HOMO to allow orbital-controlled protonation at the metal–metal bond. Implications of these conclusions on the protonation chemistry of $[CpMn(CO)_2]_2(\mu\text{-}CH_2)$ are discussed as are the reactions with other electrophiles. The differences in the reactivities of two methylidyne-bridged diiron complexes, $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CH)^+$ and $[CpFe]_2(\mu\text{-}NO)_2(\mu\text{-}CH)^+$, toward nucleophiles are also explained by consideration of their available unoccupied orbitals. For the latter complex, the electronically driven preference for bridging rather than terminal nitrosyls is discussed.

The wide variety of transition metals and ligand systems that form stable piano stool dimer complexes $[(\eta^n\text{-}C_nH_n)ML_m]_2(\mu\text{-}L')_p$ has resulted in these compounds being the subject of many experimental investigations. While there has been much research directed toward understanding the synthesis and reaction chemistry of these dimer systems, far less is known about the bonding and electronic structure of these compounds. Recently we have been utilizing approximate molecular orbital theory to investigate the electronic structure of dimeric piano stool complexes containing organic bridging units. We are primarily interested in ascertaining the influence of electronic structure upon the diverse geometric conformations and chemical reactivities observed for these complexes. Thus far, our studies have focused exclusively on the piano stool dimers of iron having the general formula $Cp_2Fe_2(CO)_3(\mu\text{-}L)_n$ (Cp = $\eta^5\text{-}C_5H_5$) where L = an organic ligand and n = 0 and 1.[1,3,4] Through the use of MO calculations we have been successful in explaining some of the observed conformations, fluxional processes, and reactivities (thermal and photochemical) displayed by compounds within this series. In this paper we extend this approach to a wider class of piano stool dimers, isovalent to the iron carbonyl system mentioned above, which fit the general formula $Cp_2M_2(EO)_m(\mu\text{-}L)$ where M = Mn, Fe, Co; E = C, N; m = 2–4; and L = CH_2, CH^+. Within this class of compounds exists a wide variety of structures and reactivities, which we feel could be better understood through a detailed examination of their bonding via molecular orbital theory.

In our most recent work, we demonstrated how altering bridging units on the same bimetallic framework ($[CpFe(CO)]_2(\mu\text{-}CO)$) sufficiently affected the electronic structure of these compounds to cause changes in their reactivity patterns.[1] Here we will concentrate on just two hydrocarbyl fragments (CH_2, CH^+) and allow them to bridge a variety of bimetallic frameworks. In this way, we will be able to investigate the electronic perturbations resulting from changing the metal and/or ancillary ligands and study the effects of these perturbations on the reactivity of the hydrocarbyl bridge. We will then use these results to predict the existence and probable reactivity of similar, but as yet unknown, piano stool dimers.

Computational Details

Molecular orbital calculations were done on an IBM 3081-D computer system using the Fenske–Hall nonempirical approximate MO method[5] and employing a fragment analysis (vide infra). All atomic basis functions were generated by using the method of Bursten, Jensen, and Fenske.[6] Contracted double-ζ representations were used for the metal 3d AO's and for the C, N, and O 2p AO's. An exponent of 1.16 was used for the hydrogen 1s AO's.[7] The basis functions for Mn, Fe, and Co were derived for the +1 oxidation state with the 4s exponents fixed at 2.0, 2.0, and 2.2, respectively, and the 4p exponents fixed at 1.8, 1.8, and 2.0, respectively. The carbonyl and nitrosyl 3σ and 6σ orbitals as well as the lowest three occupied cyclopentadienyl orbitals and all virtual orbitals above the e_2'' level were deleted from the basis transformation sets.[8]

In all calculations, the cyclopentadienyl rings were idealized to local D_{5h} symmetry and all C–H bond lengths were set at 1.08 Å. The structure assumed in the calculation of the methylene-bridged iron dimer $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ was reported in our earlier paper.[1] The structures for the other two methylene-bridged dimers, $[CpMn(CO)_2]_2(\mu\text{-}CH_2)$[9] and $[CpCo(CO)]_2(\mu\text{-}CH_2)$,[10] were taken from their crystal structures and idealized to C_s symmetry. The structures used for the model complexes $[CpCo(CO)]_2(\mu\text{-}CH_2)(\mu\text{-}L)^{n+}$ (L = H, n = 1; L = CH_2, n = 2) were constructed by using the interatomic angles of $[Cp^*Rh(CO)]_2(\mu\text{-}CH_2)_2^{2+}$[11] ($Cp^*$ = $\eta^5\text{-}C_5Me_5$) and bond lengths from $[CpCo(CO)]_2(\mu\text{-}CH_2)$[10] and idealizing the structures to C_{2h} symmetry for L = CH_2 and to C_2 for L = H. The bond lengths and angles used for the specific bridges are the following: for L = H, Co–H = 1.50 Å; for L = CH_2, Co–C = 1.9225 Å, H–C–H = 109.47°.

Since no $[CpFe(NO)]_2(\mu\text{-}CR_2)$ derivatives have been structurally characterized, the structural parameters assumed for the

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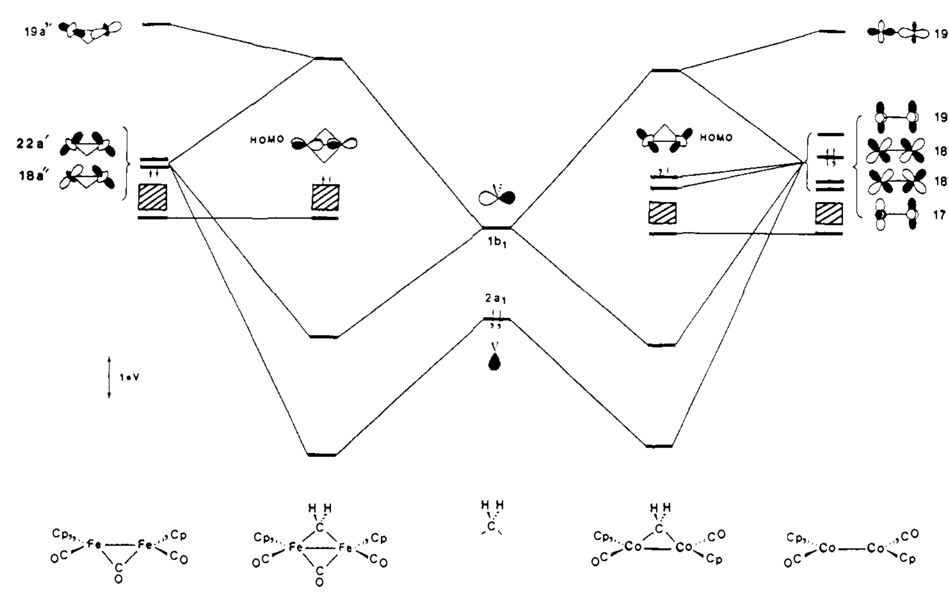


