H, 8.37. Found: C, 53.86; H, 8.24.

1-Chloro-2,5-bis(methylene)bismolane. A solution of bismuth trichloride (0.2 g, 0.6 mmol) in 3 mL of dry tetrahydrofuran was added to 0.2 g (0.6 mmol) of 1,1-dibutyl-2,5-bis(methylene)stannolane at 0 °C. After the solvent was removed under vacuum at 0 °C, the residue was washed with 10 mL of pentane to remove the dibutyltin dichloride. The solid residue was dissolved in 10 mL of tetrahydrofuran and filtered. Evaporation of the solvent at 0 °C left (0.2 g, 99%) yellow crystals that could be stored at 0 °C but decomposed at 25 °C.

^{1}H NMR (Me$_2$SO-d_6): δ 7.12 (s, 2 H), 6.12 (s, 2 H), 3.65 (s, 4 H). MS: m/z (relative intensity) 324 (5, M$^+$ for $C_6H_8\,^{35}ClBi$), 289 (50, M$^+$ − Cl), 80 (70, C_6H_8).

2,2′,5,5′-Tetrakis(methylene)bibismolane. Sodium metal (0.014 g, 0.6 mmol) was added to a solution of 0.2 g (0.62 mmol) of 1-chloro-2,5-bis(methylene)bismolane in 25 mL of liquid ammonia. A violet solid precipitated from the ammonia. After evaporation of the ammonia, the product was taken up in pentane. When the mixture was cooled to −78 °C, the product crystallized. The labile dibismuthine decomposed on warming >0 °C.

MS: m/z (relative intensity) 578 (5, M$^+$ for $C_{12}H_{16}Bi_2$), 498 (3, M − C_6H_8), 418 (32, Bi_2), 369 (15, M$^+$ − Bi), 289 (40, M$^+$ − C_6H_8Bi), 209 (100, Bi). ^{1}H NMR ($CDCl_3$): δ 6.6 (s, 4 H), 5.4 (s, 4 H), 3.2 (br d, J = 9.5 Hz, 4 H), 2.9 (br d, J = 9.5 Hz, 4 H). UV (pentane): λ_{max} 330 nm (4200 sh).

MO Calculations. The following structural parameters were used in calculations:

Compound **1′**: intermolecular Sb–Sb, 3.625 Å; Sb$_1$–Sb$_{1'}$, 2.835 Å; Sb$_1$–C$_1$, 2.14 Å; C$_2$–C$_3$, 1.32 Å; C$_5$–Sb$_1$–C$_2$, 81°; Sb$_1$–C$_2$–C$_3$, 109°; C–H, 1.08 Å. All H's are set in the bissector plane of the X–C–Y angle.

Compound **3**: same Sb–Sb distances as in **1′**; Sb$_1$–C$_2$, 2.14 Å; C$_2$–C (exo methylene), 1.34 Å; C$_5$–Sb$_1$–C$_2$, 81°; Sb$_1$–C$_2$–C$_3$, 114.9°; Sb$_1$–C$_2$–C (exo methylene), 122.5°; C(sp^2)–H, 1.08 Å; C(sp^3)–H, 1.09 Å; H–C(sp^3)–H, 104°.

Compound **5**: same Sb–Sb distances as in **1′**; Sb$_1$–C$_2$, 2.14 Å; C$_2$–C (exo methylene), 1.34 Å; C$_2$–C$_3$, 1.46 Å; C$_5$–Sb$_1$–C$_2$, 81°; Sb$_1$–C$_2$–C$_3$, 109.95°; Sb$_1$–C$_2$–C (exo methylene), 125.03°.

The assumption of identical Sb–Sb bond lengths in **1′**, **3**, and **5** is consistent with the fact that Mulliken overlap populations are calculated to be essentially the same in all three systems. This fact also means that the short-long Sb–Sb band alternation observations should be present in **3** and **5**.

