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Ab Initio Calculations of Transition-Metal Organometallics: Structure and Molecular Properties

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Contents

- I. Introduction 743
- II. Methodology 744
  - A. Atomic Basis Sets of Gaussian Functions 744
  - B. Survey of Methodology 745
- III. Results 746
  - A. Electronic States 746
    - 1. Metal Carbonyls 746
    - 2. Metal Carbides 747
    - 3. Metal Cyanides 747
    - 4. Metal Carbon Dioxide Complexes 747
    - 5. Metal Alkyls 747
    - 6. Metal Carbenes 747
    - 7. Metal Carbynes 747
    - 8. Metal Alkenes 747
    - 9. Metal Alkynes 747
    - 10. Metallocenes 748
    - 11. Binuclear Complexes 748
  - B. Electronic Spectra 748
  - C. Optimized Geometries 748
    - 1. Metal Carbonyls 749
    - 2. Metal Carbides 750
    - 3. Metal Carbon Dioxide Complexes 750
    - 4. Metal Alkyls 751
    - 5. Metal Carbenes 751
    - 6. Metal Carbynes 752
    - 7. Metal Alkenes 752
    - 8. Metal Alkynes 753
    - 9. Metallocenes and Cyclic Polyene Complexes 754
  - D. Binding Energies 754
    - 1. Metal Carbonyls 754
    - 2. Metal Carbides 755
    - 3. Metal Carbon Dioxide Complexes 755
    - 4. Metal Alkyls 755
    - 5. Metal Carbenes 756
    - 6. Metal Carbynes 756
    - 7. Metal Alkenes and Metal Alkynes 756
  - E. Other Properties 757
    - 1. Vibrational Frequencies 757
    - 2. Dipole Moment 758
    - 3. Electron Density 758
    - 4. Miscellaneous 759
  - F. Ionization Potentials and Electron Affinity 759
  - G. Nature of the Bonding 759
    - 1. Metal Carbonyls 759
    - 2. Metal Carbides 761
    - 3. Metal Cyanides 761
    - 4. Metal Carbon Dioxide Complexes 761
    - 5. Metal Alkyls 761
    - 6. Metal Carbenes and Metal Carbynes 761
    - 7. Metal Alkenes and Metal Alkynes 762
    - 8. Metallocenes 763
    - 9. Binuclear Complexes 763
- IV. Concluding Remarks 763

I. Introduction

There is considerable interest in organometallics, largely because these molecules are relevant to homogeneous catalysis. However, the electronic structure and nature of the bonding of these organometallics is not as well understood as the properties of organic molecules. In recent years, the unqualified success of theoretical calculations in the area of organic chemistry has been taken largely for granted. In contrast, ab initio calculations on transition-metal organometallics are just recently becoming commonplace as a result of considerable difficulties. For instance the Hartree–Fock approximation, which is adequate for the description of the ground state of most organic molecules,[1] is certainly less appropriate for the description of organometallics. Namely, when a CI or MC-SCF calculation is carried out for certain types of transition-metal organometallics, very often the dominant configuration does not represent an overwhelming portion of the total wave function. Also ab initio calculations for organometallics require comparatively more computer time due to the large number of electrons. For this reason they have become commonplace only with the advent of the vector computers or supercomputers.

The nature and the scope of ab initio calculations for organometallics has progressively changed over the last 20 years. During the 1970's, Hartree–Fock calculations were carried out mostly for saturated organometallic complexes, such as bis(π-allyl)nickel,[2] chromium hexacarbonyl,[3] and nickel tetracarbonyl,[3,4] since these systems usually have a low-spin ground state and no low-lying excited states. In the late 1970's and early 1980's, calculations beyond the Hartree–Fock approximation appeared both for these systems[5,6] and for the simple, unsaturated organometallic complexes,[7-10] with large basis sets used in conjunction with extensive electron correlation. In the small, unsaturated systems, the small splitting between occupied and unoccupied orbitals often leads to a number of low-lying excited states. To predict the ordering of these states and the properties of a particular state some care must be taken since different electronic states may be affected differently by increasing the size of the basis set or the amount of electron correlation. Also the early calculations were restricted to the properties of isolated

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molecules. It is only recently that they have been extended to the study of chemical reactions, including even some catalytic cycles.

The field of ab initio calculations for organometallics has received some impetus from the development of gas-phase transition-metal chemistry[11,12] together with matrix experiments.[13,14] Gas-phase experiments have provided the theoretical chemist with accurate values of relative energies. Matrix isolation techniques have provided information on unstable species.

We shall deal with transition-metal organometallic systems according to the definition which is the most commonly used, namely compounds in which the organic group or residues are attached to metal atoms by metal–carbon bonds.[15] Cluster models for the study of chemisorption and reaction on surfaces[16] will not be considered in this review. Related materials may be found in two recent books describing the state of the art and in one review article.[17–19]

II. Methodology

The methodology of ab initio calculations has been abundantly described in the literature (see for instance refs 1, 20, 21). We shall be concerned here only with some points characteristic of the ab initio calculations of organometallics.

A. Atomic Basis Sets of Gaussian Functions

Gaussian basis sets for first-row and second-row atoms of the ligands are well documented.[1,22,23] The discussion which follows will be restricted to the Gaussian basis sets for transition-metal atoms. We shall distinguish between uncontracted Gaussian basis sets, energy-optimized, and STO-*n*G basis sets which consists of expansion of Slater-type atomic orbitals (STO's) in terms of *n* Gaussian functions.

For the first transition row the early (12s6p4d) set optimized by Roos et al. for the $3d^n4s^2$ configuration[24] has been much used, usually supplemented with one p function to describe the 4p orbital[2] and in conjunction with a (8s4p) set for the first-row atoms. In addition, in order to describe accurately the $3d^{n+1}4s^1$ states where the 3d orbital is more diffuse, it is necessary to add an additional 3d function and the corresponding exponents have been optimized by Hay.[25] The contraction used is usually of the split valence type, namely one contracted function for the inner shells 1s, 2s, 2p, 3s, and 3p and two contracted functions for the shells 3d and 4s, resulting in a contracted [5s3p2d] set usually used in conjunction with a set [3s2p] for the first-row atoms. A larger set is the (14s9p5d) set optimized by Wachters[26] for the $3d^n4s^2$ configuration, supplemented with two optimized p functions to describe the 4p orbital and one diffuse 3d function.[25] The corresponding (14s,11p,6d) set is usually contracted in a way which is at least of double-ζ quality and used in conjunction with basis sets (9s5p)/[4s2p] or (10s6p)/[4s2p] for the first-row atoms. A slightly enlarged version (15s,11p,6d) has one additional s function between the s functions describing the 3s orbital and those describing the 4s orbital.[27] It has been found that the description of organometallics with long metal–metal bonds (2.9 Å in $Mn_2(CO)_{10}$) requires additional diffuse functions resulting in a (16s12p7d) set.[28] Another basis set (14s9p5d) has been reported by Huzinaga.[29] A basis set intermediate in size between the Roos and Wachters sets is the (13s7p5d) set of Hyla-Kryspin et al.[30] used in conjunction with the (9s5p) set for first-row atoms. Although optimized for the $4s^13d^{n-1}$ configuration, this basis usually requires additional diffuse functions for the 3d and 4p orbitals. A (15s8p5d) basis contracted to [4s2p1d] has been optimized by Basch et al. after contraction for the $3d^n4s^2$ configuration.[31] In order to avoid the need for additional diffuse d function, Rappe et al. have optimized (4d), (5d), and (6d) basis sets for the d^n states in conjunction with the (14s9p) primitive set of Wachters.[32] Two minimal contracted basis sets (with each atomic orbital represented by at least three Gaussians) have been optimized by Tatewaki and Huzinaga[33] and latter used as split-valence basis sets.[34] Very large basis sets, up to (16s11p8d) have been reported recently but do not seem to have been used so far for molecular calculations.[35] An even larger basis set (20s12p9d), equivalent to a (13s8p) set for first-row atoms, has been optimized by Partridge.[36]

For the second transition series, the (17s11p8d) set of Huzinaga[29] may be considered as an extension of the (14s9p5d) set for the first transition series (exponents for the supplemental basis functions have been optimized by Walch et al.[37]). In the same way the (14s,8p,7d) set of Hyla-Krypsin et al.[30] represents an extension of the (12s,6p,4d) set of Roos et al. A (12s8p7d) set contracted to a minimal basis set has been optimized for the $4d^n$ configuration.[38] A minimal basis set, with each atomic orbital represented by three Gaussians, has been developed by Huzinaga and co-workers for the second and third transition series.[39]

STO-3G minimal basis sets have been reported by Pietro and Hehre for first- and second-row transition metals.[40] They are based on expansion of Slater-type atomic orbitals in terms of three Gaussian functions, with some constraints such as orbitals of a given shell sharing a common set of Gaussian exponents. As a consequence of these constraints, the performances of the STO-3G basis sets seem inferior to those of a minimally contracted Gaussian basis set.[41] A split-valence basis set, termed 3-21G, has been constructed by Dobbs and Hehre for the first and second transition series, with the constraints of s- and p-type orbitals sharing the same exponents.[42,43]

Practically all calculations for organometallics have been carried out so far with a segmented contraction[22] (each primitive Gaussian function occurs in only one contracted basis function), although a general contraction (with each primitive contributing to each contracted function), as proposed by Raffenetti,[44] has also been used. As judged from work on small transition-metal complexes,[45] a general contraction based on the atomic natural orbitals as proposed by Almlof and Taylor[46] seems to be one promising approach for highly accurate calculations.

While d polarization functions on first-row atoms have been found essential for certain studies,[47,48] the importance of f polarization functions on transition-metal atoms has never been ascertained in detail but seems relatively minor (SCF calculations have usually been carried out without f functions, with the correlation effects included in most of the calculations with f functions). 4f orbitals with a radial density maximum near 1 Å have been used, with exponents of 0.56 or 0.67 for the iron atom of $Fe(CO)_5$[49] and 0.5 for the Mn atom in $Mn_2(CO)_9$.[50] A single contracted set of f polarization functions has been based on a three-term fit to a Slater-type orbital in a study of the transition-metal methyls at the CI level,[51] but these functions are certainly more important for the description of the correlation effects at the CI level than for the description of polarization effects at the SCF level. 4f exponents have been optimized for first-row transition-metal atoms at the CI level, but since these calculations included correlation of the (3s3p) shell the corresponding exponents are relatively high[52] (slightly different values of the optimized exponents may be found in ref 53).

B. Survey of Methodology

Since the difficulty of ab initio calculations rises rapidly with the number of electrons, the innermost functions are frequently replaced with an effective core potential (ECP), thus reducing the calculation to a more computationally feasible valence-electron problem. This subject has been reviewed in a number of books and papers.[54-57] Extensive sets of potentials for the transition metals have been reported by various authors.[58-60] These effective potentials offer a way to incorporate relativistic effects into molecular calculations without the complexity of the Dirac–Fock method. The potentials of Hay and Wadt for the second and third transition series incorporate the mass–velocity and Darwin relativistic effects.[60] In certain cases, ambiguities can arise regarding which electrons can be treated as core orbitals to be replaced by the ECP and which electrons should be treated explicitly as valence electrons. For a transition metal atom with configuration [core] $ns^2np^6nd^l(n+1)s^m$, the ns and np orbitals do not play any direct role in the chemical bonding but are of the same size as the nd valence orbitals. Since the interaction between orbitals with large overlap is not properly accounted for by a local potential, this problem has been circumvented by including all of the electrons from the ns shell in the valence space.[61] In the ECP method of Pettersson et al., the outermost core orbitals are described through frozen orbitals.[62] Relativistic effective potentials with spin–orbit operators have been reported for the first transition row.[63] While most of the effective potentials found in the literature were adjusted to orbitals, the effective potentials developed by Preuss et al. for the first-row transition metals, both nonrelativistic and quasirelativistic, were adjusted to energy differences like ionization and excitation energies.[64] Another different approach has been used in the model potential method of Huzinaga, which valence orbitals showing the correct nodal structure and the core potentials obtained directly from the atomic core orbitals.[65]

For small, unsaturated systems for which there is usually a lack of experimental data, the equilibrium geometry is generally derived from geometry optimization either at the SCF, MC-SCF, or CI level, at a computational cost which remains reasonable. For medium-size organometallics, full-geometry optimization can be carried out with the energy gradient technique at the SCF level,[66,67] and this approach is the most appropriate for the calculation of the potential energy profile for a chemical reaction. However optimization of all the geometrical parameters is an expensive process (besides the fact that geometries optimized at the SCF level are not always accurate for organometallics and that the optimization at the MC-SCF[68,69] or CI[70,71] levels represents a much more difficult problem). Quite often, geometry optimization is carried out only for the bond distances and bond angles which are the most important for the problem under study. For the same reasons, many calculations of organometallics have been carried out either for the experimental geometry or for an assumed geometry (usually on the basis of experimental bond lengths and bond angles in related systems).