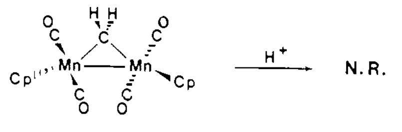
Figure 1. Comparative molecular orbital diagrams showing the formation of $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ and $[CpCo(CO)]_2(\mu\text{-}CH_2)$ via the interaction of the orbitals of CH_2 with those of the $[CpFe(CO)]_2(\mu\text{-}CO)$ and $[CpCo(CO)]_2$ frameworks.

model complex $[CpFe(NO)]_2(\mu\text{-}CH_2)$ were derived by using the interatomic angles of the isoelectronic, and in all likelihood, isostructural complex $[CpCo(CO)]_2(\mu\text{-}CH_2)$,[10] setting the bond lengths at Fe–Fe = 2.531 Å, Fe–C(Cp) = 2.109 Å, Fe–N = 1.745 Å, N–O = 1.153 Å, and Fe–(CH_2) = 1.987 Å, and idealizing the geometry to C_2 symmetry. The geometry of this framework was unchanged in the calculation of $[CpFe(NO)]_2(\mu\text{-}CH_2)^+$ with the exception of the Fe–C(CH) bond, which was set at 1.917 Å. These bond lengths were then held constant in the calculation of $[CpFe]_2(\mu\text{-}NO)_2(\mu\text{-}CH)^+$ except for the Fe–N and N–O distances, which were set at 1.917 and 1.181 Å, respectively, and the geometry idealized to C_{2v} symmetry.

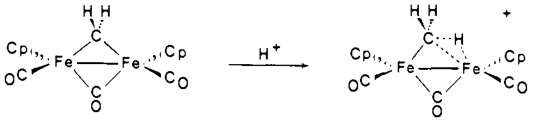
The structure assumed for the model complex $[CpMn(CO)_2]_2(\mu\text{-}CH)^+$ was derived from the structure of the corresponding methylene-bridged dimer[9] with the Mn–C(CH) bond length set at 1.955 Å. Likewise, the structure assumed for the model complex $[Cp_2Mn_2(NO)(CO)](\mu\text{-}NO)(\mu\text{-}CH)^+$ was taken from the crystal structure of $[Cp_2Mn_2(NO)(CO)](\mu\text{-}NO)(\mu\text{-}CO)$[12] with the Mn–C(CH) bond length set at 1.906 Å.

Protonation Reactions

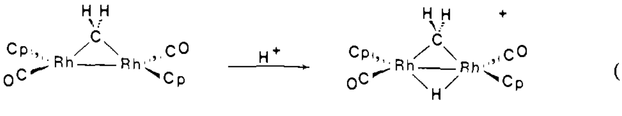
Methylene-bridged piano stool dimers have been shown to react with protonic acids in a variety of ways. For example, the treatment of three isovalent methylene-bridged dimers containing only carbonyl and cyclopentadienyl ligands with noncoordinating acids results in three apparently different reactions (eq 1–3).



(1)



(2)



(3)

Herrmann et al. found that treatment of the methylene-bridged dimanganese complex with acids such as HBF_4 or CF_3SO_3H resulted in no isolable products or apparent reactivity (eq 1).[13] In the case of the methylene-bridged iron dimer, however, Casey and co-workers discovered that protonation resulted in the formation of an agostic, asymmetrically methyl-bridged cation (eq 2).[14] We have previously described the electronic effects governing the bonding and observed fluxionality of the methyl bridge.[4] Yet, a third type of reactivity was observed when Herrmann and co-workers treated the methylene-bridged rhodium dimer with a noncoordinating acid (eq 3).[15] Rather than yielding a methyl-bridged complex, as in the diiron complex, the isolated cationic product contained both bridging methylene and bridging hydride ligands.

Although eq 1–3 seem to indicate very different reactivities of methylene-bridged complexes with acids, we believe it is likely that the products of these reactions are dictated by the electronic structural demands of the parent dimers. In contemplating this possibility, it is important to keep two considerations in mind: (1) In examining the reactants for the preferred site(s) of protonation, we will be determining the *kinetically* favored products; however, the isolated products are most probably the *thermodynamically* favored ones, which may or may not correspond to the kinetic products. (2) The methylene bridge may confer electronic and structural demands on the dimers that are not present with other bridging ligands, such as carbonyls. Hence, in the course of discussing the chemistry of the methylene-bridged complexes, we shall compare it to that of their carbonyl-bridged congeners.

Equations 2 and 3 describe protonation reactions that yield isolable protonated products. In both cases, the reactions are readily reversible, indicating that the products are most likely the thermodynamic ones. In examining these reactions, the following questions come to mind: (1) Why in one case is the product protonated at the methylene bridge while in the other one it is protonated at the metal–metal bond? (2) Is there an electronic driving force controlling the site selectivity? (3) Is there any relationship between the observed thermodynamic product and the kinetically favored site of attack? We will first address the electronic structures of the two methylene-bridged reactants, which should give an indication of the preferred site of initial protonation. Figure 1 shows the frontier orbital interactions of each dimer framework with a methylene fragment. Only the dimer framework orbitals that are of proper symmetry to interact with bridging fragments are depicted pictorially. The derivations of the frontier orbitals of the $[CpM(CO)]_2(\mu\text{-}CO)$ and $[CpM(CO)]_2$ frameworks

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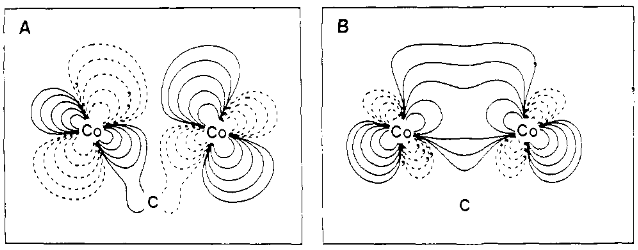


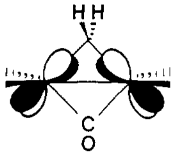
Figure 2. Contour diagrams of the second-highest (A) and highest (B) occupied molecular orbitals of $[CpCo(CO)]_2(\mu\text{-}CH_2)$.

were detailed in a separate contribution;[1] hence, they will not be discussed here. On the left half of Figure 1 is shown the interaction of $[CpFe(CO)]_2(\mu\text{-}CO)$ with a CH_2 bridge. This interaction diagram was also presented in the previous paper; therefore, the details of the electronic structure will not be discussed at length except to emphasize the strong interaction of the filled iron-based framework orbital 18a″ with the empty CH_2 π ($1b_1$) orbital, resulting in a transfer of electron density from the framework to the methylene carbon (Mulliken population of the CH_2 $1b_1$ orbital = 1.11e).[16] It is also noteworthy that the HOMO of the resulting methylene-bridged iron dimer is an Fe–Fe π^* orbital oriented perpendicular to the Fe–CH_2 plane and localized on the iron atoms.

