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Bonding of methyl groups in dinuclear complexes: terminal, symmetrically bridging, or asymmetrically bridging?

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ters[34-38] by the absence of the fifth M–M bond.

An alternative way of describing the cluster geometry is as a pentagonal bipyramid with two RuL_n fragments, two CR groups, and one NR group in the equatorial plane and two rutheniums in the axial positions. Such a description is consistent with the skeletal electron pair bonding rules which predict a closo seven-vertex cluster when eight skeletal electron pairs are present.[39]

Regarding the trapping reaction itself, the conversion, which occurs under very mild conditions, results in loss of one CO from III. From other studies[9] III (formed in situ as in this study) was found to react with CO to form $Ru_3(NH)(CO)_{10}$ and $PPN[Ru_5N(CO)_{14}]$. Consistent with this, the other two observed products in reaction 2 are $Ru_3(NH)(CO)_{10}$ and $PPN[Ru_5N(CO)_{14}]$; each in small amounts. Conceptually, the addition of the acetylene to III is easy to describe as an insertion of the C≡C into the hinge M—M bond of the cluster. Concomitant unfolding of the wings of the butterfly allow the acetylene to be stabilized by direct interaction with all four metals.

In conclusion, the trapping of $Ru_4(NH)(CO)_{12}$ (III) with diphenylacetylene has allowed the structural characterization of a stable product. Consistent with the mild reaction conditions, the structure of $Ru_4(NH)(PhCCPh)(CO)_{11}$ can be traced back to the structure proposed for III through a small number of steps. This new cluster contains an imido ligand in the novel tetrabridging bonding geometry. The NH group has been implicated as a surface-bound intermediate in the Haber process and in the decomposition of hydrazine.[40] The structure of $Ru_4(NH)(PhCCPh)(CO)_{11}$ can serve as a model for an NH group bound to a fourfold site, just as the recent structures with μ_3-NH ligands[9,13-16] model imido groups binding to threefold surface sites.

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Registry No. I, 92845-78-8; V, 100927-92-2; diphenylacetylene, 501-65-5; Ru, 7440-18-8.

Supplementary Material Available: Listings of crystallographic data, the positional and thermal parameters, and the structure factors (31 pages). Ordering information is given on any current masthead page.

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On the Bonding of Methyl Groups in Dinuclear Complexes: Terminal, Symmetrically Bridging, or Asymmetrically Bridging?

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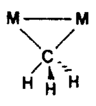
Summary: The electronic factors leading to the bridging of methyl ligands in dinuclear complexes have been investigated by using Fenske–Hall molecular orbital calculations. $[CpFe(CO)]_2(\mu\text{-}CO)(\mu\text{-}Me)^+$ (Cp = η^5-C_5H_5), which contains an agostic, asymmetrically bridging methyl group, is found to have a favorable interaction between one of the methyl C–H bonds and the iron atom to which the methyl group is not terminally bound. The asymmetric methyl bridge is slightly favored over a nonagostic, symmetric bridge for the Fe dimer.

The recognition that alkyl ligands in polynuclear complexes can bond in bridging as well as terminal fashion has resulted in much research into the synthesis and reactivity of complexes containing bridging alkyl ligands. The methyl moiety is known to adopt at least three types of bridging conformations: a symmetric pyramidal bridge (1),[2] a symmetric planar bridge (2),[3] and an asymmetric bridge (3).[4] Casey et al. prepared one of the first dimers containing an asymmetric methyl bridge (5) via protonation of the corresponding methylene-bridged complex 4 (eq 1).[4b] This type of bridge is of particular interest in that it contains an agostic M···H···C interaction which represents a possible intermediate in C–H bond activation processes.[5] Although this class of compounds is rapidly growing, little is known about the electronic demands which lead to their formation. In this communication we report the first theoretical description of an agostic methyl-bridged dimer, using 5 as our model. Further, it will be shown that for this system the asymmetric bridge is preferred over either a terminal or symmetrically bridging methyl ligand.