A variety of methods have been used to describe the electron correlation in organometallics:

(i) Configuration interaction with single- and double-excitations (SD-CI),[72] based on a SCF reference wave function, shows a slow convergence of the results as a function of the length of the CI expansion and is not size consistent (the method does not scale properly with the number of correlated electrons; for instance it does not give additive results when applied to an assembly of isolated molecules). It seems appropriate mostly when the state is relatively well described by a single configuration.

(ii) The multiconfiguration SCF (MCSCF) method, including the complete active space SCF (CASSCF) method,[73] is particularly appropriate to describe the large near-degeneracy effects that occur in transition-metal systems. The use of a MCSCF or CASSCF reference wave function in a multireference CI-SD calculation has been rather popular (it has been shown that this type of calculation represents a good approximation to a full CI calculation[74]). The generalized valence bond (GVB) description of electron correlation, developed by Goddard and collaborators,[75] represents a special case of MCSCF wave function where an electron pair is described by a pair of nonorthogonal orbitals coupled into a singlet.

(iii) The Moller–Plesset perturbation theory, usually carried out to second order and denoted MP2, MP4, etc.,[1] satisfies the size consistency requirement. This approach is valid only when the state is well described by a single configuration. However there has been some concern about the reliability of the MP2 method for transition-metal systems (for instance it fails to describe the electronic spectrum of the nickel atom[76,77] and it has been concluded that the MP method is not appropriate for certain Ni(0) complexes[78]).

(iv) Methods which include the correlation energy in a size-consistent way, like the coupled-pair functional (CPF)[79] and the modified coupled-pair functional (MCPF),[80] have been used mostly for the calculation of binding energies.

III. Results

A. Electronic States

The problem of identifying the electronic ground state of a molecule is crucial for both theoreticians and experimentalists. Mononuclear organometallics fully coordinated at the metal usually satisfy the 18e rule (although there are exceptions) and will have a closed-shell singlet ground state. On the other hand, unsaturated systems may tend to retain the electronic configuration of the metal atom with many low-lying states corresponding to different occupations of the nd, (n+1)s, and (n+1)p orbitals. This situation is exemplified by $Ni(CO)_4$ and Ni(CO), with the former having a $^1A_1$ ground state well separated from the other states and the latter showing several near-degenerate electronic states (cf. below). Polynuclear organometallics represent another class of compounds with near-degenerate electronic states, as a result of a conflict between metal–metal bonding and the loss of d–d exchange energy (the metal–metal d–d bond being inherently weak owing to the small overlap and the d–d exchange energy being large).

1. Metal Carbonyls

We start with metal carbonyls since this is a classical example of metal–ligand interaction. Early calculations addressed the question of the ground state of NiCO. Walch and Goddard found that NiCO has three bound states $^3\Sigma^+$, $^3\Pi$, and $^3\Delta$, all of s^1d^9 character on the Ni atom, with the GVB-CI calculations yielding a $^3\Delta$ ground state.[7] Rives and Fenske pointed out[8] that since the $^1A_1$ ground state of $Ni(CO)_4$ arises from a s^0d^{10} state of the Ni atom, the $^1\Sigma^+$ state of NiCO corresponding to this configuration was another candidate for the ground state, and their CI calculations effectively produced a $^1\Sigma^+$ ground state rather than a $^3\Delta$ ground state (Hartree–Fock calculations resulted in a $^3\Delta$ ground state). This assignment was confirmed later by Blomberg et al.[81] (who assigned also a $^1\Sigma_g^+$ ground state to $Ni(CO)_2$) and by Madhavan and Whitten[82] (for the ground state of NiCO, see also refs 83 and 84). Similarly, for PdCO, the $^1\Sigma^+$ state related to the d^{10} configuration is bound and lower in energy than the repulsive $^3\Sigma^+$ state originating from the s^1d^9 configuration.[84,85] For PtCO a similar energy ordering of atomic states has been found namely $^1\Sigma^+ < (^3\Sigma^+, ^3\Delta) < {}^3\Pi$ where $^1\Sigma^+$ is attractive and correlates with Pt d^{10} ^1S, with the triplet states arising from the Pt d^9s^1 ^3D (the $^3\Sigma^+$ and $^3\Delta$ being weakly attractive and the $^3\Pi$ being dissociative).[84,86] RhCO has a $^2\Sigma^+$ ground state corresponding to the d^9 configuration of Rh, with a $^4\Delta$ state (correlating with the d^8s^1 configuration) which is higher and repulsive.[85]

For ScCO the three doublet states $^2\Sigma^+$, $^2\Pi$, and $^2\Delta$ derived from the s^2d^1 atomic configuration are repulsive, the $^4\Delta$ state related to Sc d^3 is moderately attractive and the two states $^4\Sigma^-$ and $^4\Phi$ correlating to the state d^2s^1 are strongly attractive, the $^4\Sigma^-$ being the lower of the two.[87,88] For ScOC the repulsive states originating from the s^2d^1 configuration are the lowest ones,[87] the attractive states being much less stable than the corresponding states in ScCO. Davidson also arrived at the conclusion that the $^4\Sigma^-$ state must be the ground state of ScCO.[89] Three electronic states $^5\Sigma^-$, $^3\Sigma^-$, and $^3\Delta$ have been considered for FeCO, the ground state being probably the $^3\Sigma^-$ state.[90] The ground state of CuCO is a $^2\Sigma^+$ state derived from the $d^{10}s^1$ configuration, corresponding to a weakly bonded van der Waals complex, with excited states $^2\Pi$ and $^2\Sigma$ derived from the $d^{10}p^1$ configuration.[91] The same ground state has been assigned to $NiCO^-$.[92]

While the bonding in MCO systems has been described in terms of σ donation and π back-donation (cf. below), a completely different description emerged for the positive ions MCO^+ with a binding mechanism essentially electrostatic.[91,93-98] Nevertheless $CuCO^+$ has a $^1\Sigma^+$ ground state (derived from the d^{10} configuration) like NiCO[91] and $NiCO^+$ is found to have a $^2\Sigma^+$ ground state (with a $^2\Delta$ state 2 kcal/mole higher) like RhCO.[94] For $ScCO^+$ the order of electronic states is $^3\Delta$ (d^1s^1) < $^3\Pi$ (d^1s^1) < $^3\Sigma^+$ (d^1s^1) < $^3\Sigma^-$ (d^2), the order of the d^1s^1 states being a consequence of the electrostatic nature of the binding and reflecting the spatial extension of the $3d_\sigma$, $3d_\pi$, and $3d_\delta$ orbitals along the internuclear axis.[96] For $TiCO^+$ Bauschlicher found the $^4\Delta$ and $^4\Phi$ almost degenerate,[94] while Mavridis et al. considered two $^4\Sigma^-$ states, one of s^1d^2 parentage and the other of d^3 parentage, which are practically degenerate.[96] For VCO^+, Mavridis et al. considered a $^5\Delta$ state ($s^1d_{\pi x}{}^1d_{\pi y}{}^1d_\delta{}^1$ with the d^3 electrons distributed away from the incoming lone pair on CO) but pointed out that the $d_\pi{}^2d_\delta{}^2$ configuration will have an energy comparable to that of the $^5\Delta$ state and may even be lower.[96] For $CrCO^+$ they assigned the ground state as the state $^6\Sigma^+$ (d^5) with the state $^4\Pi$ $d_{\pi x}{}^2d_{\pi y}{}^1d_{\delta+}{}^1d_{\delta-}{}^1$ higher.[96] The ground state of $RhCO^+$ and $Rh(CO)_2{}^+$ has been assigned as a triplet.[99] More recently the low-lying electronic states of the first and second series mono- and dicarbonyl positive ions have been studied by Barnes et al.[98]

The low-lying electronic states of $Cr(CO)_5$ have been studied by Hay.[5] The ground state of this molecule is the $^1A_1$ state of the square pyramid (SP) structure, with low-lying states ^3E for the SP structure and $^3A_2$ for the trigonal bipyramid (TBP) structure. A triplet ground state has been predicted for $Fe(CO)_4$, in agreement with its experimental paramagnetism.[100] On the basis of SCF calculations, the ground state of $V(CO)_5$ and $Mn(CO)_5$ has been ascribed respectively to the states ^2E and $^2A_1$ of the SP structure.[101] Electronic states of $Mo(CO)_4NH_3$ have been computed for the three structures SP with the NH_3 ligand apical or basal and TBP with the NH_3 ligand equatorial, the ground state being the $^1A'$ state of the SP with NH_3 basal.[102] The ground state of $HCo(CO)_3$ has been a matter of controversy, being assigned either to a triplet state of a distorted tetrahedral structure[103] or to the closed shell $^1A_1$ state of the C_{3v} structure.[104]

2. Metal Carbides

The ground state of PdC is a $^3\Sigma^-$ state (originating from the configuration $4d^{10}\ 2s^2\ 2p\pi^1\ 2p\bar{\pi}^1$) at both SCF and CI levels, with a $^1\Delta$ state at 1.38 eV higher at the CI level.[105] The ground state of CrC^+ is a $^4\Sigma^-$ state (derived from Cr^+ $3d^5\ ^6S$ and C $2s^22p^2\ ^3P$) with an excited state $^4\Pi$ 0.8 eV higher at the CI level.[106]

3. Metal Cyanides

ScCN has a set of closed-lying states $^{1,3}\Sigma^+$, $^{1,3}\Pi$ and $^{1,3}\Delta$, with the $^3\Delta$ state being the lowest.[107]

4. Metal Carbon Dioxide Complexes

Although $RhCl(AsH_3)_4(CO_2)$ has a pseudooctahedral structure with a d^8 electron configuration, the ground state is calculated to be a singlet.[108]

5. Metal Alkyls

The low-lying electronic states of $NiCH_3$ have been discussed in ref 109. The electronic states of $Ni(CH_3)_2$ have been studied first at the SCF level[110] and later at the CI level,[111] the ground state being a triplet with a linear structure (see also ref 112 for more accurate calculations). The ground state of MCH_3^+ (for M = Sc,Cr,Mn,Y,Mo,Tc,Pd) has A_1 symmetry except for $ScCH_3^+$ (of E symmetry) and is derived from the ground state of M^+ by forming a single bond with the methyl ligand.[113-115] Bauschlicher et al. assigned the ground state for both the neutral and positive ions of all of the first and second series transition-metal methyls.[51] They noticed some changes in ground states between the first and second series compounds (for instance $MnCH_3$ has a $^7A_1$ ground state, $TcCH_3$ has a $^5A_1$ ground state), this being mostly a consequence of a change in the order of (or in the gap between) the atomic asymptotes d^ns^2 and $d^{n+1}s^1$. The complexes $MH(CH_3)$ and $M(CH_3)_2$ with M = Pd or Pt have a closed-shell singlet ground state.[116] McKee obtained at the MP3 level a ^6E ground state for $FeCH_3$ but concluded that the state ^4E is in reality lower[117] (in agreement with the conclusions of Bauschlicher et al.[51]).

6. Metal Carbenes

Electronic states of $MnCH_2$ and $MnCH_2^+$ have been studied at the SCF level, the ground state being assigned to a $^8B_1$ state arising from the state ^6S of the Mn atom and the state $^3B_1$ of CH_2, the interaction of the state ^6S of Mn with the singlet carbene being essentially repulsive.[118] While SCF calculations predict a $^7B_1$ ground state for $MnCH_2^+$ and a $^6B_1$ ground state for $CrCH_2^+$,[119] electron correlation has a dramatic effect since the GVB-CI calculations yield a $^4B_1$ ground state for $CrCH_2^+$.[113,120] The lower states of $NiCH_2$ correspond to Ni having the character s^1d^9 and the CH_2 fragment in the $\sigma^1\pi^1$ state, the ground state being the state $^1A_1$ with a weak π bond.[109,121] The ground state $^1A_1$ of $ScCH_2^+$ is doubly bonded, the two valence electrons of Sc^+ ^3D coupling to the two valence electrons of CH_2 ($^3B_1$).[115] The ground states $^1A_1$ of $ScCH_2^+$, $^2A_2$ of $TiCH_2^+$, $^3A_2$ of VCH_2^+ and $^4B_1$ of $CrCH_2^+$ all have a metal–carbon double bond and correlate with the ground state $^3B_1$ of CH_2.[122] For $RuCH_2^+$, the electronic state spectrum reveals five states close in energy.[123] The ground state has the $^2A_2$ symmetry and is of the metal–methylidene type (namely it is related to the triplet $\sigma^1\pi^1$ ground state of CH_2), with a $^2A_1$ state of the same character 1 kcal/mol higher. A cluster of three degenerate excited states $^4A_2$, $^4B_1$, and $^4B_2$, 13 kcal/mol higher, is of the metal–carbene type (namely it derives from the singlet σ^2 excited state of CH_2) (a $^4B_1$ ground state has been reported for $FeCH_2^+$[117]). The carbene complex $Cl_4W{=}CH_2$ has two states $^1A_1$ and $^3B_2$ very close in energy.[124]