The right half of Figure 1 displays the frontier orbital description of the cobalt analogue of the methylene-bridged rhodium complex.[17] The interaction of the $[CpCo(CO)]_2$ framework with a methylene moiety results in a somewhat different electronic picture than was found for the iron dimer. The cobalt dimer framework contains a group of four closely spaced orbitals (17b, 18a, 18b, 19a), all of which are of the correct symmetry to interact with the orbitals of a methylene bridge. The ligation of a single bridging ligand, in this case CH_2, causes these orbitals to mix, resulting in four new hybrid orbitals. Two of the four hybrids interact strongly with the CH_2 occupied σ ($2a_1$) and empty π ($1b_1$) orbitals while the other two hybrids remain as nonbonding orbitals. The Mulliken population of the CH_2 $1b_1$ orbital in $[CpCo(CO)]_2(\mu\text{-}CH_2)$ is 1.17e, indicating even more efficient back-bonding and a higher degree of electron density being transferred to the methylene carbon than in the case of the iron dimer. This results in a greater negative charge associated with the carbon atom of the methylene bridge ($q_C = -0.62$ for $[CpCo(CO)]_2(\mu\text{-}CH_2)$ and $q_C = -0.52$ for $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$). The two nonbonding hybrids are directed toward the "empty" bridge position and ultimately become the HOMO and SHOMO of the methylene-bridged cobalt dimer. As we will discuss shortly, it is the presence of these two "high-energy" orbitals, particularly the mirror-symmetrical HOMO, that influences the chemistry of this complex.

This electronic description of $[CpCo(CO)]_2(\mu\text{-}CH_2)$ is similar to that obtained by Hofmann on the analogous $[CpRh(CO)]_2(\mu\text{-}CH_2)$ from extended Hückel theory.[18] Contour plots of the HOMO and SHOMO as calculated by the extended Hückel method greatly resemble those obtained from Fenske–Hall calculations, which are shown in Figure 2. Most important, the HOMO calculated by either method is the symmetrical nonbonding orbital directed toward the empty bridge position.[19]

We believe there is an intimate connection between the above descriptions of the electronic structures of $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ and $[CpCo(CO)]_2(\mu\text{-}CH_2)$ and the protonation reactions in eq 2 and 3. The site of protonation can depend either on the nature and accessibility of the HOMO (orbital control) or on the most negatively charged site in the molecule (charge control). In the methylene-bridged iron dimer, the HOMO is a π^* orbital localized on the Fe atoms, and it is oriented in the same plane as the Cp and terminal CO ligands. The orientation of this orbital makes it sterically inaccessible to the proton; therefore, we believe that this reaction is charge controlled, causing the proton to attack the most negative site, i.e. the methylene carbon. It is important to note that although orbital-controlled electrophilic attack (protonation, in this case) is generally considered to be directed by the HOMO of the species undergoing attack, it is conceivable that a different high-energy filled orbital could play a role in such reactivity. In the case of $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$, there is a block of five occupied metal-based orbitals that lie close in energy to the HOMO. The most sterically accessible of these orbitals is the Fe–Fe π-type orbital directed toward the $\mu\text{-}CH_2$ ligand



This metal-based orbital remains high in energy since the $\mu\text{-}CH_2$ ligand has no orbital of appropriate symmetry and energy to interact with and stabilize it. Therefore, it appears that if this orbital were to contribute to the site selectivity of protonation, it would direct it toward the metal center, but more importantly, to the side of the molecule that has the methylene bridge. It is also apparent, given the observed product, that we believe that the kinetic site of protonation leads to the thermodynamically most favored product. We will discuss this point shortly.

Inasmuch as the protonation of the iron dimer is charge controlled, the rhodium dimer presents a fascinating comparison of charge vs. orbital control. As noted above, the methylene carbon of the cobalt analogue to the rhodium dimer is calculated to be even more negative than that of the iron dimer, a factor that would seem to favor charge control in the protonation of $[CpRh(CO)]_2(\mu\text{-}CH_2)$. However, as also noted above, the HOMO of this dimer is a readily accessible orbital that is directed toward the empty bridging position, thus indicating that, unlike the iron dimer, orbital control is certainly possible. The thermodynamic product is the result of protonating the HOMO to yield a symmetric μ-hydrido bridged dimer. While it may be the case that protonation occurs directly at the HOMO to yield the product, there is strong chemical evidence for either a more complex or a competitive mechanism for protonation. Herrmann et al. have found that treatment of $[CpRh(CO)]_2(\mu\text{-}CH_2)$ with D^+ leads to the formation of the thermally labile complex $[CpRh(CO)]_2(\mu\text{-}CH_2)(\mu\text{-}D)^+$.[15] Treatment of this complex with base converts it back to the neutral methylene-bridged precursor, and under either slow or rapid deprotonation, deuterium is incorporated into the methylene ligand. This rapid $\mu\text{-}CH_2/\mu\text{-}H$ exchange might occur via an equilibrium between $[CpRh(CO)]_2(\mu\text{-}CH_2)(\mu\text{-}H)^+$ and $[CpRh(CO)]_2(\mu\text{-}CH_3)^+$; Herrmann et al. have postulated that protonation occurs at the Rh–Rh bond (orbital control), followed by a rapid equilibration with the $\mu\text{-}CH_3$ isomer.[15] This is certainly a reasonable proposal in view of the electronic structure of the neutral dimer. An alternative explanation, which also is consistent with our calculations, would be the competition between protonation at the Rh–Rh bond and at one of the Rh–CH_2 bonds, i.e. a kinetic competition between the two sites. The resolution of this mechanistic problem awaits further experimental and theoretical studies.

Protonation of $[CpRh(CO)]_2(\mu\text{-}CH_2)$ leads to the formation of $[CpRh(CO)]_2(\mu\text{-}CH_2)(\mu\text{-}H)^+$ as the exclusive product; the cationic μ-methyl complex proposed above has not been directly

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(16) If the bridging methylene ligand is formally considered to be a dianion (CH_2^{2-}) rather than a neutral ligand, as it often is, then the π electron transfer would be from the occupied methylene $1b_1$ orbital to the now empty 18a″ orbital of $[CpFe(CO)]_2(\mu\text{-}CO)^{2+}$. The final picture of the Fe–CH_2–Fe bonding will be the same.