Atomic parameters: reference previous paper.[5]

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Registry No. **1′**, 108036-04-0; **3**, 108036-00-6; **4**, 108036-03-9; **5**, 108036-05-1; **6**, 71566-70-6; **7**, 108035-99-0; **8**, 108035-98-9; **9**, 108036-01-7; **10**, 108036-02-8; dichlorophenylstibine, 5035-52-9; 1,2-dibromoethane, 106-93-4; dibutyltin dichloride, 683-18-1; bismuth trichloride, 7787-60-2.

Agostic Bonds in $(MCH_3)^+$ Fragments. Implications for M^+–CH_3 Bond Dissociation Energies

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Available data for transition-metal fragments ML$^+$ show that M$^+$–CH$_3$ bonds are stronger than M$^+$–H bonds, in opposition to the trend observed for coordinatively saturated complexes, for which D(M–CH$_3$) is significantly lower than D(M–H). Extended Hückel molecular orbital calculations on some MCH$_3$$^+$ systems indicate that strong agostic interactions may be responsible for that "reversed" trend.

The energetics of transition-metal–carbon and -hydrogen bonds in coordinatively saturated complexes and in organometallic fragments and ions has been the subject of many recent studies.[1-3] Available data for saturated complexes show that M–H bond energies are higher (by ca. 60–100 kJ/mol)[4] than M–CH$_3$ bond energies, while an opposite conclusion is drawn for the unsaturated species MCH$_3$$^+$ and MH$^+$: metal–hydrogen bonds are weaker (by ca. 2–75 kJ/mol)[1a,3a,b] than metal–methyl bonds. Data for neutral MCH$_3$ fragments are still rather scarce,[5] but the "reversed" trend may also hold. However, it is probably less pronounced than in the case of the ions.

The stability of MCH$_3$$^+$ fragments, as compared to MH$^+$, was discussed by Mandich, Halle, and Beauchamp, the conclusion being that the resonant charge stabilization of the methyl cation, favored for the more polarizable, more easily ionized methyl ligand, was the main reason for the unexpectedly large bond dissociation energy.[6] This has recently been supported by a correlation showing that

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(1) (a) Martinho Simões, J. A.; Beauchamp, J. L. *Chem. Rev.*, to be submitted for publication. (b) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41. (c) Skinner, H. A.; Connor, J. A. *Pure Appl. Chem.* **1985**, *57*, 79. (d) Pilcher, G.; Skinner, H. A. In *The Chemistry of the Metal-Carbon Bond*; Hartley, F. R., Patai, S., Ed.; Wiley: New York, 1982; Chapter 2.

(2) Some recent examples from which the energetics of M–CH$_3$ and M–H bonds in coordinatively saturated complexes can be compared include (a) Alibrandi, G.; Minniti, D.; Romeo, R.; Cum, G.; Gallo, R. *J. Organomet. Chem.* **1985**, *291*, 133. (b) Moloy, K. G.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7051. (c) Nolan, S. P.; Lopez de la Vega, R.; Hoff, C. D. *J. Organomet. Chem.* **1986**, *315*, 187. (d) Calhorda, M. J.; Dias, A. R.; Minas da Piedade, M. E.; Salema, M. S.; Martinho Simões, J. A. *Organometallics*, in press.

(3) Recent gas-phase results enabling comparisons between M$^+$–CH$_3$ and M$^+$–H (or between M–CH$_3$ and M–H) bond energies in MR$^+$ (or MR) species include: (a) Aristov, N.; Armentrout, P. B. *J. Am. Chem. Soc.* **1984**, *106*, 4065. (b) Elkind, J. L.; Armentrout, P. B. *J. Phys. Chem.* **1985**, *89*, 5626. (c) Weil, D. A.; Wilkins, C. L. *J. Am. Chem. Soc.* **1985**, *107*, 7316. (d) Sallans, L.; Lane, K. R.; Squires, R. R.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 4379.

(4) A larger difference (228 kJ/mol, recalculated value) has been estimated for platinum complexes. See ref 2a.

(5) D(Co–H) is close to D(Co–CH$_3$). See ref 1a.

(6) Mandich, M. L.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 4403.