7. Metal Carbynes

For ScCH a $^3\Pi$ has been found below a $^5\Pi$ state[107] but the possible occurrence of a state $^1\Sigma^+$ (corresponding to the formation of a triple bond) as the ground state has not been ruled out. The ground state of $ScCH^+$ is a $^2\Pi$ state corresponding to the formation of a double bond between Sc^+ $s^1d^1\ ^3D$ and CH in the $^4\Sigma^-$ state.[115,125] The ground state of $CrCH^+$ has been assigned to the state $^3\Sigma^-$ corresponding to the formation of a triple bond between Cr^+ ^6S and CH in the $^4\Sigma^-$ state.[113] The ground states of VCH^+ (2Δ) and $TiCH^+$ ($^1\Sigma^+$) are also characterized by a metal–carbon triple bond.[125] A $^3\Delta$ ground state has been reported for $FeCH^+$ and HFeCH.[117]

8. Metal Alkenes

Electronic states of MnC_2H_4 have been investigated at the SCF level but the results have not been reported in detail.[126] Species $Ni(C_2H_4)_m$ (where m = 1, 2, 3) and $Ni_2(C_2H_4)_m$ (where m = 1, 2) have been identified experimentally[127] and have been the subject of several theoretical studies.[127-131] The early calculations[127,128] agreed that the ground state of NiC_2H_4 must be a $^3A_1$ state corresponding to the interaction of a Ni atom in the state $d^9s^1\ ^3D$ with ground-state ethylene, with the higher four d-hole states associated with this configuration lying between 0.5 and 1 eV above the ground state. Subsequent calculations by Widmark et al.[130] establish that the $^3A_1$ state is not bound except for a weak van der Waals type interaction at large Ni–C distances and that the ground state must be the state $^1A_1$ derived from the state ^1D of Ni. The ground state of the π-$Ni_2C_2H_4$ complex has been assigned either to a $^3A_2$ state,[127] to a $^3A_1$ state,[10] or to a $^1A_1$ state.[131] SCF calculations favor a $^3B_{3u}$ ground state (of parentage d^9s^1) for $Ni(C_2H_4)_2$ with a planar D_{2h} structure[129] but calculations at the CI level yield a singlet ground state with a twisted D_{2d} structure.[132] The $^2A_1$ ground state of the π-CuC_2H_4 complex arises from a weak interaction between ethylene and a copper atom in its $d^{10}s^1$ configuration, with three bound excited states corresponding to the $d^{10}p^1$ configuration.[133] The ordering of the states $^2A_1 < {}^2B_2 < {}^2B_1 < {}^2A_1$ is the same for the π-complexes of ethylene with copper, silver, and gold.[134] The same low-lying electronic states have been described at the SCF level for the mono- and diligand complexes $Ag(C_2H_4)_{1,2}$.[135]

9. Metal Alkynes

The ground state of the π-MnC_2H_2 complex was found repulsive at the SCF level, a consequence of the s^2d^5 configuration of the Mn atom.[126] For π-NiC_2H_2, the lowest electronic states were at first assigned to the five different possible occupations of the d shell in the

d^9s^1 triplet state.[128] A later study assigned the ground state to the state $^1A_1$ originating from the Ni state d^9s^1, with the $^3A_1$ state higher and essentially repulsive.[136] A singlet ground state was also assigned to the π-PdC_2H_2 complex, corresponding to the d^{10} configuration of Pd.[136] The low-lying electronic states of $Ag(C_2H_2)_{1,2}$, arising from the $d^{10}s^1$ and $d^{10}p^1$ states, have been described at the SCF level.[135]

10. Metallocenes

A $^5E_2$ ground state has been assigned to $FeC_5H_5^+$ and $HFeC_5H_5$.[117] The spectrum of electronic states of the ferricenium ion has been studied at the SCF level, with a ground state $^2E_{2g}$.[137,138] A $^2E_{1g}$ ground state has been predicted for cobaltocene at the SCF level.[139]

11. Binuclear Complexes

The singlet–triplet separation has been computed for the following binuclear complexes: $[(C_5H_5)V]_2C_8H_8$,[140,141] $[(C_5H_5)V(C_4H_8)]_2$,[142] $[(C_9H_7)V)]_2$,[143] $[(C_5H_5)VH]_2C_6H_6$,[143] and $[Cp_2Zr(\mu\text{-}PH_2)]_2$.[144] The ground state of $(\mu\text{-}NO)_2[Co(\eta^5\text{-}C_5H_5)]_2$ has been found to be a triplet at the levels of DCSCF and CASSCF calculations,[145,146] but experimental measurements indicate a diamagnetic ground state.[147] A closed-shell ground state has been assumed for the complex $Fe_2(CO)_6(HC_2H)$ although the SCF calculations yield a triplet ground state.[148] Singlet closed-shell ground states have been reported for $Fe_2(CO)_9$,[149] *trans*-$[(C_5H_5)Fe(CO)(\mu\text{-}CO)]_2$, and $Fe_3(CO)_{12}$.[150]

B. Electronic Spectra

Attempts to predict the electronic spectra of organometallics have been rather scarce and this results probably from two factors: (i) reasonably accurate calculations of excitation energies (with an accuracy better than half an electronvolt) require extended basis sets and multireference CI calculations based on better than SCF reference wavefunctions; (ii) electronic spectra of organometallics are usually poorly resolved, a consequence of the high density of states (for a relatively simple system like $Fe(CO)_5$, 18 electronic states have been numbered within an interval of 20 000 cm^{-1} [100]).

The 17 excited states of NiCO which are found within 2.7 eV of the ground state may be divided into a lower manifold, principally involving the Ni $3d^94s^1$ configuration, and a higher manifold associated with the charge-transfer $Ni^+(3d^9)CO^-(\pi^*)$ configuration.[82] No energy gap is found between the two manifolds.

In the π-NiC_2H_4 complex, the large number of excited states is due to the very large number of possible excitations in the d^9s^1 nickel atom alone (3d → 4p, 3d → 4s, 4s → 4p) coupled with ligand field splittings of the 3d and 4p orbitals and the possibilities of charge transfer transitions.[10] Ligand field (LF) states have been computed between 0.5 and 1 eV, an allowed mixed 4s → π^* and 4s → 4p state is predicted at ~2.2 eV, the metal-to-ligand charge transfer (MLCT) is spread over several states from 4.9 to 5.8 eV due to mixing with the 3d → 4p transition and corresponds probably to the state observed at 4.4 eV.[10] Comparable results have been obtained in ref 127, with the $\pi \rightarrow \pi^*$ and 4s → π^* state as 2 eV and the MLCT state at 6.1 eV. For CuC_2H_4, the calculated energies for the 4s → 4p excitations are 2.84, 2.97, and 3.39 eV, in good agreement with the observation of bands at 2.95 and 3.25 eV.[133] A similar agreement has been observed for AuC_2H_4.[134] For AgC_2H_4 the observed spectrum is rather different and, since this feature is not reproduced in the calculations, the assignment of the spectrum to AgC_2H_4 has been questioned.[134]

Early calculations, in the 1970's, of the electronic spectrum of large organometallics were carried out at the SCF level or at the level of CI restricted to single excitations with qualitatively reasonable results but errors on the excitation energies which could be larger than 1 eV.[4,151] More recently this approach has been used by Vanquickenborne to study the ligand field spectrum of cyanides[152-154] and the spectrum of d^6 $M(CO)_6$ complexes.[155]

Calculations at the CI level, using a SCF reference wave function, seem to yield reasonably accurate excitation energies (within 1 eV of the experimental values). For $Cr(CO)_5$, Hay computed a low-lying excited state ^1E (resulting from the $e \rightarrow a_1$ d → d excitation) at 1.5 eV, corresponding probably to the absorption band observed at 2.0–2.5 eV (calculated oscillator strength $f = 0.025$, experimental $f \approx 0.03$).[5] The pronounced variation of the absorption band with the type of solid matrix is readily explained from the nature of the excited state a_1 orbital. The sequence of LF and MLCT excited states of $Cr(CO)_6$ is reproduced correctly by the calculation, but the theoretical excitation energies are too high by 0.4 to 0.9 eV.[156] The first excited singlet of $Fe(CO)_5$ has been computed at 4.4 eV,[100] but the experimental spectrum is known to start at 3.5 eV.[157,158] The calculated LF excitation energies of $Mo(CO)_4NH_3$ are in the range 1.8–2.2 eV.[102]

The most accurate estimates of excitation energies are based on MR-CI calculations using a CASSCF reference wave function and seem to yield theoretical values which are probably accurate to within 0.5 eV. For $HMn(CO)_5$, the allowed LF excitation is computed at 4.7 eV and corresponds to a shoulder observed at 4.3 eV, with an allowed $d_\pi \rightarrow \sigma^*_{Mn-H}$ excitation computed at 5.2 eV and corresponding probably to the band at 5.8 eV.[158] The LF state $^1E'$of $Fe(CO)_5$ is computed at 4.1 eV but estimated at 3.6 eV (introducing an empirical correction for the fact that the CASSCF orbitals have been optimized for the ground state).[158] For $H_2Fe(CO)_4$ the lowest singlet states are computed to be the states $^1B_2$ and $^1A_1$ (both involving an excitation of a 3d electron into an orbital localized on the FeH_2 moiety) at 4.4 eV,[159] with a shoulder in the experimental spectrum at 4.6 eV.[160] The lowest singlet state of $HCo(CO)_4$ is a ^1E state corresponding to a $d_\delta \rightarrow \sigma^*_{Co-H}$ excitation and a first calculation yielded an excitation energy of 4.5 eV,[27] but a subsequent study produced a much lower value of 2.9 eV.[103] A new estimate of this excitation energy, based on an accurate calculation of the corresponding triplet, produced a value of 4.2–4.5 eV,[104] with the experimental spectrum starting at 4.5 eV.[161]

C. Optimized Geometries

Very often experimental geometry is lacking and the first step of a theoretical study consists in geometry optimization. The description of geometry for molecules containing first- and second-row elements has been extremely successful at the Hartree-Fock level with a split-valence or even minimal basis set.[1] At which level of theory should geometry optimization be carried out for the transition-metal organometallics? There is no simple answer to this question although a few general rules have emerged. For instance STO-3G calculations at the SCF level do not perform well,[40] with the calculated bond lengths to carbon usually too small, by as much as 0.25 Å in $Ni(CO)_4$ and the axial Fe–C bond of $Fe(CO)_5$ too long by 0.19 Å but the equatorial bond too short by 0.18 Å. The calculated Fe–C distances in ferrocene are somewhat better but as the result of a fortuitous cancellation of errors.[40] The results seem to improve slightly by using a minimal GTO basis set.[41] Structures calculated with a split-valence basis set appear generally superior but not as good as those for compounds containing main-group elements only.[42,162,163] Worst is the fact that the Hartree–Fock model fails to reproduce correctly the metal-to-ligand distances in a number of organometallics, mostly the carbonyls[49,101] and the metallocenes.[164]

1. Metal Carbonyls

The Sc–C bond distance in ScCO is around 2.1 Å for the $^4\Sigma^-$ state but around 4.4 Å for the $^2\Pi$ state (corresponding to a van der Waals minimum).[87,89] For TiCO a Ti–C bond length of 2.06 Å has been reported.[94] For FeCO, the optimized Fe–C bond length is 1.81 Å for the $^3\Sigma^-$ state and 1.90 Å for the $^5\Sigma^-$ state.[90] For NiCO the value of 1.74 Å for the Ni–C bond length in the state $^1\Sigma^+$ is probably the most accurate one.[81] In general, it was found that the inclusion of correlation strengthens the Ni–C interaction through increased backbonding, thus shortening r(Ni–C) and lengthening r(C–O).[8,81,84,165] Ni–C bond lengths between 1.9 and 2.1 Å have been reported for the states $^3\Delta$, $^3\Sigma^+$, and $^3\Pi$.[92] The CuCO $^2\Sigma^+$ state shows a weak van der Waals interaction around 4 Å.[91] The Ni–C bond length in the state $^2\Sigma^+$ of $NiCO^-$ is much shorter, between 1.70 and 1.75 Å,[92,97] as a result of the electron occupying an orbital with a large amount of 4p character. Rather different values have been reported for the Rh–C bond length in the state $^2\Sigma^+$ of RhCO, either 1.86 Å (optimized at the Hartree–Fock level)[99] or 2.05 Å (at the CI level).[85] For the state $^1\Sigma^+$ of PdCO, values range from 1.86 Å[166] or 1.88 Å[84] to 2.13 Å[16,85,167] (the latter obtained with a nonrelativistic effective core potential). For the state $^1\Sigma^+$ of PtCO, values of 1.71 Å[86] and 1.98 Å[84] have been reported for the Pt–C bond length. The Ni–C bond length in $Ni(CO)_2$ is significantly longer, by 0.11–0.12 Å, than the corresponding value in NiCO.[81,93]