(17) The calculation was performed on the Co compound analogue rather than the Rh compound in order to provide a more direct comparison to the Fe systems. Calculations on the Rh complex yield results that are very similar to those for the Co complex.

(18) Hofmann, P. *Angew. Chem.* **1979**, *91*, 591–593; *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 554–556.

(19) Although it may seem at first that the metal–metal bonding HOMO should be at lower energy than the metal–metal antibonding SHOMO, it is the effect of the methylene bridge on these orbitals that causes this apparent energy reversal. The CH_2 $2a_1$ orbital destabilizes the HOMO, while the CH_2 $1b_1$ orbital stabilizes the SHOMO.

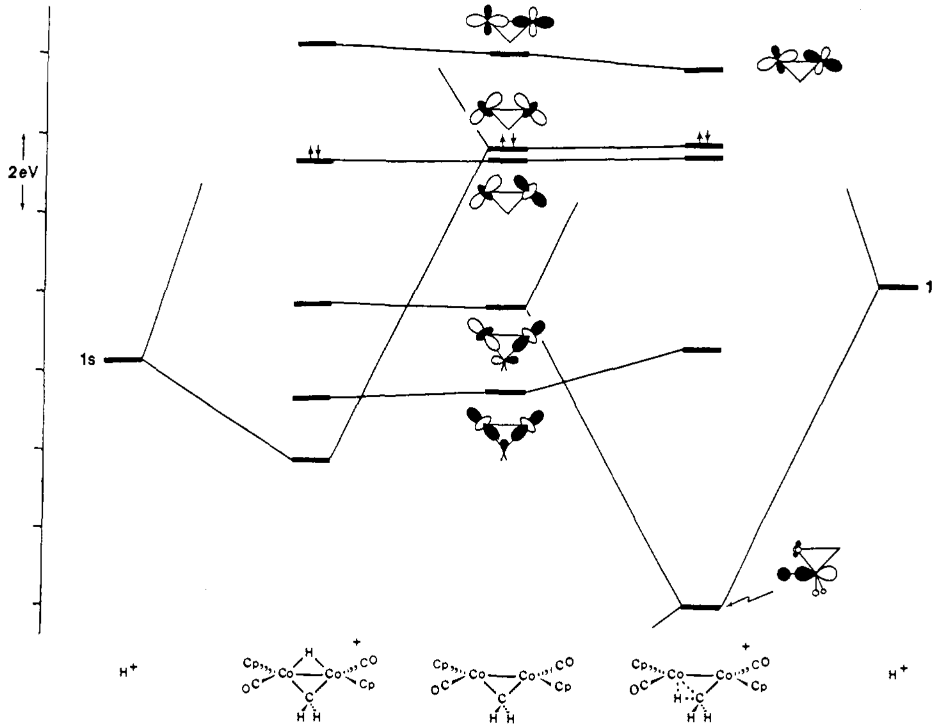

Figure 3. Abbreviated molecular orbital diagram showing the important orbital interactions involved in the formations of $[CpCo(CO)]_2(\mu\text{-}CH_2)(\mu\text{-}H)^+$ and $[CpCo(CO)]_2(\mu\text{-}CH_3)^+$ from $[CpCo(CO)]_2(\mu\text{-}CH_2)$ and H^+.

observed. It is of interest to compare the electronic structures of the two possible products, namely $[CpRh(CO)]_2(\mu\text{-}CH_2)(\mu\text{-}H)^+$ and $[CpRh(CO]_2(\mu\text{-}CH_3)^+$. Figure 3 is an abbreviated MO diagram for the Co analogues of these cationic complexes, showing the principal interactions that occur when H^+ interacts with either the Co–Co or Co–CH_2 bond of $[CpCo(CO)]_2(\mu\text{-}CH_2)$. In the former case, a classic three-center, two-electron Co–H–Co bond is formed between the H 1s orbital and the HOMO of $[CpCo(CO)]_2(\mu\text{-}CH_2)$. In a purely formal sense, this may be viewed as a transfer of the two electrons from the HOMO of $[CpCo(CO)]_2(\mu\text{-}CH_2)$ to the proton, leading to the "usual" description of hydrogen as an anionic ligand. The large orbital stabilization observed and the removal of electrons from the HOMO of the neutral dimer are both favorable factors for the formation of the μ-H complex.

When H^+ is allowed to interact with a Co–CH_2 bond to form the asymmetrically methyl-bridged complex $[CpCo(CO)]_2(\mu\text{-}CH_3)^+$, several effects are noted. First, the hydrogen interacts primarily with the methylene carbon to form a strong C–H bond. To achieve this, there is severe rehybridization of both of the metal–methylene bonding orbitals, resulting in a nearly pure C–H bond and a Co–C σ bond involving principally only one of the Co atoms. These interactions are contained in the lowest two orbitals shown for the μ-CH_3 complex in Figure 3. Somewhat surprisingly, and in contrast to what was seen for $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CH_3)^+$,[4] the agostic interaction of the C–H bond is very small, and the resultant MO of $[CpCo(CO)]_2(\mu\text{-}CH_3)^+$ contains less than 5% Co character. As was the case for the μ-H dimer, this rearrangement of the metal-based orbitals is consistent with the formal two-electron oxidation of the dicobalt framework; however, in this case, two electrons are transferred from one of the lower lying Co–CH_2 bonding orbitals to the methyl group rather than from the nonbonding HOMO. In addition, the Co–CH_3 σ bonding orbital is slightly destabilized and the LUMO is slightly stabilized by this rehybridization, and as a result, the HOMO–LUMO separation decreases.

In the absence of calculated total energies for the two protonated species, it is not possible to determine which is more thermodynamically stable. However, since the μ-CH_3 product is never actually observed, it appears that the stabilization of a high-energy metal-based orbital upon protonation at the metal–metal bond is, in this case, favored over the formation of a C–H bond resulting from protonation at the μ-CH_2 ligand.