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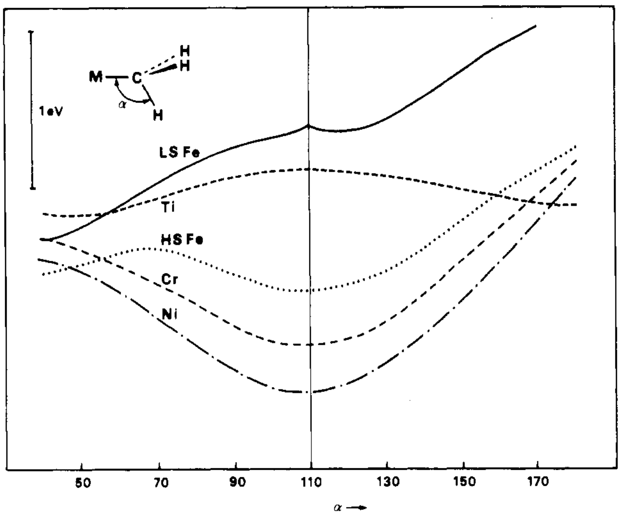

Figure 1. Change of total energy with M–C–H angle (α) in MCH_3^+ fragments [M = Ti (high-spin triplet state), Cr (high-spin quintet state), Fe (low-spin and high-spin triplet), and Ni (low spin)].

$D(M^+–C_nH_{2n+1})$ increases as n increases.[7] Also, identical reasoning has been used to account for "small" M–H and M–CH_3 bond energy differences in coordinatively saturated thorium complexes.[2b]

While we see no reason to challenge the above explanation, it is possible to deal with the same problem from another angle. Brookhart and Green[8] have recently suggested that when discussing metal–alkyl bond energies, it is necessary to distinguish between agostic and nonagostic systems. Later theoretical work has shown that when the C–H bond donates electrons to the metal center, forming a metal–hydrogen bond, a strengthening of the metal–carbon and a weakening of the carbon–hydrogen bond also occur, the net effect being the stabilization of the whole system.[9] We decided to look for the existence of such interactions in some MCH_3^+ systems, by means of extended Hückel molecular orbital calculations.[10]

One of the largest $D(M^+–CH_3) - D(M^+–H)$ differences observed is for M = Fe. The calculations involving $FeCH_3^+$ may indicate a large decrease in energy associated with an agostic interaction (Fe–C–H angle decreasing as the hydrogen approaches the iron atom in the xz plane, the CH_3 group being kept pyramidal with H–C–H angles of 109.47°), as shown in Figure 1. In order to understand this behavior, we start by looking at the interaction between a methyl group and a metal ion (Figure 2). The methyl group can interact through its high-energy n_{CH_3} orbital and the two low-energy π_{CH_3} orbitals. These two match xz and yz in symmetry, but their interaction is small owing to the large energy difference. The strongly bonding molecular orbital derives from z^2 and n_{CH_3}, with some mixture of z and s. xy and $x^2 - y^2$ are nonbonding. The symmetry labels refer to the symmetry plane (xz) that is kept throughout the distortion. For $FeCH_3^+$, the highest occupied molecular orbitals are 3a″ and 5a′, with one electron each. The behavior of these orbitals when the M–C–H angle, α, is allowed to change is shown in the Walsh diagram (Figure 3). The orbitals derived from xz and z^2 begin to mix, as they now have the same symmetry.