The M–C bond lengths in the monocarbonyl positive ions have been optimized in a number of papers,[91,94,96–99] besides the systematic work of Barnes et al.[98] In general, M–C bond lengths are longer than for the neutral carbonyls, a consequence of the electrostatic character of the interaction, since they range from 3.16 Å for $ScCO^+$ $^3\Sigma^+$ to 1.91 Å for $CoCO^+$.[98] M–C bond lengths for the ground states become progressively smaller as one moves from the left to the right in the periodic table.[96,98] For $NiCO^+$ the value of 1.94 Å given by Bauschlicher[94] is significantly shorter than the value of 2.13 Å reported by Blomberg et al.[97] A similar disagreement is found for $TiCO^+$ between the two values of 2.18 and 2.66 Å reported in refs 94 and 96, respectively. Geometries have also been optimized in a systematic way for the first- and second-series dicarbonyl ions $M(CO)_2^+$.[98]

For saturated metal carbonyls, metal–carbon bond lengths obtained at the Hartree–Fock level are in striking disagreement with experiment. In $Fe(CO)_5$, an early calculation found the axial iron to carbonyl distance to be 0.17 Å longer than the experimental value,[101] and this was confirmed by subsequent SCF calculations[49,163] (the disagreement increases with the size of the basis set and reaches 0.24 Å at a near-Hartree–Fock level[49]). Similar deviations have been reported for the axial and equatorial bonds of $H_2Fe(CO)_4$.[168] The same trend is observed for $Ni(CO)_4$,[84,121,163,169–171] although the disagreement is less severe with an error at the near-Hartree–Fock level close to 0.10 Å.[171] The geometries of the nickel carbonyls $Ni(CO)_n$ (n = 1–4) have been optimized at the SCF level, but the satisfactory agreement with the experimental data has been traced to a cancellation of errors.[165] Similar discrepancies are observed for $Pd(CO)_4$ and $Pt(CO)_4$.[84] The error in the Cr–C bond length of $Cr(CO)_6$ is comparable, the theoretical value with an extended basis set being 1.99 Å[172] vs an experimental value of 1.91 Å.[173] For $Fe(CO)_5$ a dramatic improvement is observed at the CI level, with an axial bond length of 1.785 Å vs an experimental value of 1.807 Å.[49] For $Ni(CO)_4$ correlation effects decrease the Ni–C bond length to 1.87–1.88 Å.[81,84,174] Relativistic corrections result in a Ni–C bond contraction of 0.026 Å,[171] the remaining error being probably the consequence of the lack of f functions in the nickel basis set.[81] Optimization of the Rh–C distance in $RhCl(PH_3)_2CO$ yields a result which is overestimated by ca. 0.1 Å.[175] The cause of the inequivalent chromium–carbonyl bond lengths in $Cl(CO)_4Cr{\equiv}CCH_3$ turns out to be a tilt of the methyl group caused by crystal packing.[176,177] Metal–hydrogen bond lengths in hydridocarbonyl complexes such as $HMn(CO)_5$, $H_2Fe(CO)_4$, and $HCo(CO)_4$, when calculated at the SCF level, are generally within 0.03–0.04 Å from the experimental value.[104,168,178] However metal–hydrogen bond lengths which are too long by 0.15 Å have also been obtained with split valence basis sets.[42,179] The Fe–H, Fe–CH_3, Fe–C (formyl), and Fe–C (acetyl) bond lengths have been optimized in the hydridoacetyl complex $Fe(CO)_4(COCH_3)(H)$ and in the methylformyl complex $Fe(CO)_4(CHO)(CH_3)$.[180] In order to understand the insertion reaction of CO_2 into the metal–hydride bond, the geometry of the adduct $[Cr(CO)_5H{\cdots}CO_2]^-$ has been optimized at the SCF level and shows an η^1 C-coordination with an OCO angle of 134°. The CH distance is short, 1.15 Å, and close to the value expected in the formate ligand.[181] Geometries have been optimized at the SCF level, by using the analytical gradient techniques, for the pentacarbonyls $M(CO)_5L$ (M = Cr, L = PH_3 or NH_3; M = Mn, L = H or Cl) and for the fragments formed by carbonyl loss.[178] Angles formed by bonds originating from the metal are generally within 5–6° (or better) from their experimental values.[168,178]

Five-coordinate metal carbonyls $M(CO)_5$ and $M(CO)_4L$ may adopt a variety of structures (TBP, or SP with L either apical or basal). The relative stabilities of these structures has been studied at the SCF[101] and CI[5] levels, with the conclusion that the d^6–d^7 systems $M(CO)_5$ prefer the SP structure but that the d^8 systems $Fe(CO)_5$, $Mn(CO)_5^-$, $Co(CO)_5^+$ and $Fe(CO)_4(C_2H_4)$ favor the TBP structure. SCF calculations on the systems $Tc(CO)_4Cl$ and $Mo(CO)_4L$ (with L = NH_3, PMe_3, C(OMe)H, C_2H_4), for the lowest closed-shell state, indicate that the most stable structure should be a distorted TBP (with the heteroligand L equatorial and an angle of 90° between the equatorial carbonyl ligands) followed by the SP with the ligand L basal.[102] The relative stabilities of different structures for $Mo(CO)_4NH_3$ remain practically unchanged when going from the SCF to the CI level.[102] $M(CO)_4L$ complexes (M = Cr, L = NH_3 or PH_3; M = Mn, L = H or Cl) with L apical have SP structures with almost 90° angles but the complexes obtained upon cis loss from $M(CO)_5L$ adopt a structure close to a distorted TBP.[178] Complete geometry optimization at the SCF level has yielded for $HCo(CO)_4$ a TBP structure with the hydrogen atom equatorial.[179] This conclusion was reversed in a subsequent study at the CI level, the TBP structure with the hydrogen axial becoming more stable but marginally (the energy difference being less than 1 kcal/mol).[103] In a later study, the TBP structure with the hydrogen atom axial was found more stable than the other one by 15 kcal/mol, in agreement with the experimental structure.[104] For $Co(CO)_4(CH_3)$ the TBP with the methyl ligand axial represents the most stable structure.[101]

Exploration of the potential energy surface of $Fe(CO)_4$ in its ground state (with fixed bond lengths) favored a structure of C_{2v} symmetry, in agreement with the structure deduced from the infrared spectrum.[100] A SCF study yields a structure of C_{3v} symmetry for $Co(CO)_4$.[182] For $HCo(CO)_3$ various structures have been considered both at the SCF and CI levels[103,104,179,182] with the latest calculation in favor of the C_{3v} structure.[104] The molecular geometry of formylcobalt tricarbonyl, (η^2-ethylene)hydridocobalt tricarbonyl, and ethylcobalt tricarbonyl has been investigated at the SCF and CI level.[183]

For the dihydrogen complex $W(CO)_3(PH_3)_2(H_2)$ the geometries of the three forms of H_2 coordination (two sideways η^2-bonded and the end-on η^1-bonded) have been optimized at the Hartree–Fock level by using a rigid $W(CO)_3(PH_3)_2$ fragment.[184] The lower energy η^2 form (with H_2 parallel to the PWP axis) shows a slight lengthening (from 0.74 to 0.80 Å) of the H–H bond from uncomplexed H_2 with a W–H distance of 2.15 Å, in reasonable agreement with the experimental structure. Geometries were also optimized for the seven-coordinate dihydride $W(CO)_3(PH_3)_2H_2$. In a more recent study, the calculated W–H bond distance (1.91 Å) and H–H separation (0.81 Å) in $W(CO)_3(PH_3)_2(H_2)$ are in excellent agreement with the experimental values (1.89 and 0.82 Å, respectively), and theoretical values of these parameters have also been obtained for the Mo complex.[185] The theoretical barrier height hindering the H_2 rotation in these systems agrees well with the observed value.[185] A number of structures have been optimized at the Hartree–Fock level for $Cr(CO)_4(H_2)_2$.[186] The cis compound with the H_2 molecules oriented in an upright position relative to the equatorial plane corresponds to the most stable structure. Pacchioni has optimized a number of geometrical parameters for different isomers of $Cr(CO)_5(H_2)$ and $Cr(CO)_4(H_2)_2$.[187]

Several studies have addressed the problem of the relative stabilities of the cis and trans isomers of $M(CO)_4L_2$ and $M(CO)_2L_4$ systems. SCF calculations predict the trans isomer of $H_2Fe(CO)_4$ to be the most stable one and the inclusion of correlation effects was necessary to reproduce the experimental energy ordering (with the cis isomer more stable).[188] A study of the cis–trans isomerism in the disubstituted d^6 metal carbonyls $M(CO)_4L_2$ (M = Cr, Mo and L = NH_3, PH_3, C_2H_4) and $M(CO)_4LL'$ (M = Mo, L = C_2H_4, L' = CH_2) leads to the following conclusions: (i) for L = NH_3, PH_3 the cis isomer is more stable than the trans one and correlation effects contribute predominantly to this greater stability of the cis isomer for L = NH_3, but their effect is much smaller for L = PH_3; (ii) for L = C_2H_4, CH_2 the trans isomer is more stable than the cis one with the correlation effects contributing significantly to the greater stability of the trans isomer for $Cr(CO)_4(C_2H_4)_2$; (iii) going from Cr to Mo increases the stability of the cis isomer for L = NH_3, PH_3 but decreases it for L = C_2H_4.[186] SCF calculations carried out on the two structures cis and trans of the model compound $Mo(CO)_2(NH_2)_4$ account for the cis configuration of the two carbonyl groups in $Mo(CO)_2(TTP)$ (TTP = tetratolylporphine dianion).[189]

2. *Metal Carbides*

The optimized bond length for the ground state $^4\Sigma^-$ of CrC^+ is 1.74 Å. The $^4\Pi$ excited state has a much larger bond length of 2.06 Å.[106]

3. *Metal Carbon Dioxide Complexes*

Carbon dioxide complexes of transition metals pose several questions of theoretical interest. The first one concerns the mode of coordination. One would like to find out which of the three coordination modes, the η^2 side-on mode, the η^1 C mode, or the η^1 end-on mode, is the most favorable. Another problem is concerned with the CO_2 distortion caused by the coordination. Geometry optimization has been generally limited to the parameters of importance for the specific problem, for instance the MC distance and the OCO angle in the C mode. The side-on coordinated $Ni(PH_3)_2(CO_2)$ was the most stable structure, with optimized values of 138° for the OCO angle, Ni–C = 1.87 Å and Ni–O = 2.02 Å.[190] In contrast $[Cu(PH_3)_2(CO_2)]^+$ has the largest stabilization in the end-on mode, the result of a strong electrostatic interaction between Cu(I) and the negatively charged oxygen of carbon dioxide. CASSCF calculations (with assumed geometries) for $Ni(NH_3)_2(CO_2)$ find the η^1 end-on structure to be only 1 kcal/mol higher in energy than the η^2 side-on structure.[191] Optimization of the OCO angle in the η^1 end-on structure yields similar values, 130° and 136°, at the SCF and CASSCF levels.[192] The geometry of the $Ni(CO_2)(C_2H_4)$ entity has been optimized in the $[Ni(NH_3)_2(\eta^1\text{-}CO_2)(C_2H_4)]$ system.[192] For the complex $[Co(alcn)_2(CO_2)]^-$ (alcn = $HNCHCHCHO^-$) the optimized OCO angle is 135° in the C mode and 153° in the side-on mode, and the η^1 C coordination mode is calculated to be the most stable one (with a CoC distance of 2.02 Å).[193,194] Study of the complex $RhCl(AsH_3)_4(CO_2)$ was restricted to the η^1 C coordinated structure, with optimized values of 2.02 Å (SCF level) and 2.13 Å (MP2 level) for the Rh–C distance.[108]

Knowledge of the structure of the intermediate *trans,mer*-$Mo(C_2H_4)(CO_2)(PH_3)_3$ is a prerequisite for understanding the coupling mechanism of the ethylene and CO_2 ligands. Four rotamers were considered, corresponding to the rotation of CO_2 around the axis going through the metal and the coordinated C–O bond. The two structures with the CO_2 ligand in the plane of the Mo–P bonds are the most stable ones, with two rotation barriers of 11 and 35 kcal/mol.[195]

4. *Metal Alkyls*

Geometries for the first and second series transition-metal methyl neutrals and positive ions have been determined with the assumption of C_{3v} symmetry.[51] For $ScCH_3^+$ and $CuCH_3^+$ a full geometry optimization was performed at the correlation level. For both the first and second series metal methyls the MCH angle varies by only about 4°, which is consistent with an sp^3-hybridized CH_3 covalently bonded to the metal. Although it had been suggested that there should be an agostic interaction between the metal atoms on the left side of the row and CH_3 arising from the donation of the C–H bonding electrons into empty d orbitals, the fact that the hydrogen atoms bend further away from the metal for these atoms argues against an agostic interaction. The M–C bond distances show a general decrease with increasing nuclear charge, with small deviations associated with differences in the bonding mechanism or a half or full closure of the d shell.[51] The bond lengths reported by McKee for $FeCH_3$[117] are about 0.2 Å longer than the values given by Bauschlicher et al. (the same trend is observed for $FeCH_3^+$). For $NiCH_3$ the different values reported in the literature[51,109,196] are all in the range 1.87–1.93 Å. A slightly greater value of 2.00 Å has been obtained at the SCF level for $Ni(CH_3)_2$.[110] Bauschlicher et al. found that the variation in the MCH angle is larger for the positive ions (spanning a range of 15°) than for the neutrals.[51] These large variations have been rationalized in terms of charge donation and of the relative energies of the planar and tetrahedral structures in CH_3^+, CH_3, and CH_3^-. For the systems MCH_3^+ considered by Schilling et al. (M = Sc, Cr, Mn, Y, Mo, Tc, Pd),[114] the M–C bond lengths are 0.05–0.1 Å longer than those obtained by Bauschlicher et al., who concluded that the M–C bond length is more sensitive to the level of calculation than the MCH bond angle.[51] If for $ScCH_3^+$ the Sc–C bond lengths reported in the literature.[51,11,115] are reasonably close (being in the range 2.20–2.25 Å), the spectrum of values reported for the Cr–C bond length in $CrCH_3^+$ [51,113,114] is broader (2.02–2.14 Å).