The apparent competition between orbital and charge control in $[CpRh(CO)]_2(\mu\text{-}CH_2)$ prompted us to investigate further whether this possibility exists for the protonation of $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$. Accordingly, we have calculated the electronic structure of the hypothetical $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CH_2)(\mu\text{-}H)^+$ cation, the presumed product of protonation of the Fe–Fe bond by analogy to that in the dirhodium system. In order to achieve any sizable interaction between the proton and the Fe–Fe bond, the parent dimer had to be severely distorted; we found a reasonable interaction only if the dihedral angle between the Fe–CH_2–Fe and Fe–CO–Fe planes was substantially reduced, in this case from the observed[20] 164 to 120°. Even in this case, the HOMO of the complex cannot interact with the proton and little orbital stabilization results. It is apparent that "tying up" the appropriate metal-based orbitals with additional ligands (the μ-CO in the case of the diiron complex) precludes their interaction with electrophiles. In fact, piano stool dimers of the type $[CpML]_2(\mu\text{-}L)_2$ seem only able to form μ-H products if the bridging ligands transform to terminal ones. $[CpFe(CO)]_2(\mu\text{-}CO)_2$ reacts with strong acids to form $[CpFe(CO)_2]_2(\mu\text{-}H)^+$ in which there are no bridging carbonyl ligands.[21] More recently, Heinekey and Chinn have structurally characterized $[CpRu(CO)(PMe_3)]_2(\mu\text{-}H)^+$ and have found only terminal ligands and a nonbonding Ru–Ru distance of 3.06 Å.[22] Treatment of the cation with base yields the ligand-bridged, metal–metal bonded dimer $[CpRu(PMe_3)]_2(\mu\text{-}CO)_2$, which has a Ru–Ru bond length of 2.75 Å.[23] Similar results are seen for isoelectronic nitrosyl-containing $[CpML_2]_2(\mu\text{-}H)^+$ systems; both $[CpRe(CO)(NO)]_2(\mu\text{-}H)^{+\,24}$ and $[CpW(NO)_2](\mu\text{-}H)^{+\,25}$ contain only terminal ligands and probably do not possess metal–metal bonds. In all of these $[CpML_2]_2(\mu\text{-}H)^+$ systems, the M–H–M bond is probably best described as a

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(20) Crystal structure of *cis*-$[CpFe(CO)]_2(\mu\text{-}CO)_2$: Bryan, R. F.; Greene, P. T.; Newlands, M. J.; Field, D. S. *J. Chem. Soc. A* **1970**, 3068–3074.

(21) Legzdins, P.; Martin, D. T.; Nurse, C. R.; Wassink, B. *Organometallics* **1983**, *2*, 1238–1244, and references therein.

(22) Chinn, M. S.; Heinekey, D. M. *Abstracts of Papers*, 191st National Meeting of the American Chemical Society, New York, NY; American Chemical Society: Washington, DC, 1986; INOR 357.

(23) Heinekey, D. M.; Graham, W. A. G.; Ball, R., unpublished result.[24]

(24) Graham, W. A. G., personal communication, Dec 19, 1986.

(25) Hames, B. W.; Legzdins, P. *Organometallics* **1982**, *1*, 116–124.

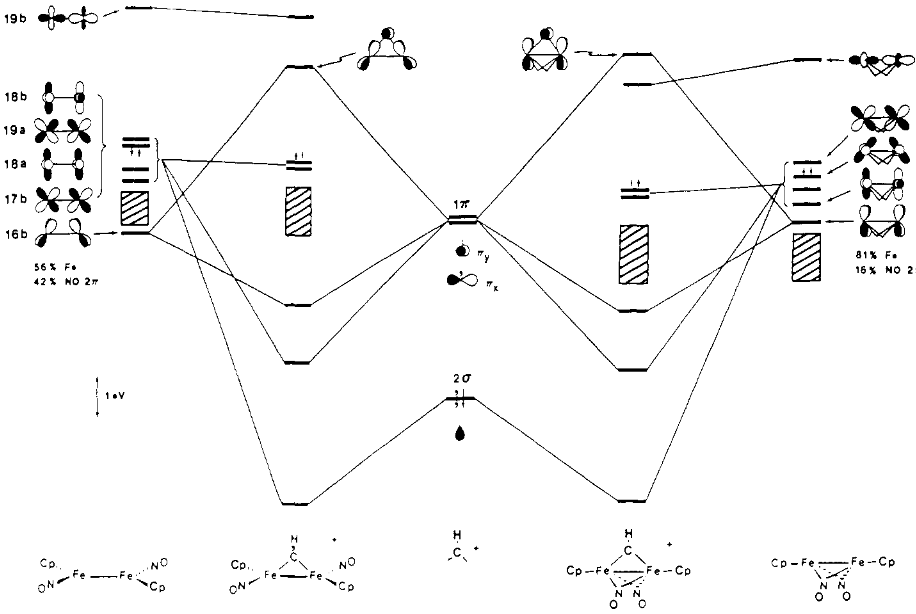

Figure 4. Comparative molecular orbital diagrams of $[CpFe(NO)]_2(\mu\text{-}CH)^+$ and $[CpFe]_2(\mu\text{-}NO)_2(\mu\text{-}CH)^+$.

three-center, two-electron interaction between two 17-electron $CpML_2$ fragments and a proton, in analogy with other non-metal–metal bonded, hydrido-bridged systems.[26] If $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$ were to react with H^+ in an analogous fashion to $[CpFe(CO)]_2(\mu\text{-}CO)_2$, the methylene ligand would be required to adopt a terminal conformation. Although bridge-to-terminal conversion is a facile process for carbonyl ligands, it is much less common (and, presumably, much less favored) for the CH_2 ligand,[27] and thus this mode of reactivity is not possible.

The unfavorable situation described above for the addition of H^+ to the M–M bond of $[CpML]_2(\mu\text{-}L)_2$ could be alleviated if one of the bridging ligands were removed, thus yielding $[CpML]_2(\mu\text{-}L)$ and freeing the orbital necessary to react with the proton. This is indeed the case for $[CpFe(NO)]_2(\mu\text{-}CH_2)$, a complex that is isoelectronic with $[CpCo(CO)]_2(\mu\text{-}CH_2)$. MO calculations on $[CpFe(NO)]_2(\mu\text{-}CH_2)$ indicate that the HOMO and SHOMO are very similar to those of $[CpCo(CO)]_2(\mu\text{-}CH_2)$, and the replacement of the carbonyls with nitrosyls (and the concomitant replacement of Co with Fe) does not affect these orbitals markedly. Although the protonation of $[CpFe(NO)]_2(\mu\text{-}CH_2)$ has not been studied as extensively as the Co system, Herrmann and co-workers have found that the protonation of the second-row analogue, $[CpRu(NO)]_2(\mu\text{-}CH_2)$, does indeed give the hydride-bridged cation $[CpFe(NO)]_2(\mu\text{-}CH_2)(\mu\text{-}H)^+$.[28]