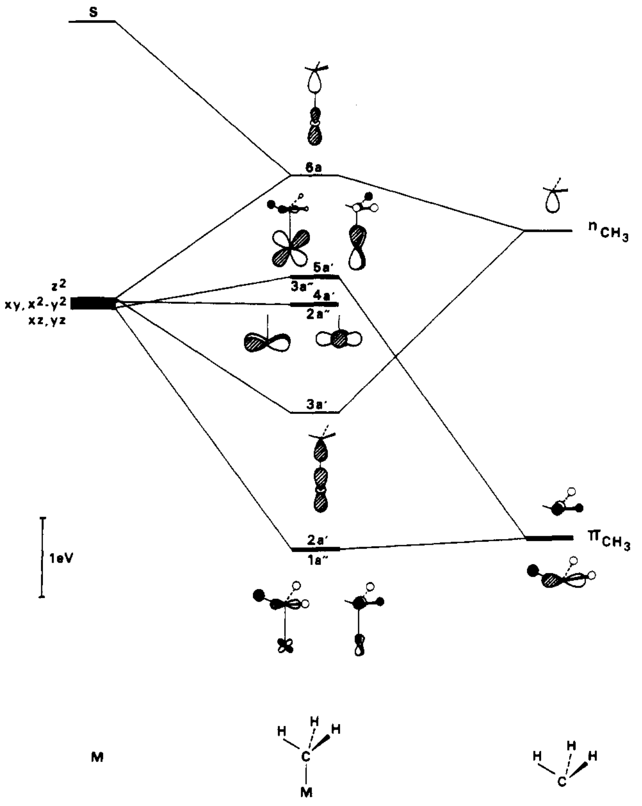

Figure 2. Molecular orbital diagram showing the interaction between a methyl group and a metal ion.

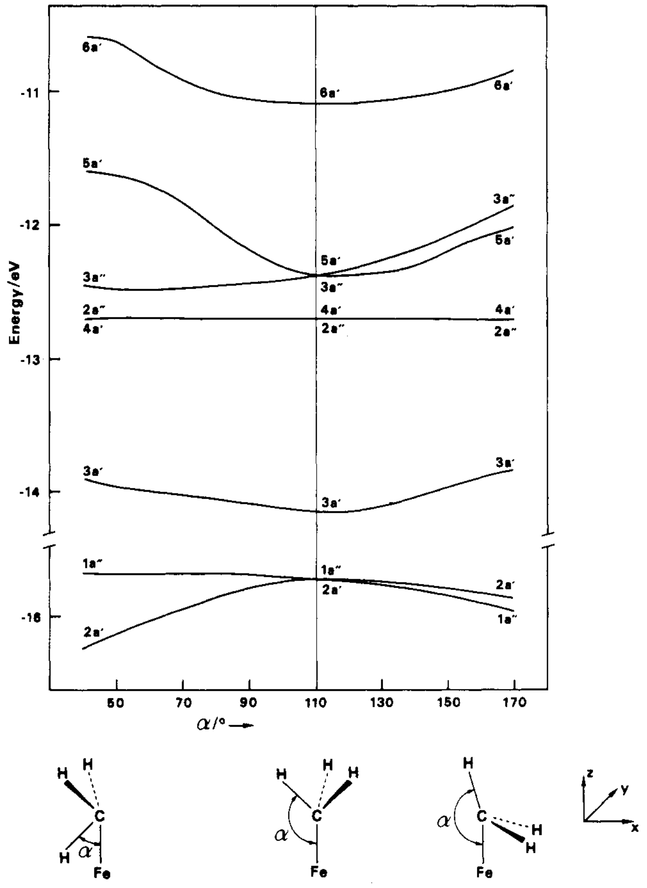

Figure 3. Walsh diagram for $FeCH_3^+$.

If we look at what happens for small α, we can see that the overlap between n_{CH_3} and z^2 has decreased, 1.

On the other hand, a strong interaction has developed between that methyl orbital and xz, 2.

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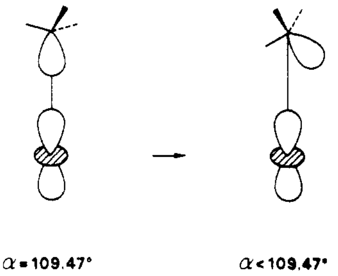
[7] Radecki, B. D.; Allison, J. *Organometallics* **1986**, *5*, 411.

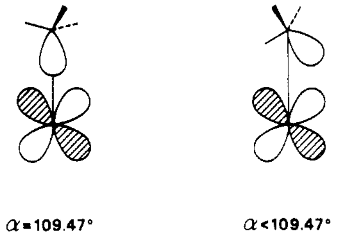
[8] Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

[9] Eisenstein, O.; Jean, Y. *J. Am. Chem. Soc.* **1985**, *107*, 1177.