Geometry optimization has been carried out for the dimethyl positive ions $M(CH_3)_2^+$, all of these systems being bent with an angle of approximately 90°.[19] Low and Goddard optimized the geometries of the complexes $MH(CH_3)$ and $M(CH_3)_2$, M = Pd or Pt.[116] The bond distances for Pd–CH_3 and Pt–CH_3 bonds are nearly identical (1.96 ± 0.01 Å) for all complexes, but the bond angles for $MH(CH_3)$ and $M(CH_3)_2$ vary considerably, being 80° and 92° for Pd and 89° and 98° for Pt, a consequence of a R–R bonding interaction in the d^{10} resonance structure. The geometries of the complexes $Pt(H)(CH_3)(PH_3)_2$,[197,198] $M(CH_3)_2(PH_3)_2$ with M = Pd or Pt and $PtCl_2(CH_3)_2(PH_3)_2$[198] have been optimized at the Hartree–Fock level by using analytic gradient techniques. A good agreement was obtained with the X-ray structures on related molecules, indicating that the Hartree–Fock level is reasonable for geometry optimization of Pd and Pt complexes.[198] In the cis compound $Pt(H)(CH_3)(PH_3)_2$ both of PtH and PtC bonds have smaller bond distances that in the trans compound, the trans influence of a CH_3 ligand being larger than that of a PH_3 ligand.[197] The structure of $Pd(CH_3)(H)(CO)(PH_3)$ has been optimized.[199]

In Cl_3TiCH_3 the TiCH angle is calculated to be close to tetrahedral geometry with little flattening of the hydrogen atoms.[200,201] These atoms bend away from the titanium atom as the Ti–C distance is shortened, showing that the Ti–H interactions are repulsive and not attractive. It was concluded that agostic interactions are not strong enough to symmetrically flatten a methyl group.[201] Structural optimization of $Ti(CH_3)(PH_3)_2Cl_3$ shows a distorted methyl group with a TiCH angle of 99.6° and a TiH distance of 2.51 Å.[202] Optimization of the geometry of $Ti(C_2H_5)(PH_3)_2Cl_2H$ shows a CCTi bond angle of 89° (much smaller than expected in the sp^3 hybridization) and a distance between H_β of the ethyl group and the Ti atom of 2.23 Å (a very small value indicating a direct H···Ti interaction).[203] The distortion of the ethyl group is largely influenced by the other ligands, since both complexes $Ti(C_2H_5)(PH_3)_2H_3$ and $Ti(C_2H_5)(PH_3)_2(H)_2Cl$ have an undistorted alkyl group. The optimized geometry of $Pd(C_2H_5)(H)(PH_3)$ shows a distorted ethyl group, indicating an agostic interaction, with a PdH_β distance of 2.13 Å and a PdCC bond angle of 88°.[204] The agostic interaction is much weaker in $Pd(CH_2CHF_2)(H)(PH_3)$ and $Ni(C_2H_5)(H)(PH_3)$, and a general guideline favoring the agostic interaction has been deduced.[204]

Dedieu calculated the relative stabilities of various stereoisomers of $HRhCl(PH_3)_2(C_2H_5)$ (the nine possible isomers corresponding to a flat square pyramid and two TBP isomers) with the assumption of idealized geometries and fixed bond lengths, the most stable structure being a SP with the ethyl ligand axial.[205] Daniel et al. optimized the geometry of this isomer with the Hartree–Fock energy gradient method and found signs of a very strong agostic interaction with a small RhCC angle of 80° and a short RhH_β distance of 1.86 Å.[206]

The geometry of the allylcopper complex $Cu(C_3H_5)$ has been optimized at the SCF level, the conformer with a dihedral angle of 90° having the lowest energy with two rotational barriers of 3 and 7 kcal/mol corresponding, respectively, to the syn and anti isomers.[207]

The geometry of the dichlorotitanacyclobutane has been optimized at the GVB level.[208,209] The configuration at the β carbon is nearly tetrahedral, but there are substantial departures from the tetrahedral configuration at the α carbons, with skeletal angles of 88°. This structure shows a good agreement with the experimental one reported for the cyclopentadienyl analogue. The structure optimized at the STO-3G level for the dihydridotitanacyclobutane[210] shows a reasonable agreement with the higher level structure of ref 209. The geometry of the palladacyclobutane has been optimized at the CASSCF level.[211]

5. *Metal Carbenes*

Geometry optimization at the SCF level for the state $^8B_1$ of $MnCH_2$ yields a MnC distance of 2.16 Å.[118] This is contrasted to the NiC bond length of 1.78 Å obtained for $NiCH_2$ at the GVB-CI level (with an HCH angle of 114° quite different from its value of 135° in the ground state of CH_2)[109] (structures optimized at the SCF level agree rather well with a NiC bond length of 1.74–1.78 Å and an HCH angle of 112° [121,212]). The calculated MC bond length decreases slightly in the series MCH_2^+ M = Sc to Cr, from 2.00 Å for $ScCH_2^+$ to 1.96 Å in $TiCH_2^+$ and VCH_2^+ and 1.92 Å in $CrCH_2^+$.[122] For $ScCH_2^+$ the optimized ScC bond length is 2.00 Å for the ground state $^1A_1$ and 2.26 Å for the state $^3A_1$, the increased bond length in the latter being consistent with the loss of the π component of the ScC double bond.[115] The same trend is found in $CrCH_2^+$, with a CrC bond length of 1.91–1.92 Å in the $^4B_1$ state and 2.06–2.07 Å in the $^6B_1$ state.[113,120,213] The optimized geometry of the single-bonded donor–acceptor $^6A_1$ state (Cr–C = 2.32 Å and HCH = 109°) differs considerably from the covalently single-bonded $^6B_1$ state (Cr–C = 2.07 Å and HCH = 118°) with a much smaller HCH angle close to that in free singlet CH_2 (102°).[213] For $MnCH_2^+$ the optimized bond length for the doubly bonded ground state is 2.01 Å[214] and a value of 2.08 Å has been reported for the singly bonded state $^7B_1$.[119] Goddard observed that the MnC bond in $MnCH_2^+$ is substantially longer than the CrC bond of $CrCH_2^+$ because Mn bonds to CH_2 by using the larger 4s orbital to make the σ bond, whereas the σ bond in $CrCH_2^+$ is half sp and half 3d in character and hence is much smaller.[120] For doubly bonded $FeCH_2^+$ in the state $^4B_1$, the FeC bond length of 2.07 Å optimized by McKee[117] is much longer than the value of 1.96 Å reported by Goddard[214] and longer than the values of 2.03 and 2.06 Å optimized for the sextet states of singly bonded $FeCH_2^+$.[117] Optimized geometries have been reported for two different states of $RuCH_2^+$, the $^2A_2$ ground state (with a covalent double bond to the triplet carbene, a RuC bond length of 1.88 Å and an HCH angle of 122°) and the low-lying excited state $^4A_2$ (with a σ-donor and π-acceptor bond from the singlet carbene, a RuC bond length of 1.93 Å and an HCH angle of 113°).[123] The decrease in the HCH bond angle reflects the fact that this angle is 103° in the singlet state of CH_2, whereas it is 133° in the triplet state.

Franci et al. optimized the structures of substituted titanium carbenes $R_2Ti = CHX$ (with R = H, Cl, Me, or Cp, X = H, F, CN, NH_2, or Li) at the STO-3G level.[210] They found a number of significantly distorted geometries such as the one of $H_2Ti{=}CH(CH_3)$ with a TiCC angle of 165°, a manifestation of hyperconjugation associated with the electron deficiency at the metal (with a significant shortening of the metal–carbon linkage). Geometries optimized for $Cl_2Ti{=}CH_2$ at the Hartree–Fock level with different basis sets are in reasonable agreement.[209,210]

Of the two TBP structures for $(CO)_4Fe{=}CHOH$ the one with the carbene ligand at the axial position is more stable, by 8 kcal/mol, than the equatorial isomer.[215] The MC bond lengths seem, on the average, to be slightly longer in the Fischer-type complexes (2.00 Å for the complexes $(CO)_5Cr{=}CHOH$ and $(CO)_4Fe{=}CHOH$[215]) than in the Shrock-type complexes (1.83 Å in $(CO)_3NiCH_2$,[121] 1.87 Å in $Cl(H)Ru{=}CH_2$,[216] 1.89 Å in $H_2(CH_3)Nb{=}CH_2$,[217] 1.91 Å in $MoOCl(CH_3)(CH_2)$,[212] 1.99 Å in $CpCl_2Nb{=}CH_2$,[218] and 2.00 Å in $Cl_4W{=}CH_2$[124]). The rotational barriers in the Schrock-type complexes tend to be relatively high (15 kcal/mol in $CpCl_2Nb{=}CH_2$[218] and 11 kcal/mol in $H_2(CH_3)Nb{=}CH_2$[217]) compared to the barriers in the Fischer-type complexes (0.4 kcal/mol for $(CO)_5Cr{=}CH(OH)$ and 2.9 kcal/mol for $(CO)_4Fe{=}CH(OH)$[215]) (the low value of 0.2 kcal/mol for the barrier in $(CO)_3Ni{=}CH_2$ resulting probably from the 6-fold symmetry[121]). A high barrier of 31 kcal/mol has been reported for $MoOCl(CH_3)(CH_2)$ and linked to the presence of an oxo ligand in the coordination sphere.[212] The structure of lowest energy for $Cl_4W{=}CH_2$ is a TBP with the carbene ligand in the equatorial plane.[124] The most stable conformation of the *trans*-$Mo(CO)_4(CH_2)_2$ complex has the two carbene ligands mutually perpendicular and eclipsing the Mo–C bonds, with a rotation barrier close to 0.[219]

6. Metal Carbynes

For ScCH, optimized bond lengths of 1.86 and 2.24 Å have been reported for the doubly bonded and singly bonded states $^3\Pi$ and $^5\Pi$, respectively.[107] Comparable values of 1.94 and 2.18 Å have been obtained for the doubly bonded $^2\Pi$ and singly bonded $^4\Pi$ states of $ScCH^+$.[115,125] The bond length of 1.77 Å for the triply bonded $^3\Sigma^-$ state of $CrCH^+$ is, according to the authors, probably too long as a consequence of computational limitations at the CI level.[113] $CrCH^+$, VCH^+, and $TiCH^+$ are all characterized by a metal–carbon triple bond of similar length (1.77, 1.74, and 1.76 Å, respectively).[125] For $FeCH^+$ the bond length of 1.96 Å reported for the triply bonded $^3\Delta$ state appears rather long, furthermore the bond length of 2.04 Å for the singly bonded $^7\Delta$ state is only slightly longer (slightly longer values of 2.05 and 2.12 Å have been obtained for the states $^3\Delta$ and $^7\Delta$ of HFeCH).[117]

The bond length of the Cr≡C bond is calculated at the SCF level as 1.65 Å for $(CO)_5Cr{\equiv}CH^+$ and 1.62–1.65 Å (depending on the basis set) for $Cl(CO)_4Cr{\equiv}CX$ (X = H or CH_3).[176,217,220] CASSCF calclations produce some elongation of the computed CrC distance to 1.71–1.72 Å (in better agreement with the experimental value of 1.71 Å).[220]