Finally, it is not clear from an electronic standpoint why no isolable products are obtained when $[CpMn(CO)_2]_2(\mu\text{-}CH_2)$ is treated with acids (eq 1).[13] The HOMO of this complex, reported earlier by Lichtenberger et al.[29] and reconfirmed by our calculations, is an antibonding orbital similar to that found for $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CH_2)$. Like that of the Fe dimer, the HOMO of the Mn dimer is sterically inaccessible, and the formation of $[CpMn(CO)_2]_2(\mu\text{-}CH_2)(\mu\text{-}H)^+$ is not possible. As in the other methylene-bridged dimers discussed above, however, the bridging carbon is the most negative site in the manganese complex ($q_C = -0.53$), and hence it would not be unreasonable to expect proton attack at this carbon. Calculations on the hypothetical $[CpMn(CO)_2]_2(\mu\text{-}CH_3)^+$ cation in which the methyl bridge was allowed to adopt both the symmetrical and asymmetrical conformations indicate that the asymmetric bridge is favored. Both conformations achieve less stabilization from the agostic interaction than was found for $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CH_3)^+$,[4] however, and are thus probably less stable thermodynamically than the iron system. Therefore, although a methyl bridge would be expected kinetically, perhaps it is its thermodynamic instability with respect to $[CpMn(CO)_2]_2(\mu\text{-}CH_2) + H^+$ that prevents its formation. If this is the case, the treatment of $[CpMn(CO)_2]_2(\mu\text{-}CH_2)$ with D^+ might lead to H/D exchange even though the methyl bridge itself is unstable. This exchange reaction has not been attempted to our knowledge. In addition, given the enhanced stability of $Cp_2Fe_2(\mu\text{-}dppm)(\mu\text{-}CO)(\mu\text{-}CH_3)^+$ over $Cp_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}CH_3)^+$,[30] it is possible that the substitution of more basic ligands (such as phosphines) for the carbonyls in $[CpMn(CO)_2]_2(\mu\text{-}CH_2)$ could generate a more basic dimer and allow the methyl-bridged complex to be isolated.

Reactions of Other Electrophiles

As discussed above, there are still unanswered questions concerning the kinetically favored site of protonation of $[CpRh(CO)]_2(\mu\text{-}CH_2)$. There is, however, additional evidence that the HOMO of this complex can be directly attacked by electrophiles (although it may not be the favored site). Faraone et al. have investigated the reactions of electrophiles with $Cp_2Rh_2(\mu\text{-}dppm)(\mu\text{-}CO)$.[31] This dirhodium complex is electronically similar to $[CpRh(CO)]_2(\mu\text{-}CH_2)$ and has virtually the same HOMO. The reaction of $Cp_2Rh_2(\mu\text{-}dppm)(\mu\text{-}CO)$ with the electrophiles H^+, $AuPPh_3^+$, and AgO_2CCH_3 yields, in each case, $Cp_2Rh_2(\mu\text{-}dppm)(\mu\text{-}CO)(\mu\text{-}E)$, structurally analogous to $[CpRh(CO)]_2(\mu\text{-}CH_2)(\mu\text{-}H)^+$. This reactivity is not surprising since all three electrophiles have a LUMO of σ symmetry that can interact strongly with and stabilize the nonbonding HOMO of the rhodium dimer. Charge-controlled electrophilic addition to $Cp_2Rh_2(\mu\text{-}dppm)(\mu\text{-}CO)$ would dictate attack of the carbonyl oxygen atom, and while this cannot be ruled out,[32] there is no evidence that it occurs.

None of the three electrophiles discussed above has an empty orbital of π symmetry that would be needed to interact favorably

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(26) See, for example: Bau, R.; Teller, R. G.; Kirtley, S. W.; Koetzle, T. F. *Acc. Chem. Res.* **1979**, *12*, 176–183, and references therein.

(27) (a) Herrmann, W. A.; Bauer, C. *Organometallics* **1982**, *1*, 1101–1102. (b) Messerle, L.; Curtis, M. D. *J. Am. Chem. Soc.* **1982**, *104*, 889–891.

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(29) Calabro, D. C.; Lichtenberger, D. L.; Herrmann, W. A. *J. Am. Chem. Soc.* **1981**, *103*, 6852–6855.

(30) Dawkins, G. M.; Green, M.; Orpen, A. G.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1982**, 41–43.

(31) (a) Schiavo, S. L.; Bruno, G.; Francesco, N.; Piraino, P.; Faraone, F. *Organometallics* **1985**, *4*, 2091–2096. (b) Schiavo, S. L.; Bruno, G.; Piraino, P.; Faraone, F. *Organometallics* **1986**, *5*, 1400–1404.

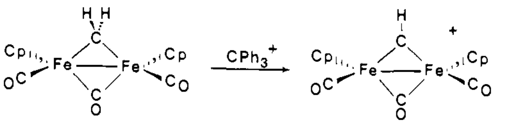
(32) Piano stool dimers such as $[CpFe(CO)]_2(\mu\text{-}CO)_2$ have been shown to interact with *strong* Lewis acids (such as AlR_3) at the oxygen atoms of the bridging carbonyl ligands. See, for example: Nelson, N. J.; Kime, N. E.; Shriver, D. F. *J. Am. Chem. Soc.* **1969**, *91*, 5173–5174.

with the SHOMO of either $Cp_2Rh_2(\mu\text{-dppm})(\mu\text{-CO})$ or $[CpRh(CO)]_2(\mu\text{-CH}_2)$; therefore, the SHOMO remains nonbonding. However, an electrophile containing two unoccupied orbitals of appropriate energy, one of σ and one of π symmetry, should be able to stabilize both the HOMO and SHOMO of either dimer. The CH_2^{2+} fragment satisfies these requirements. One could imagine removing two electrons from the CH_2 fragment in Figure 1 to yield empty $2a_1$ and $1b_1$ orbitals, each energetically near the nonbonding HOMO and SHOMO of either dimer and of the correct symmetries to interact with and stabilize these orbitals. Consistent with this analysis, Maitlis and co-workers have prepared and structurally characterized such a complex,[11] namely $[Cp^*Rh(CO)]_2(\mu\text{-CH}_2)_2^{2+}$, which may be formally considered as the result of electrophilic addition of CH_2^{2+} to $[Cp^*Rh(CO)]_2(\mu\text{-CH}_2)$.

This analogy can just as easily be extended to transition-metal fragments.[33] The neutral 14-electron fragments $Ni(CO)_2$ and Cp_2Ti have frontier orbital configurations resembling that of CH_2^{2+}, i.e. both metal fragments contain empty, low-lying σ and π orbitals. This should enable either fragment to interact favorably with the HOMO and SHOMO of $[CpCo(CO)]_2(\mu\text{-CH}_2)$ (or one of its electronically equivalent analogues). A common synthetic ploy used in the preparation of trimers containing two cobalt triad metal atoms has been the exploitation of the electron-rich metal–metal double bond of $Cp_2M_2(\mu\text{-CO})_2$ (M = Co, Rh, Ir) to which unsaturated (16-electron) fragments can be added.[34] Our calculations suggest that similar use could be made of the high-energy HOMO and SHOMO of the $[CpM(CO)]_2(\mu\text{-L})$ (M = Co, Rh) complexes in the synthesis of transition-metal clusters.