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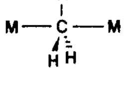

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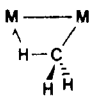

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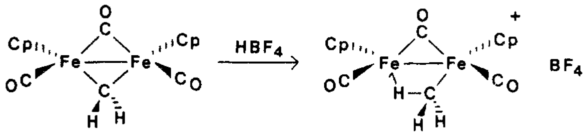

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The calculations were performed by using the Fenske–Hall molecular orbital method.[6] Figure 1 depicts the

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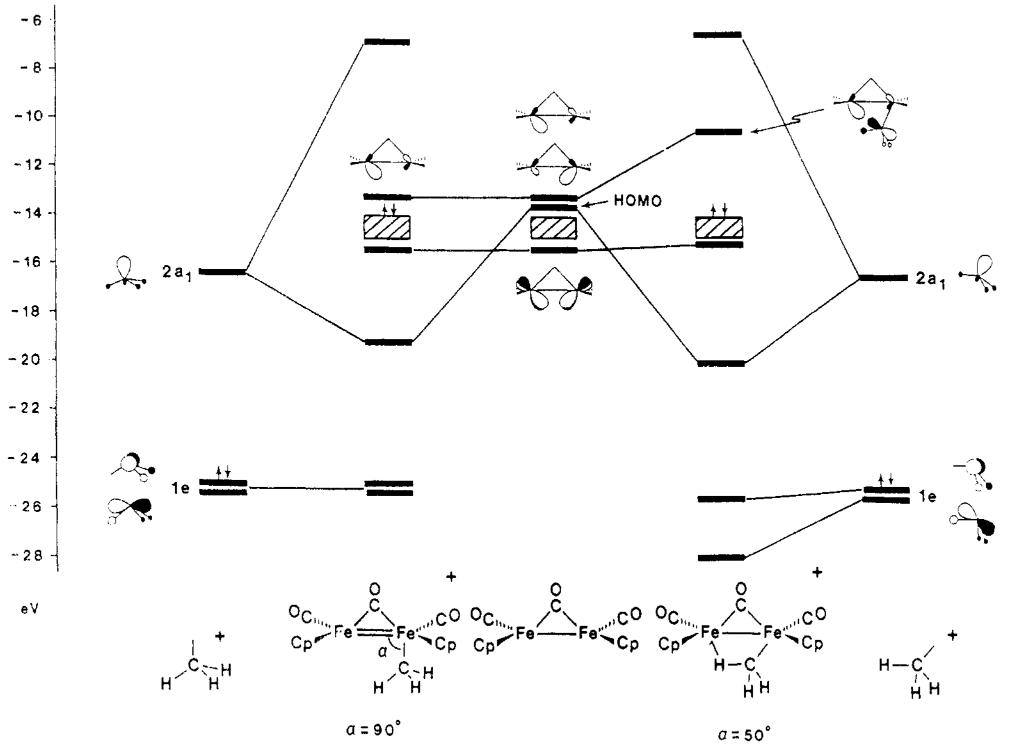

Figure 1. Molecular orbital diagram showing the interaction of a Me^+ ligand with the $[CpFe(CO)]_2(\mu\text{-}CO)$ framework at Fe–Fe–C(Me) angles of 90° and 50°. For clarity, only the frontier orbitals of the iron dimer fragment are shown.

molecular orbital diagrams for both the terminal and bridged conformations of **5**, constructed by allowing the orbitals of a Me^+ ligand to interact with those of a *cis*-$[CpFe(CO)]_2(\mu\text{-}CO)$ (Cp = η^5-C_5H_5) fragment.[7] Although this fragment contains a plane of symmetry, the HOMO and LUMO of the dimer fragment may be considered as localized, one on each Fe atom; such localization in fact results when the symmetry is reduced by asymmetric methyl ligation. The left half of Figure 1 shows the interactions in a model terminal complex in which the Fe–Fe–C(Me) angle, denoted α, is equal to 90°. Like $Cp_2Fe_2(\mu\text{-}CO)_3$,[8] this complex would contain a formal Fe–Fe double bond. In this geometry, the LUMO of the complex is quite low in energy and is localized on the Fe atom to which the methyl group is not bound. The right half depicts the orbital interaction diagram which results from pivoting the methyl ligand into a bridging position ($\alpha < 90°$). As α decreases, two important effects are noted. First, the Fe–C σ bonding is increased due to an increased overlap between the empty Me $2a_1$ orbital and the HOMO of the diiron fragment. Second, and more important, one of the C–H bonds of the methyl ligand interacts with the empty orbital localized on the electron-deficient Fe atom. This interaction stabilizes the filled C–H bonding orbital and raises the energy of the LUMO. Similar interactions have been found by Hoffmann[9] and by Eisenstein[10] in mononuclear agostic complexes, although the M···H···C interaction appears to have an even greater stabilizing effect in the dinuclear systems since the C–H bond can overlap strongly with an empty orbital on the *other* metal atom.