7. Metal Alkenes

Several studies have been devoted to the structure of the nickel ethylene complexes. For the π-NiC_2H_4 complex, early studies[10,128] found that the geometry changes only slightly from that of the free molecule, with a CC bond length increased by ~0.02 Å and the CH bonds bent back 2° out of the ethylene molecular plane, the NiC bond distance being in the range 2.07–2.13 Å. Contrary to these findings, Widmark et al. found for the singlet ground state a considerably distorted C_2H_4 moiety with a CC bond length of 1.45 Å and the hydrogen atoms tilted away 21° from the CC axis, with a much shorter NiC bond distance of 1.97 Å.[130] In the case of $Ni_2C_2H_4$, Ozin et al. found essentially no change in the geometry relative to their results for NiC_2H_4.[127] Widmark and Roos considered four geometric arrangements, the end-on π-bonded structure being the only one bound with a NiC distance of 2.14 Å, a CC bond length of 1.37 Å, and a bending angle of 11°.[131] In the π-CuC_2H_4 complex the ethylene geometry appears as rather unperturbed by the weak van der Waals interaction in the $^2A_1$ ground state, with a CC distance of 1.37 Å, a bending angle of 3°, and a Cu–C_2H_4 distance of 2.37 Å.[133] The changes in the ethylene geometry become important in the excited state $^2B_2$ (with a CC distance of 1.51 Å, a bending angle of ~30°, and a Cu–C_2H_4 distance of 2.17 Å). Similar changes in the ethylene structure have been obtained by Cohen and Basch for the $^2B_1$ state of the π-AgC_2H_4 complex from Hartree–Fock calculations (with a CC distance of 1.46 Å and a bend angle of 25°).[135] Nicolas and Spiegelmann compared the potential energy curves for the ground state $^2A_1$ of MC_2H_4 with M = Cu, Ag, or Au, the gold complex having the shortest equilibrium distance.[134] Geometry optimization for the π-$ScC_2H_4^+$ complex yields a Sc–C distance of 2.19 Å with a CC bond length of 1.47 Å and a bend angle of 18°.[221] SCF calculations find the twisted (D_{2d}) and "planar" (D_{2h}) conformations of $Ni(C_2H_4)_2$ extremely close in energy (within 1 kcal/mol in ref 222 and 0.1 kcal/mol in ref 129). However, with the geometries optimized at the CASSCF level, the twisted D_{2d} structure is 10 kcal/mol lower than the planar D_{2h} structure at the CI level[132] (this D_{2d} structure has a geometry which is similar to the π-NiC_2H_4 structure, with a NiC distance of 1.95 Å, a CC distance of 1.41 Å and a tilt angle of 18°). For $Ni(C_2H_4)_3$ the planar conformation is 24 kcal/mol lower than the upright form at the SCF level.[129] For $Ag(C_2H_4)_2$ only the D_{2h} geometry was investigated at the SCF level and shows longer Ag–C distance and smaller ligand geometry changes compared to the monoligand complex.[135]

For a number of Ni(0) and Ni(II) ethylene complexes $NiX_2(C_2H_4)$ with various ligands (X = F^-, Cl^-, NH_2^-, CN^-, CH_3^-, H_2O, NH_3, PH_3), the CC distance optimized at the SCF level was in all cases longer than in the free ethylene, the Ni(0) complexes having longer CC bond distances than the Ni(II) complexes.[223] The geometry of the NiC_2H_4 moiety has been optimized at the SCF level for $Ni(NH_3)_2(C_2H_4)$ and $Ni(PH_3)_2(C_2H_4)$, the increase in the CC bond length of ethylene was calculated to be 0.1 Å (in rather good agreement with the results of ref 223), the bending angle being 32° and 26° for the ligands NH_3 and PH_3, respectively.[224] The effect of electron correlation on the Ni–C distance in $Ni(PH_3)_2(C_2H_4)$ has been studied with the SD-CI, MP2, and MP4 methods. SD-CI calculations lengthen the Ni–C distance by 0.05 Å, whereas the MP2 and MP4 calculations increase it by 0.3–0.4 Å (a comparison with the experimental values suggest that the SD-CI method is more reliable than the MP method in these complexes).[78] In the square-planar system $RhCl(PH_3)_2(C_2H_4)$, the geometry of the $Rh(C_2H_4)$ moiety was optimized at the SCF level (Rh–C = 2.36 Å, C–C = 1.34 Å, with a bending angle of 7°) and the structure with the ethylene perpendicular to the $RhCl(PH_3)_2$ plane is more stable than the in-plane structure by 11 kcal/mol.[175] The calculated Rh–C distance seems to be overestimated by 0.24 Å and several reasons have been considered: (i) the $RhCl(PH_3)_2$ geometry is kept fixed when optimizing the Rh–C distance; (ii) the electron correlation is neglected; (iii) the relativistic effects which tend to yield rather long bond distances are missing. Dedieu considered (but without geometry optimization) the 12 geometries possible for the $H_2RhCl(PH_3)_2(C_2H_4)$ system (with the restriction that C_2H_4 is eclipsed with respect to two of the cis rhodium–ligand bonds).[205] The relative stabilities of these 12 stereoisomers are controlled by three main factors: the steric interaction and the two orbital interactions of the Dewar–Chatt model. The upright conformers (with the ethylene ligand perpendicular to the equatorial plane) tend to be more stable than the planar conformers and this has been traced to less steric repulsion. Daniel et al. optimized with the Hartree–Fock energy gradient method the geometry of the isomer with the olefin cis to one hydride ligand and trans to the other.[206] They found very long Rh–C bonds of 2.60 and 2.58 Å (which could be reduced somewhat by electron correlation). This was not an artifact of the calculation since the Rh–C bond length in square-planar $RhCl(PH_3)_2(C_2H_4)$ (with ethylene trans to chloride) is calculated with the same basis set to be 2.11 Å in good agreement with the experimental value of 2.12 Å. This suggests that these long rhodium–ethylene distances are due to the strong trans influence of the hydride that is trans to ethylene.[206] In fact the M–C bond lengths calculated in similar nickel- and palladium–ethylene cis dihydride complexes $H_2M(PH_3)(C_2H_4)$ are 2.50 and 2.54 Å for M = Ni and 2.49 and 2.50 Å for M = Pd.[204] Since the Rh–C distance in $HRh(PH_3)_2(C_2H_4)$ is calculated to be 2.41 Å, the Rh–C distances in $H_2RhCl(PH_3)_2(C_2H_4)$ are still longer and suggest that there is some effect of cis ligands as well. To check this point, Daniel et al. optimized the structure of $H_3Rh(PH_3)_2(C_2H_4)$, with the Rh–C distances being 2.41 Å, hence shorter by 0.2 Å than those in $H_2RhCl(PH_3)_2(C_2H_4)$. This indicates that a cis chloride makes the metal–ethylene bond distance longer than a cis hydride.[206]

The geometries of the π-complexes $[MCl_3(C_2H_4)]^-$ (M = Pd or Pt) were optimized at the Hartree–Fock level (with the MCl_3 fragment held rigid) and compared with the structure determined for the Zeise's salt.[225] For the Pt compound, the calculated metal–olefin bond distance of 2.11 Å is 0.09 Å longer than the observed bond length but the distortions of the ethylene ligand upon coordination are well represented: bending of 13° compared to 16° experimentally and lengthening of the CC bond length by 0.053 Å (0.037 Å experimentally). The upright form is more stable than the planar one and the calculated barrier to rotation of 15 kcal/mol agrees well with the experimentally observed barriers in the range 10–14 kcal/mol. The barriers decrease in the order Pt > Pd. Geometry optimization was carried out for the complex $PdF_2(NH_3)(C_2H_4)$,[226] and the results agree well with those of Hay for $[PdCl_3(C_2H_4)]^-$ [225] (CC bond length of 1.34 Å vs 1.35 Å and bending angle of 7° vs 8°, Pd–C_2H_4 distance of 2.29 Å vs 2.25 Å).

The relative energies of the different conformations for the complexes *trans*-$MoL_4(C_2H_4)_2$ (with L = PH_3 or CO) have been discussed by Bachmann et al.,[222] the most stable one having the two ethylene ligands mutually perpendicular and eclipsing the Mo–L bonds. For L = PH_3, a barrier of 16–17 kcal/mol has been estimated for the rotation about the metal–olefin bond and compares well with the experimental value of 15 kcal/mol.

8. Metal Alkynes

Geometry optimization has been carried out for the triplet state of the Ni–acetylene complex, with the geometry changing only slightly from that of the free ligand (the CC bond length increasing by 0.02 Å with a bending angle of 5°) and a calculated Ni–C distance of 2.01 Å.[128] When the optimization is performed for the singlet ground state, the Ni–C is appreciably shorter (1.94 Å), the CC bond length increases by 0.08 Å with a bending angle of 32°.[136] Search on the Pd(C_2H_2) singlet surface yields a minimum for a Pd–C distance of 2.30 Å, a CC bond length increased by 0.03 Å, and a bending angle of 17°.[136] Geometry optimization at the SCF level for the Ag(C_2H_2) complex points to an increase in the CC bond length of 0.10 Å with a bending angle of 37° and an Ag–C distance of 2.28 Å.[135] The change compared to the free ligand is much smaller for the diacetylene complex, the CC bond length increasing by 0.03 Å only with a bending angle of 15° and an Ag–C distance of 2.50 Å. The geometrical parameters optimized for Ni(PH_3)$_2$(C_2H_2) are not very different from those reported for Ni(C_2H_2), with the CC bond length stretched by 0.09 Å, a bending angle of 40°, and a Ni–C distance of 1.89 Å.[224]

9. *Metallocenes and Cyclic Polyene Complexes*

Rather large errors characterize the metal–ring distance of the metallocenes optimized at the SCF level: the theoretical value of 1.88 Å in ferrocene differs appreciably from the experimental value of 1.65 Å.[164] Optimization of the ligand geometry did not improve the results. Comparable errors were reported for VCp_2 (0.19 Å), $MnCp_2$ (0.21 Å), $CoCp_2$ (0.23 Å), and $NiCp_2$ (0.16 Å).[227] The error is smaller for the positive ions (0.11–0.12 Å for $FeCp_2^+$ and $CoCp_2^+$) and for the half-sandwich compounds (0.10 Å for NiCpNO).[227] Large CI expansions bring the theoretical distance in ferrocene down to 1.72–1.74 Å, but these values are still off by nearly 0.1 Å (relativistic effects appear to be of minor importance and the remaining error has been ascribed to the incompleteness of the basis sets used and of the CI expansion).[228,229] The staggered (D_{5d}) conformer has an energy 0.6 kcal/mol above that of the eclipsed (D_{5h}) conformer.[164]

For the dibenzenechromium [$Cr(C_6H_6)_2$], the Cr–benzene distance optimized at the SCF level with a split-valence basis set is 0.07 Å longer than the experimental value (the error in ferrocene with this basis set amounts to 0.18 Å).[163] The same error of 0.07 Å has been obtained for the metal–ring distance in the benzenechromium tricarbonyl [$Cr(C_6H_6)(CO)_3$] (the optimized CC bond lengths are within 0.004 Å of experimental results and alternate long and short, the CC bonds eclipsed with the carbonyls being longer by 0.02 Å).[163] In $MnCp(CO)_3$ the calculated metal–ring distance is too long by 0.12 Å.[163] Unlike the geometry optimizations on the cyclopentadiene and benzene complexes which yield metal–ring distances too long, the calculated metal–ring distance in bis(cyclobutadiene)nickel[$Ni(C_4H_4)_2$] tends to be too short. Structural optimization at the SCF level for the D_{4h} conformation yielded a Ni–ring distance of 1.72 Å (experimental value 1.74 Å for $NiCl_2(C_4Me_4)$) and a CC distance of 1.45 Å with a bending angle of 5°.[230] The eclipsed (D_{4h}) conformation is estimated to lie 1.3 kcal/mol below the staggered (D_{4d}) form. The error on the Ni–ring distance increases (to 0.06 Å too short) when a smaller basis set is used.[163]

Most of geometry optimizations in ferrocene were carried out with the assumption of a D_{5h} or D_{5d} symmetry.[163,164,228,229] STO-3G calculations yield a structure of C_s symmetry (with the iron atom coordinated in an η^5 position for one ring and at η^3 for the other) 37 kcal/mol below that optimized with a D_{5h} symmetry constraint.[231] By using a split-valence basis set, this relative energy difference is reduced to 5 kcal/mol. The relative stability of structures exhibiting alternative coordination modes of the cyclopentadienyl ligand (η^1, η^2, and η^5 modes) has been estimated in $TiCl_3Cp$, $TiCl_2Cp_2$, $TiClCp_3$, $TiCp_4$, and $TiCp_2$.[232]

Symmetry-adapted SCF calculations carried out on μ-$(NO)_2[Fe(C_5H_5)]_2$ with a planar $(FeNO)_2$ core yield a conformation with staggered cyclopentadienyl rings to be more stable by 60 kcal/mol than a conformation with eclipsed rings.[233] This barrier, about 2 orders of magnitude higher than the barrier expected for the rotation of a cyclopentadienyl ring, is an artifact resulting from the different levels of symmetry constraints for the two isomers.

D. Binding Energies

The estimate of dissociation energies for the bound states represents a challenge for a number of reasons. Major sources of error include the basis set superposition error and the size consistency problem.[1,234] Most often the bond energies are not very large. The SCF approximation usually leads to very poor results and SCF errors of 40–80 kcal/mol for binding energies are typical. For instance the $^1\Sigma^+$ state of NiCO is unbound by 68 kcal/mol at the SCF level and bound by 16 kcal/mol at the CI level.[76] The CI approach as currently used at the SD level breaks down due to size inconsistency, namely the calculated correlation energy does not scale properly with the number of correlated electrons. One has then to turn to size-consistent methods such as the CPF and MCPF methods.