[10] Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397; **1964**, *40*, 2745. Metal–carbon distances were taken as 210 pm and carbon–hydrogen distances as 109 pm; M–C–H angles equal 109.47°.

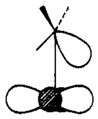


1



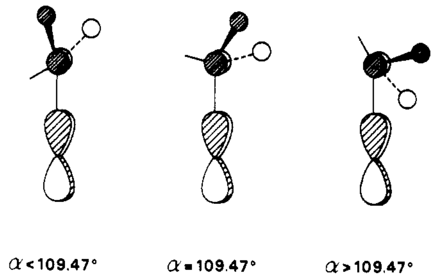
2

These effects result in a stabilization of the *xz*-derived bonding molecular orbital 2a′ and changes in the other a′ orbitals. Interactions involving π_{CH_3}(a′) also change upon distortion but with a smaller effect. Also, an interaction between n_{CH_3}(a′) and $x^2 - y^2$ can occur, 3, but it is so weak that no noticeable change in energy is observed for the $x^2 - y^2$ orbital (4a′).



3

A small change in energy occurs for 1a″ (slight destabilization) and 3a″ (slight stabilization) for small α. The reason for this lies in the smaller overlap between *yz* and the hydrogen 1s orbitals, 4.



4

The opposite behavior is seen for large α, explaining why 1a″ and 3a″ change in an asymmetric way (Figure 3).

An agostic interaction is, therefore, expected in a MCH_3^+ fragment, for small α, for instance, if the *xz* orbital (5a′) is empty, that is, for a low-spin $FeCH_3^+$ species. The distorted high-spin ion has an energy comparable to that of the undistorted one, but there is a small energy barrier between them. Although the undistorted $FeCH_3^+$ has probably a triplet ground state, this might not be the same in a distorted ion, but extended Hückel calculations cannot give us a reliable answer.

For Ti and Cr derivatives, the energy changes are only shown for the high-spin species (Figure 1). An agostic interaction is expected to occur for $TiCH_3^+$, but not for $CrCH_3^+$. These results may be derived from the Walsh diagram which are a little bit different from that for $FeCH_3^+$. For $TiCH_3^+$, 2a′ is stabilized, 3a′ does not change much, and both 5a′ and 6a′ become more antibonding. On the other hand, for $CrCH_3^+$, 3a′ is destabilized, and that makes the distortion unfavorable. This comes from the fact that orbitals change from one metal to the other.[11] As the behavior of the molecular orbitals depends on a delicate balance between stabilizing and destabilizing interactions (as shown, for instance, in 1 and 2), it is not surprising that it may be upset by changing the metal orbitals involved.

Another possible distortion obtained by decreasing the three M–C–H angles simultaneously, keeping the C_{3v} symmetry of the fragment, was explored. Only small changes in energy were observed (less than 0.1 eV), both for cromium and iron derivatives.

The values for $D(M^+{-}CH_3) - D(M^+{-}H)$ are 42, 9, and 17 kJ/mol for M = Fe, Cr, and Ti, respectively.[1a] They parallel the tendency of the metal to form agostic bonds to the methyl group if a low-spin distorted $FeCH_3^+$ may exist. For M = Ni no trace of agostic bonds could be found in our calculations [$D(Ni^+{-}CH_3) - D(Ni^+{-}H) = 24$ kJ/mol].[1a] Indeed, for this metal, the two extra electrons will occupy antibonding molecular orbitals that are strongly destabilized as distortion proceeds.

Although it is obvious that a more sophisticated type of calculations should be used in a detailed study of those small systems, our results strongly indicate that the possibility of allowing the distortions of methyl groups should be made, as they seem to play an important role in understanding the surprisingly strong $M^+{-}CH_3$ bonds.

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Registry No. $FeCH_3^+$, 90143-29-6; $TiCH_3^+$, 107987-12-2; $CiCH_3^+$, 89612-53-3; $NiCH_3^+$, 90624-35-4.

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[11] Albright, T. A.; Hofmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* 1977, *99*, 7546.