Hydride Abstraction Reactions

In our previous paper, we examined the electronic effects involved in the reaction of $[CpFe(CO)]_2(\mu\text{-CO})(\mu\text{-CH}_2)$ with CPh_3^+, which results in a net hydride abstraction from the methylene bridge to produce a methylidyne-bridged cation (eq 4).[14] An isovalent dimer results when the three carbonyl ligands are replaced with two nitrosyl ligands to yield $[CpFe(NO)]_2(\mu\text{-CH}_2)$. Casey and Roddick found that, under the correct conditions, the reaction of $[CpFe(NO)]_2(\mu\text{-CH}_2)$ with CPh_3^+ also yielded a methylidyne-bridged cation as one of the products (eq 5).[35]



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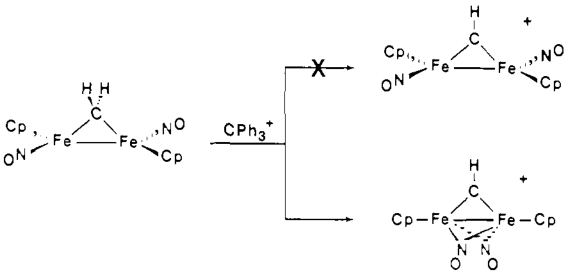
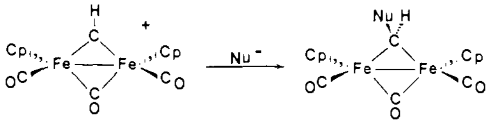


(5)

Interestingly, infrared spectroscopy indicated that the nitrosyl ligands change conformation from terminal to bridged upon hydride abstraction to form the methylidyne product. Moreover, in direct contrast to the iron carbonyl methylidyne dimer,[36] the methylidyne carbon of the iron nitrosyl methylidyne dimer does not undergo nucleophilic addition (eq 6 and 7); rather, the complex shows no reaction or decomposes when treated with nucleophiles.[35]



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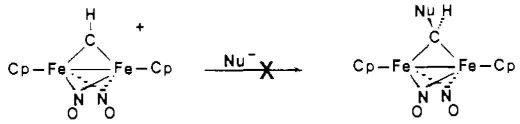

(7)

Inasmuch as the replacement of three carbonyls by two nitrosyls can induce great changes in electronic structure, it seems likely that the differences between the carbonyl- and nitrosyl-containing dimers are electronic in origin. Therefore, we will attempt to elucidate an electronic driving force responsible for the bridging of the nitrosyl ligands in the methylidyne complex and to provide an explanation for its lack of reactivity with nucleophiles.

The methylene-bridged dimer $[CpFe(NO)]_2(\mu\text{-CH}_2)$ has been shown spectroscopically to contain linear terminal nitrosyl ligands, while the methylidyne-bridged dimer $[CpFe]_2(\mu\text{-NO})_2(\mu\text{-CH})^+$ apparently contains bridging nitrosyl ligands. Why does the CH^+ moiety prefer a geometry with bridging nitrosyls? To answer this, let us compare the molecular orbital diagrams for a methylidyne-bridged dimer in the two possible geometries, i.e. one with two linear nitrosyls and one with two bridging nitrosyls. These are shown in Figure 4.

The replacement of a CH_2 bridge with a CH^+ bridge changes the fragment orbital picture in one important respect: The LUMO of the CH^+ moiety is a doubly degenerate set of π orbitals, including the $1\pi_y$ orbital, which is perpendicular to the Fe–CH–Fe plane and has no counterpart in the CH_2 fragment. We will show that the presence of this orbital ultimately determines the geometry of the complex. The terminal nitrosyl framework (left side of Figure 4) is isoelectronic to the cobalt carbonyl framework shown in Figure 1 and contains a similar group of four orbitals (17b, 18a, 18b, 19a), which are of the correct symmetry to interact with bridging fragments. Coordination of the CH^+ bridge causes these four orbitals to mix, producing two orbitals that interact strongly with the CH^+ 2σ and $1\pi_x$ orbitals and two orbitals that remain as the nonbonding HOMO and SHOMO. In the bridging nitrosyl geometry (right side of Figure 4), the framework orbital $13a_1$ interacts with the CH^+ 2σ, while the $8b_1$ and $9b_1$ framework orbitals mix to yield one orbital that interacts with the CH^+ $1\pi_x$ and a nonbonding orbital that becomes the SHOMO of the complex. As was alluded to earlier, the most important new interaction is that of the CH^+ $1\pi_y$ orbital with the dimer frameworks. In the terminal nitrosyl geometry the CH^+ $1\pi_y$ is of appropriate symmetry to interact with the 16b orbital. However, the geometry of the terminal nitrosyl complex dictates that those d orbitals that can interact strongly with the CH^+ $1\pi_y$ orbital can (and will) also interact strongly with the NO 2π orbitals. That this is the case is evident in the population analysis of the fragment 16b orbital; the orbital contains nearly as great a contribution from the NO 2π orbitals (42%) as from the Fe 3d orbitals (56%). Thus, in the terminal geometry, the CH^+ $1\pi_y$ and the NO 2π orbitals are competing for the *same* Fe 3d orbitals. In the bridging nitrosyl geometry, the CH^+ $1\pi_y$ orbital interacts almost exclusively with the $8b_2$ orbital of the framework. In contrast to the case for the terminal NO geometry, the $8b_2$ orbital, by virtue of the geometry, is much more localized on the Fe 3d orbitals (81%) and contains a relatively small (16%) contribution from the NO 2π orbitals. Hence, by achieving a conformation in which the NO ligands bridge, the competition for the Fe 3d orbitals between the CH^+ $1\pi_y$ and NO 2π orbitals is mitigated, resulting, in particular, in a stronger interaction between the CH^+ $1\pi_y$ orbital and the dinuclear framework. We will see next how this strong CH^+ $1\pi_y$ interaction affects the chemistry of the complex, particularly at the methylidyne carbon.

A variety of nucleophiles react with the μ-methylidyne complex $[CpFe(CO)]_2(\mu\text{-CO})(\mu\text{-CH})^+$, resulting in addition to the methylidyne carbon atom in all cases.[36] We have previously proposed that this reactivity is dependent upon the nature of the LUMO,

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[33] Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729–1742.

[34] See, for example: Cirjak, L. M.; Huang, J.; Zhu, Z.; Dahl, L. F. *J. Am. Chem. Soc.* **1980**, *102*, 6623–6626.