1. *Metal Carbonyls*

For ScCO dissociation energies of 25 kcal/mol have been reported for the states $^4\Sigma^-$ and $^4\Pi$ with respect to the Sc ^4F d^2s^1 asymptote.[87] Frey and Davidson estimate the $^4\Sigma^-$ minimum to be bound by 5 kcal/mol and have presented a detailed analysis of the bond energies (both SCF and correlated) in terms of s → d promotion energy of the metal, distortion energy of the carbonyl, SCF interaction energy, and dispersion energy.[89] The SCF interaction energy has been partitioned into components via the Morokuma analysis.[235] A dissociation energy of 28 kcal/mol has been reported for the state $^3\Sigma^-$ of FeCO.[90] Difficulties associated with the calculation of dissociation energies are exemplified for NiCO. A dissociation energy of 20–30 kcal/mol relative to the ^1D state of the nickel atom has been calculated for the state $^1\Sigma^+$ of NiCO.[81,90] A value of 18 kcal/mol relative to the ^3D state has also been reported.[82] It was found that correlation of the two σ lone-pair electrons was important for the dissociation energy, which decreases from 30 to 25 kcal/mol if only the 10 nickel electrons are correlated.[81] Inclusion of f functions in the nickel basis set and d functions in the carbon and oxygen basis sets have practically no effect on the binding energy.[81,97,236] A value of 33 kcal/mol (relative to the ^3D state of the nickel atom) was obtained with all 20 valence electrons correlated (the experimental prediction being about 40 kcal/mol).[97] A close value of 30 kcal/mol has been obtained by Bauschlicher et al. using a coupled pair functional method, with all the valence electrons correlated.[174] A dissociation energy of 26 kcal/mol was initially reported[7] for the state $^3\Delta$ which was later characterized as unbound.[81] Finally all three triplet states a$^3\Delta$, b$^3\Sigma^+$, and c$^3\Pi$ were found to be bound by 11, 10, and 4 kcal/mol, respectively.[92,174] A dissociation energy of 28 kcal/mol has been obtained for the state $^2\Pi$ of CuCO.[91] Dissociation energies of 4 and 7–8 kcal/mol have been reported for the low-spin states $^2\Sigma^+$ of RhCO and $^1\Sigma^+$ of PdCO, respectively (their high-spin states were found to be repulsive).[16,85] (A value of 18 kcal/mol was reported for PdCO by the same authors using a different ECP.[167]) For the doublet state of RhCO, a value of 42 kcal/mol is 1 order of magnitude larger.[99] For PdCO Blomberg et al. report a much larger value of 33 kcal/mol (with a relativistic contribution of 11 kcal/mol).[166,237] The value of 37 kcal/mol obtained by Rohlfing and Hay at the MP2 level[84] has been considered as somewhat fortuitous since the binding energy of 58 kcal/mol obtained for NiCO at the same level seems overestimated.[84,186] Binding energies of 43 and 45 kcal/mol have been obtained for PtCO at the CI and MP2 levels, respectively.[84,86]

In MCO$^+$ systems, pure electrostatic interactions are dominant, the leading ones being the charge–dipole and charge–induced dipole interactions. Since the dipole moment of CO is known to be sensitive to correlation effects, correlation on CO is likely to be more important than correlation on the metal. A CI calculation yields a binding energy of 26 kcal/mol for NiCO$^+$ (replacing the Ni ion with a simple point charge leads to a binding energy of 28 kcal/mol which is increased to 31 kcal/mol by enlarging the basis set on the carbonyl ligand).[97] It was then concluded that the experimental binding energy of 48 kcal/mol is at least 10 kcal/mol too large. The same conclusion was reached from the calculation of ref 94, with the 19 valence electrons correlated and a computed dissociation energy of 34 kcal/mol. With a large basis set, the binding energy of TiCO$^+$ has been estimated to 28 kcal/mol.[94] A value of 27 kcal/mol has been reported for the binding energy of CuCO$^+$.[91] Mavridis et al. compared the binding energies calculated for MCO$^+$ (M = Sc, Ti, V, and Cr) with a purely electrostatic interaction and correlate them with the M–C bond length.[96] Barnes et al. have reported binding energies for the first and second series transition metal carbonyl ions, using large basis sets.[98] These binding energies are largest when the metal ion has a d^{n+1} ground state. They are generally in good agreement with experimental data, with the exception of Mo(CO)$^+$. A binding energy of 31 kcal/mol has been obtained at the MP3 level for RhCO$^+$.[99]

The binding energy of 20 kcal/mol calculated for NiCO$^-$ compares well with the experimental value of 21 ± 15 kcal/mol.[97] Bauschlicher et al. obtained a value of 18 kcal/mol but estimated that a basis set enlargement would increase it to 22 kcal/mol.[92] However their last value obtained with a large basis set is 18 kcal/mol.[174]

Blomberg et al. found that the binding energy of Ni(CO)$_2$ relative to the dissociated system Ni(^{1}D) + 2CO is 57 kcal/mol, almost twice the binding energy of NiCO (30 kcal/mol at the same level of calculation)[81] (a CASSCF value of 56 kcal/mol has also been reported[93]). The binding energy of 20 kcal/mol obtained for Rh(CO)$_2$ at the MP3 level (with respect to the fragments Rh + 2CO) is less than half the binding energy of 42 kcal/mol reported for the monocarbonyl system RhCO.[99] The same anomalous behavior is observed for the cations RhCO$^+$ and Rh(CO)$_2$$^+$, with respective binding energies of 31 and 33 kcal/mol.[99] This should be compared to the values of 31 and 59 kcal/mol obtained by Barnes et al.[98] These authors reported binding energies for the first and second series transition-metal dicarbonyl positive ions, which are in general close to (or even larger than) twice the binding energies for the monocarbonyl ions.

Calculation of accurate total binding energies for saturated carbonyls represents a challenge due to the large number of electrons of these systems. For Ni(CO)$_4$ an early CI calculation correlating the Ni 3d electrons gives a binding energy of 86 kcal/mol when the experimental values are 120 and 140 kcal/mol.[81] The agreement between theory and experience has been much improved in a calculation which included correlation effects for the ligands and produced a binding energy of 120 kcal/mol[76] (a close value of 118 kcal/mol has been obtained in a similar calculation[174]). Most noteworthy is the fact that theory predicts a much more regular trend in the carbonyl binding energies of Ni(CO)$_4$ than what is obtained from experiment. The dissociation energies obtained at the MP2 level for M(CO)$_4$ with M = Ni, Pd, or Pt are sizable overestimates of the experimental values but reproduce the experimental order of stability Ni > Pt > Pd.[84]

The dissociation energy of a single carbonyl ligand from Cr(CO)$_6$ is 50 kcal/mol at the SCF level (with the assumption of a frozen geometry) and the corresponding value of 31 kcal/mol for Cr(CO)$_6$$^+$ is in good agreement with the experimental value of 33 kcal/mol.[238] A value of 43 kcal/mol has been obtained at the CI level for the dissociation energy of the first carbonyl ligand from Fe(CO)$_5$ and should be compared to the experimental value of 55 ± 11 kcal/mol.[100] The low value of 22 kcal/mol for the dissociation energy of the axial carbonyl ligand of HCo(CO)$_4$ probably results from the large trans influence of the hydride ligand.[27] A binding energy of 36 kcal/mol has been reported at the SCF level for the carbonyl ligand of RhCl(PH$_3$)$_2$(CO) and partitioned according to the energy decomposition of Morokuma.[175]

2. *Metal Carbides*

The dissociation energy calculated for the PdC molecule is 29 kcal/mol.[105] For CrC$^+$, the binding energy (with approximate size-consistency) is 32 kcal/mol for the ground state $^4\Sigma^-$ and 13 kcal/mol for the excited state $^4\Pi$.[106]

3. *Metal Carbon Dioxide Complexes*

The binding energy of CO$_2$ to Ni(PH$_3$)$_2$ (side-on coordination) and Cu(PH$_3$)$_2$$^+$ (end-on coordination) has been calculated as 27 and 14 kcal/mol, respectively, and decomposed into its various components.[190] For the complex RhCl(AsH$_3$)$_4$(CO$_2$) the correlation effects significantly influence the binding energy (27 kcal/mol at the MP2 level but slightly negative at the HF level).[108] The SCF binding energy of CO$_2$ in $[\mathrm{Co(alcn)_2(CO_2)}]^-$ (in the η^1-C mode) is 6 kcal/mol but increases to 20 kcal/mol in the presence of a Li$^+$ cation.[194]

4. *Metal Alkyls*

Bauschlicher et al. have reported metal–carbon bond dissociation energies for the first and second series transition-metal methyls using large basis sets, with the valence electrons of the metal and the methyl ligand correlated.[51] The relativistic contribution was included through first-order perturbation theory for the first transition series and through the ECP for the second series. The computed D_0 values agree well with the experimental values for the methyls of the first transition series. Previous theoretical work on $NiCH_3$ yielded binding energies of 60 kcal/mol[109] and 45 kcal/mol,[196] the latest being close to the result of ref 51.

The study of Bauschlicher et al. produced a quite good agreement between the theoretical and experimental D_0 values for the methyl positive ions, with the theoretical values slightly smaller than experiment.[51] It was suggested that the experimental D_0 values for $RuCH_3^+$, $RhCH_3^+$, and $PdCH_3^+$ are of the order of 10 kcal/mol too large. The bond dissociation energies obtained by Schilling et al. for the ions MCH_3^+ (M = Sc, Cr, Mn, Y, Mo, Tc, Pd) are in excellent agreement with the values of Bauschlicher et al., within 3 kcal/mol or less.[114] The binding energies reported for $ScCH_3^+$,[115] $CrCH_3^+$,[113] and $FeCH_3^+$ [117] are systematically smaller than the values of Bauschlicher et al. (according to Harrison et al., this error should be traced to the CI function correlating only the CH_3 electrons which participate in the σ bond with Cr^+, with the consequence that the polarizability of CH_3 is not well represented[113]).

Binding energies have been reported for the dimethyl positive ions $M(CH_3)_2^+$ of the first and second transition series.[19] The influence of the ligand L (L = C_2H_4, C_2F_4, CO, PH_3, N_2, H_2O, Cl^-) on the interaction energies calculated for the complex LNi(H)(CH_3) relative to LNi and CH_4 has been correlated to the amount of covalent metal–ligand bonding. The larger the covalent metal–ligand bonding, the larger is the destabilization of the M–R bonds (R = H, CH_3).[237]

5. Metal Carbenes

$MnCH_2$ in the state $^8B_1$ is bound by 33 and 35 kcal/mol at the SCF and CI levels, relative to ^6S Mn and $^3B_1$ CH_2.[118,239] A binding energy of 65 kcal/mol has been calculated for $NiCH_2$.[109] The bond energy decreases in the series $ScCH_2^+$ (68 kcal/mol), $TiCH_2^+$ (67 kcal/mol), VCH_2^+ (62 kcal/mol), and $CrCH_2^+$ (39 kcal/mol) (these calculated bond energies being smaller than the experimental values of 97 kcal/mol for $ScCH_2^+$ and 80 ± 8 kcal/mol for VCH_2^+).[122] Bond dissociation energies of 41 and 22 kcal/mol have been obtained for the excited states $^7B_1$ of $MnCH_2^+$ and $^6B_1$ of $CrCH_2^+$, relative to ^7S Mn^+ or ^6S Cr^+ and $^3B_1$ CH_2.[119] Carter and Goddard obtained a binding energy of 44 kcal/mol for the ground state $^4B_1$ of $CrCH_2^+$ dissociating into the fragments ^6S Cr^+ and $^3B_1$ CH_2.[120] They estimate the fully correlated limit to be 49 kcal/mol, which may be compared to the experimental value of 65 ± 7 kcal/mol. The same complex in the excited state $^6A_1$ (corresponding to a carbene bond of the donor–acceptor type) has a much lower bond energy of 39 kcal/mol.[213] The same authors calculated a bond energy of 68 kcal/mol for $^2A_2$ $RuCH_2^+$ dissociating into the fragments ^4F Ru^+ and $^3B_1$ CH_2 and estimate the exact value to be 74 kcal/mol.[123] The bond strength for the state $^4A_2$ of $RuCH_2^+$ (corresponding to a σ-donor, π-acceptor bond) is of the same magnitude, 66 kcal/mol. The bond energy increases to 85 kcal/mol for the larger complex $ClRuH(CH_2)$, due to the loss of exchange coupling on the metal (a consequence of the presence of additional ligands).