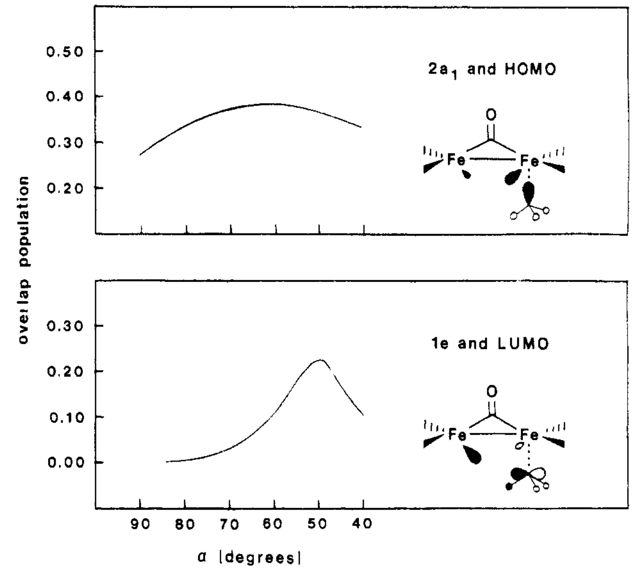

Figure 2. Plots of the variations in overlap populations between the Me^+ $2a_1$ and 1e orbitals with the appropriate diiron orbitals as a function of the Fe–Fe–C(Me) angle.

The stabilization of the asymmetrically bridged conformation of **5** is also evident in the overlap populations of the Me $2a_1$ and 1e orbitals with the HOMO and LUMO of the dimer framework. Figure 2 shows the variation of these overlap populations as α is varied from 90° to 40°. Both of these maximize in the range of 50–60°, in good agreement with the Fe–Fe–C(Me) angle of 54° found for the closely related complex $[Cp_2Fe_2(dppm)](\mu\text{-}CO)(\mu\text{-}Me)^+$ (dppm = bis(diphenylphosphino)methane).

Although the above calculations correctly account for the preference of bridging rather than terminal coordination of the methyl ligand, the geometry of the bridging methyl ligand could be either symmetric pyramidal (**1**) or asymmetric (**3**), assuming the retention of an Fe–Fe bond. Calculations performed on these two conformations offer further support for the importance of an agostic M···H···C

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[7] The results reported for the diiron complexes are for the cis complex. There are no significant differences between calculations on the cis and trans isomers. For a discussion of the frontier orbitals in iron dimers see: Jemmis, E. D.; Pinhas, A. R.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2576–2585.

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interaction.[11] The overlap population of the Me $2a_1$ orbital with the dimer fragment HOMO is only slightly greater for the asymmetric than the symmetric bridge (0.381 and 0.376, respectively). However, the overlap population of the Me 1e (C–H bond) orbital with the dimer fragment LUMO is substantially greater for the asymmetric bridge (0.180) than the symmetric one (0.125). This preference for an asymmetric bridge is also evident in the molecular orbital energies, and the net stabilization of the asymmetric geometry over the symmetric one is ca. 0.5 eV. NMR experiments have shown that the μ-CH_3 protons are fluxional,[4b] and, with the assumption that the symmetric bridge is the transition state for this process, the net stabilization of 0.5 eV should roughly correspond to the barrier to fluxionality. The small value calculated is consistent with the experimental observation that all three protons and both iron atoms are equivalent down to at least −86 °C.

As has been found for the monomeric alkenyl agostic systems of Brookhart and Green, the LUMO of **5** is the antibond of the agostic interaction (Figure 1).[12] Thus the formal addition of two electrons should destroy the interaction and cause the methyl ligand to coordinate in a terminal fashion. The compound $[CpFe(CO)]_2(\mu\text{-}CO)(CH_3)^-$ is not as yet known, but the isovalent dimer $[(\eta^5\text{-}C_5Me_5)Rh(CO)]_2(CH_3)^-$, recently prepared by Bergman and Krause,[13] does contain a terminal methyl ligand. Protonation of the methylene-bridged rhodium dimer $[CpRh(CO)]_2(\mu\text{-}CH_2)$ (**6**) might be expected to lead to the dimer $[CpRh(CO)]_2(\mu\text{-}CH_3)^+$ by analogy to the chemistry of **4**. **6** exhibits markedly different reactivity toward protons than does **4**, however. Rather than adding to the methylene, the proton adds to the Rh–Rh bond of **6** to form $[CpRh(CO)]_2(\mu\text{-}CH_2)(\mu\text{-}H)^+$.[14] We believe that this difference in reactivity is dictated by the nature of the HOMO's of the methylene-bridged complexes. A detailed explanation of this effect along with a description of the electronically induced reactivity of similar hydrocarbyl-bridged dimers will be presented in a later publication.