[35] Casey, C. P.; Roddick, D. M. *Organometallics* **1986**, *5*, 436–438.

[36] (a) Casey, C. P.; Fagan, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 4950–4951. (b) Casey, C. P.; Fagan, P. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 7360–7361.

J. Am. Chem. Soc. 1987, 109, 6059-6067

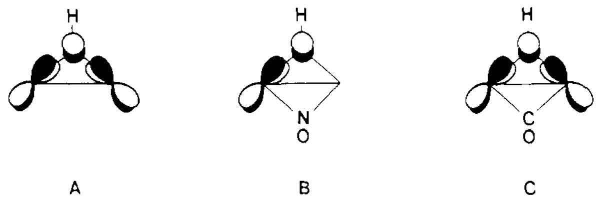

Figure 5. Lowest unoccupied molecular orbitals of (A) $[\mathrm{CpMn(CO)_2}]_2(\mu\text{-CH})^+$, (B) $[\mathrm{Cp_2Mn_2(CO)(NO)}](\mu\text{-NO})(\mu\text{-CH})^+$, and (C) $[\mathrm{CpFe(CO)}]_2(\mu\text{-CO})(\mu\text{-CH})^+$.

which for $[\mathrm{CpFe(CO)}]_2(\mu\text{-CO})(\mu\text{-CH})^+$ is essentially an energetically isolated $p\pi$ orbital localized on the methylidyne carbon and oriented perpendicular to the Fe–CH–Fe plane. This orbital is easily accessible to nucleophiles. Looking once again at Figure 4, the interaction of the $\mathrm{CH^+}$ $1\pi_y$ orbital with the $[\mathrm{CpFe}(\mu\text{-NO})]_2$ framework $8b_2$ orbital is strong enough that the antibonding counterpart (the orbital that is analogous to the LUMO of $[\mathrm{CpFe(CO)}]_2(\mu\text{-CO})(\mu\text{-CH})^+$) is pushed above the Fe–Fe σ^* orbital. Therefore, the LUMO here is not a primarily $\mathrm{CH^+}$-based orbital but rather is localized on the Fe atoms and directed along the metal–metal bond, thereby making this orbital sterically inaccessible and preventing facile nucleophilic addition.

The fact that $[\mathrm{CpFe}(\mu\text{-NO})]_2(\mu\text{-CH})^+$ does not react with nucleophiles, and in particular alkenes, is disappointing since it was hoped the "hydrocarbation" reactions exhibited by $[\mathrm{CpFe(CO)}]_2(\mu\text{-CO})(\mu\text{-CH})^{+\,37}$ could be duplicated in a different system. This reaction is an important model of catalytic processes since it involves carbon–carbon bond formation between small organic fragments on a transition-metal dimer. Since we now understand what is required electronically for such reactivity, perhaps we can make use of this to predict what other bimetallic frameworks could form stable methylidyne-bridged complexes capable of exhibiting "hydrocarbation" reactivity. Calculations performed on two other (to our knowledge unknown) piano stool dimers indicate that they may provide the necessary electronic properties to induce such reactivity: $[\mathrm{CpMn(CO)_2}]_2(\mu\text{-CH})^+$ and $[\mathrm{Cp_2Mn_2(CO)(NO)}](\mu\text{-NO})(\mu\text{-CH})^+$. The LUMO's calculated for each of these complexes are shown in Figure 5, along with the LUMO of $[\mathrm{CpFe(CO)}]_2(\mu\text{-CO})(\mu\text{-CH})^+$. The similarity of the LUMO's of the two methylidyne-bridged manganese complexes with the iron dimer LUMO makes these compounds electronically well suited for similar reactivity with nucleophiles.

Acknowledgment. We gratefully acknowledge Dr. C. P. Casey, Dr. D. M. Roddick, Dr. W. A. G. Graham, and Dr. D. M. Heinekey for stimulating discussions and results prior to publication. R.H.C. is grateful for a Presidential Fellowship from The Ohio State University Graduate School.

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Magic Angle Spinning NMR Studies of Silicon Carbide: Polytypes, Impurities, and Highly Inefficient Spin–Lattice Relaxation

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Abstract: Silicon carbide polytypes give distinctive ^{29}Si and ^{13}C MAS NMR spectra that can be related to the number and types of lattice sites present, which differ in their next-nearest-neighbor environment. It is shown that only four next-nearest-neighbor silicon (and carbon) environments are possible in crystalline silicon carbide regardless of polytype. A local-site designation system is developed for these and related to the various existing polytype designation systems. Carbon and silicon sites are isostructural, and the almost exact mirror-image relationship between ^{29}Si and ^{13}C chemical shifts of the 6H polytype indicates that the same structural factors determine chemical shifts of both nuclei. ^{13}C spin–lattice relaxation times can be extremely long and can differ considerably for nonequivalent lattice sites in the same sample, detracting from the reliability of ^{13}C MAS NMR as a tool for polytype studies. In the extreme case of cubic silicon carbide a ^{13}C signal has not yet been detected under a range of conditions that do give ^{29}Si spectra, consistent with ^{13}C spin diffusion being far less efficient than spin diffusion among the more abundant ^{29}Si atoms. Due to the long T_1's of atoms in crystalline silicon carbide sites, minor short T_1 impurities can be selectively detected by rapid pulsing, with little interference from signals of the bulk crystalline material. Hydrofluoric acid washing modifies the ^{29}Si short T_1 impurity signals to varying extents in different samples, indicating that they arise in part from surface oxide species.

The structure of silicon carbide is simultaneously very simple and very complex. All forms of silicon carbide are based on the diamond structure, with both silicon and carbon tetrahedral and with alternating silicon and carbon atoms. The basic structural types (polymorphs) are therefore hexagonal α–SiC (wurtzite structure) and cubic β–SiC (zinc blende structure). However, silicon carbide distinguishes itself from diamond in having many crystalline α–SiC modifications called polytypes.[1] These arise from the numerous possible stacking sequences of the silicon and carbon layers. The resulting unit cells have the same dimensions in two directions but differ in the third (the stacking direction.) A few short-period polytypes are stable under definite thermodynamic conditions; their transformations have been studied.[2] However, it is often observed that many different polytypes grow under the same conditions of temperature and pressure, several polytypes sometimes occurring side by side in the same crystal.[1]

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(1) Verma, A. R.; Krishna, P. *Polymorphism and Polytypism in Crystals*; Wiley: New York, 1966.

(2) Jepps, N. W.; Page, T. F. In *Crystal Growth and Characterization of Polytype Structures*; Krishna, P., Ed.; Pergamon; Oxford, 1983; pp 259–307.

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