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Transition-Metal Chemistry of Octafluorocyclooctatetraene. Synthesis and X-ray Structure of a Novel Five-Coordinate *cis*-Dialkyl Nickel Complex

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Summary: Reaction of $Ni(COD)_2$ with 2 equiv of the phosphines PMe_3 or $PPhMe_2$ (L) in the presence of octafluorocyclooctatetraene (OFCOT) affords the first examples of Ni(0) compounds containing two coordinated fluoroolefins $[Ni(1,2,5,6\text{-}\eta\text{-OFCOT})L_2]$ (**1**); use of exactly 2 equiv of *t*-BuNC instead of a phosphine yields the metallacyclic complex $[Ni(C_8F_8)(t\text{-BuNC})_2]$ (C_8F_8 = perfluorobicyclo[3.3.0]octadienediyl) (**2**) which does not undergo reductive elimination in the presence of exogenous ligands to give perfluorosemibullvalene (**3**) but instead forms the first stable examples of five-coordinate *cis*-dialkyl complexes of nickel $[Ni(C_8F_8)(t\text{-BuNC})_2L]$ (**4**) (L = *t*-BuNC, PMe_3, PPh_3), one of which, **4b** (L = PMe_3), has been characterized by a single-crystal X-ray diffraction study at −110 °C.

Reductive elimination reactions of square-planar d^8 metal complexes are of considerable importance in homogeneous catalysis and have been reviewed recently.[3] The detailed mechanism of elimination is still the focus of a great deal of theoretical and experimental work. Kinetic and theoretical studies have indicated that reductive elimination from square-planar Pd(II) and Au(III) complexes involves initial *dissociation* of a ligand to give a T-shaped intermediate.[4] In corresponding Ni(II) systems, however, theoretical studies[3] together with recent kinetic observations on catalytic hydrocyanation reactions[5] have provided powerful evidence that the key reductive elimination step is preceded by *association* with an exogenous ligand to give a five-coordinate *cis*-dialkyl nickel species. We now report the isolation and crystallographic characterization of the first stable example of such a complex.

While Ni(1,5-cyclooctadiene)$_2$ $[Ni(COD)_2]$ and $Ni(C_2H_4)L_2$ (L = PPh_3, PPh_2Me) do not react with octafluorocyclooctatetraene[6] (OFCOT), reaction of $Ni(COD)_2$ with OFCOT in the presence of 2 equiv of the more basic tertiary phosphine ligands PMe_3 or $PPhMe_2$ affords the thermally and photochemically inert 18-electron diolefin complexes **1**[7] which exhibit characteristic ^{19}F NMR spectra containing only two fluorine resonances. Cyclopentadienyl complexes of cobalt(I) and rhodium(I) adopt this mode of coordination with both OFCOT[8] and its hydrocarbon analogue cyclooctatetraene (COT),[9] but there are no ana-

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[7] **1a**: mp 120–122 °C dec; ^{19}F NMR (C_6D_6, shifts in ppm upfield from internal $CFCl_3$) δ 118.12 (4 F, m), 155.74 (4 F, m); ^1H NMR (C_6D_6) δ 0.65 (9 H, d, J_{P-H} = 6.2 Hz, CH_3); IR (KBr) 1708 (ν(C=C)), 1252, 1288 cm^{-1} (ν(CF)). Anal. Calcd for $C_{14}H_{18}F_8NiP_2$: C, 36.65; H, 3.95. Found: C, 36.58; H, 4.09. **1b**: mp 145–147 °C dec; ^{19}F NMR (C_6D_6) δ 117.46 (4 F, m), 151.62 (4 F, m); ^1H NMR (C_6D_6) δ 0.86 (6 H, d, J_{P-H} = 7.61 Hz, CH_3), 6.9 (5 H, m, Ph); IR (CH_2Cl_2) 1718 (ν(C=C), 1295, 1260 cm^{-1} (ν(CF)). Anal. Calcd for $C_{24}H_{22}F_8NiP_2$: C, 49.44, H, 3.80. Found: C, 49.30, H, 3.61.

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