SCF bond energies of 44 and 37 kcal/mol have been reported for the Fischer-type compounds $(CO)_5Cr{=}CH(OH)$ and $(CO)_4Fe{=}CH(OH)$ dissociating to the singlet fragments[215] (bond energies at the HF level are probably reasonable for carbene complexes of the donor–acceptor type[123,213]). A SCF value of 112 kcal/mol has been obtained for the dissociation energy of the Nb=C bond in $H_2(CH_3)Nb{=}CH_2$ to the closed-shell singlet fragments (with a value of 48 kcal/mol for the dissociation to the triplet fragments).[217] Taylor and Hall report a dissociation energy of 50 kcal/mol at the SCF level for $(CO)_5Mo{=}CH(OH)$, which increases to 60 kcal/mol at the CI level.[218] Their computed dissociation energies for $CpCl_2Nb{=}CH(OH)$ and $(CO)_5Mo{=}CH_2$ are rather comparable (58 and 56 kcal/mol) but the value obtained for $CpCl_2Nb{=}CH_2$ is appreciably higher, 74 kcal/mol (the absolute accuracy of these dissociation energies may be in error by 10–15 kcal/mol).[218]

6. Metal Carbynes

A lower limit of 60 kcal/mol has been proposed for the bond energy of ScCH.[107] M–C bond strengths in the carbyne cations MCH^+ (M = Sc, Ti, V, Cr) have been computed at the CI level in a size-consistent way. The computed values of 79, 96, 91, and 54 kcal/mol, respectively, are probably lower bounds[125] (the experimental value of D_e for VCH^+ being 115 kcal/mol). The POL-CI technique yields for $CrCH^+$ a slightly larger value of 61 kcal/mol.[113] Ushio et al. obtained a dissociation energy of 175 kcal/mol to the singlet closed-shell fragments for the Cr=C bond of $(CO)_5Cr{\equiv}CH^+$ at the SCF level.[217] For $Cl(CO)_4Cr{\equiv}CH$, the Cr=C bond energies corresponding to the fissions into the doublet and quartet fragments are 58 and 41 kcal/mol at the SCF level,[217] but it has been shown that these positive values result from a cancellation of errors introduced by the use of a limited basis set and the lack of correlation effects, since the fragments in their quartet states have an energy lower by 5 kcal/mol than that of the carbyne complex when a larger basis set is used at the SCF level.[220] A bond energy of 115 kcal/mol has been obtained at the CASSCF level with respect to both fragments computed in the quartet states[220] and this value is reduced to 109 kcal/mol by accounting for the basis set superposition error. A dissociation energy of 102 kcal/mol has been computed for the Cr=C bond of $Cl(CO)_4Cr{\equiv}CCH_3$ with respect to the superposition of the metal fragment in its $^4A_2$ ground state and CCH_3 in its ^2E ground state (the corresponding value for $Cl(CO)_4Cr{\equiv}CH$ being 107 kcal/mol).[117]

7. Metal Alkenes and Metal Alkynes

A bond energy of about 60 kcal/mol has been mentioned for the interaction of Ni(I) ($3d^9$) with ethylene or acetylene[128] (compared to a binding energy of 80 kcal/mol for the interaction of Ni(II) with ethylene[223]), these large values resulting probably from the electrostatic interactions. The bond energy for the neutrals is smaller, also as a consequence of the repulsive interactions with the 4s orbital. Early calculations reported binding energies of 6–14 kcal/mol for Ni–ethylene and 17 kcal/mol for Ni–acetylene in the triplet state.[10,128] A SCF value of 27 kcal/mol was obtained for Ni–ethylene with the electronic state assumed to be a closed-shell singlet.[223] For the $^1A_1$ ground state of Ni–ethylene, the computed binding energy was 20 kcal/mol relative to Ni ($d^9s^1\ ^1D$) and the triplet state was found to be essentially unbound.[130] The binding energy in MC_2H_4 complexes (M = Cu, Ag, Au) is small for the ground state of these van der Waals complexes (2–3 kcal/mol for copper and silver, with a larger value of 12 kcal/mol for the gold complex as a consequence of relativistic effects).[134] It increases to larger values (in the range 19–66 kcal/mol) for the excited states, the dissociation energies of the AuC_2H_4 states being about twice those of CuC_2H_4 and AgC_2H_4. The binding energies obtained at the SCF level for the excited states of $Ag(C_2H_4)_n$ and $Ag(C_2H_2)_n$ with n = 1 or 2 are of the same order of magnitude.[135]

In the Ni(II) complexes $X_2Ni(C_2H_4)$, the presence of a ligand X decreases the binding energy, this being especially true when X is negatively charged (in fact no neutral Ni(II) complexes have been isolated). On the contrary the binding energy for the Ni(0)–ethene complexes are increased on the addition of ligands.[223]

The SCF binding energy is larger in the acetylene complex $Ni(PH_3)_2(C_2H_2)$ (37 kcal/mol) than in the ethylene complex $Ni(PH_3)_2(C_2H_4)$ (30 kcal/mol).[224] There is a reasonable agreement between the SCF binding energies of refs 223 and 224, respectively, 54 and 64 kcal/mol for $Ni(NH_3)_2(C_2H_4)$ and 36 and 30 kcal/mol for $Ni(PH_3)_2(C_2H_4)$. More recently the binding energy of $Ni(PH_3)_2(C_2H_4)$ has been investigated at different levels of theory: it increases from 29 kcal/mol at the HF level to 35 kcal/mol at the MP2 level, with the full CI value estimated at 35 kcal/mol and the experimental value close to 30 kcal/mol.[78] A SCF value of 24 kcal/mol has been reported for the binding energy of the ethylene ligand in the complex $RhCl(PH_3)_2(C_2H_4)$.[175] The influence of the cis and trans ligands on the $Rh-C_2H_4$ binding energy in a series of complexes $RhLL'L''(PH_3)_2(C_2H_4)$ (L, L', L'' = vacancy, H, Cl) has been studied at the SCF level, with the binding energy ranging from 8 kcal/mol in $RhH_2Cl(PH_3)_2(C_2H_4)$ (with an hydrogen atom in trans) to 35 kcal/mol in $RhCl(PH_3)_2(C_2H_4)$ (with the chlorine atom in trans).[206] Binding energies were also reported for the corresponding Pt complexes. In the complex $[MCl_3(C_2H_4)]^-$ the ethylene was calculated to be bound by 28 kcal/mol for M = Pt and 12 kcal/mol for M = Pd.[225] The binding energy of a series of complexes $PdF_nL_{3-n}(C_2H_4)$ (n = 1–3, L = NH_3 or PH_3) range from 16 to 24 kcal/mol at the SCF level.[226]

Two close values of 36 and 34 kcal/mol have been reported for the binding of ethylene to the $CH_3TiCl_2^+$ complex at the SCF level, which increases to 49 kcal/mol at the MP2 level.[240,241] A much lower value of 16 kcal/mol was obtained at the MP2 level for the binding of ethylene to the complex $[Cp_2Ti(CH_3)]^+$.[241] A change of 5 kcal/mol in the free energy has been reported for the complexation of ethylene to $MOCl_2(CH_2)(LB)$ (M = Cr, Mo, W and LB = Lewis base), together with a complexation enthalpy of 18 kcal/mol for the interaction of ethylene with Cl_2TiO.[242]

E. Other Properties

1. Vibrational Frequencies

Calculated vibrational frequencies together with their intensities should be helpful for the identification of unstable species in inert gas matrices and gas-phase experiments. The knowledge of complete force fields is also profitable for the determination of thermodynamic data. Vibrational frequencies are usually obtained by taking finite differences of analytical energy gradients.

Carbonyl frequency shifts of 330, 280, and 240 cm^{-1} have been predicted for ScCO, TiCO, and VCO, respectively.[243] Frequencies have been reported for the stretching modes of ScCO (ν_{ScC} = 33 cm^{-1} and ν_{CO} = 2123 cm^{-1} in the van der Waals state $^2\Pi$, ν_{ScC} = 416 cm^{-1} and ν_{CO} = 1906 cm^{-1} for the ground state $^4\Sigma^-$, in good agreement with the experimental value ν_{CO} = 1950 cm^{-1}).[89] Blomberg et al. obtained for NiCO a frequency ν_{CO} = 2030 cm^{-1} (experimental value 2028 cm^{-1}) and a frequency shift compared to the free carbonyl of 143 cm^{-1} in excellent agreement with the experimental shift of 142 cm^{-1}.[97] Bauschlicher et al. estimated the Ni–C stretching modes for the ground state of NiCO and $NiCO^-$ and the excited states of NiCO.[92] Their value of 510 cm^{-1} for the ground state of NiCO is close to the value of 505 cm^{-1} of ref 8. The vibrational frequencies (and the infrared intensities) in the series of nickel carbonyls $Ni(CO)_n$ with n = 1–4 have been studied by Carsky and Dedieu at the SCF level (with MP2 calculations for NiCO).[165] The MP2 values were in rather good agreement with experiment for CO and NiCO, with SCF frequencies overestimated by as much as 20%. For $Ni(CO)_4$ A_1 Ni–C stretching frequencies of 418 and 277 cm^{-1} have been obtained at the SCF level, the experimental value being 371 cm^{-1}.[165,169] Blomberg et al. have performed rather accurate calculations of the CO stretching modes in Ni(CO) and $Ni(CO)_2$, with the trends in the experimental frequency shifts rather well reproduced (the best results being obtained from the calculations with all the carbonyl valence electrons correlated).[76] The force constants for the totally symmetric metal–ligand stretching vibrations of $Fe(CO)_5$ turn to be rather sensitive to correlation effects.[49] For the dihydrogen complex $W(CO)_3L_2(H_2)$ (L = phosphine) both theory and experiment show a marked decrease in the H–H stretching frequency from free H_2 (calculated 4561 cm^{-1}, experimental 4401 cm^{-1}) to the complex (calculated 2474 cm^{-1}, experimental 2690 cm^{-1}).[184] These SCF calculations apparently underestimate the degree of $M-H_2$ bonding as measured by the $M-H_2$ stretching frequency of 808 cm^{-1} compared with 1575 cm^{-1} observed experimentally.[184]

A vibrational frequency of 726 cm^{-1} has been predicted for the ground state of CrC^+.[106]

Force constants for the $M-CH_3$ stretch and the MCH symmetric bend have been obtained for the ions MCH_3^+ (M = Sc, Cr, Mn, Y, Mo, Tc, Pd).[114] Vibrational frequencies for the $M-CH_3$ stretch have been reported for the first and second series transition-metal methyls and their positive ions and turn out to be quite similar for the different metals except $CuCH_3^+$ and $AgCH_3^+$.[51] SCF vibrational frequencies have been computed at the SCF level for $ScCH_3$ and $CuCH_3$, with the CH stretching frequencies being reduced relative to the free methyl (for $CuCH_3$ the SCF modes disagree with the experimental assignment with respect to the order of the symmetric and asymmetric C–H stretches).[51] The vibrational frequencies of *cis*- and *trans*-$PtH(CH_3)(PH_3)_2$ have been obtained at the HF level.[197] The Pt–C stretching frequency is 520 cm^{-1} for the trans compound and 560 cm^{-1} for the cis one, with experimental values in the range 516–566 cm^{-1}. From the vibrational frequencies calculated at the HF level for H_3TiCH_3 and H_3GeCH_3, a large difference of 401 cm^{-1} was found in the methyl rocking mode frequency of these two compounds, which accounts for the experimental difference of 245 cm^{-1} observed between Cl_3GeCH_3 and Cl_3TiCH_3 (the potential energy surface as a function of the rock angle being flatter for the titanium compounds).[200]

The vibrational frequencies have been obtained for the state $^4B_1$ and $^6B_1$ of $CrCH_2^+$,[120] for the states $^2A_2$ and $^4A_2$ of $RuCH_2^+$ and for the $^1A'$ ground state of $ClRuH(CH_2)$.[123] The M=C frequencies correlate with the bond strength in the order $Cr^+ < Ru^+ < ClRuH$. Approximate vibrational frequencies have been calculated at the SCF level for the M=C bond of $(CO)_5Cr{=}CH(OH)$, $(CO)_4Fe{=}CH(OH)$ and $H_2(CH_3)Nb{=}CH_2$.[215,217] One-dimensional determinations of the frequency shift for the symmetric C–C stretch has produced a value of 276 cm^{-1} for $Ni(C_2H_4)$ (experimental 130 cm^{-1}).[236] The symmetric metal–ring stretching frequency for ferrocene is 244 cm^{-1} at the SCF level and should be compared to the experimental value of 301 cm^{-1} (for decamethylferrocene, both values are equal to 179 cm^{-1} but the agreement is certainly fortuitous).[164]

2. Dipole Moment

Dipole moments have been calculated for the mono and dicarbonyls of Sc, Ti, and V.[243] Dipole moments based on CASSCF wave functions (which do not include sufficient correlation to give quantitatively accurate properties) have been reported for four electronic states of NiCO, for $^5\Sigma^-$ FeCO, and for $^2\Sigma^-$ CuCO.[90] Dipole moments were calculated by Bauschlicher et al. with large basis sets and all the valence electrons correlated for the same electronic states of NiCO, for three electronic states of $NiCO^+$, and for $NiCO^-$.[92,174] Theoretical values of the dipole moment have been used to analyze the bonding in $TiCO^+$ and $NiCO^+$.[94] Dipole moments were also evaluated for the first and second series transition-metal carbonyl and methyl positive ions and for the neutral methyls.[51,98] For the methyl ions, the dipole moment changes sign with increasing Z, since the donation switches from metal to CH_3, for the early metals, to CH_3 to metal, in the later ones.[51] For the state $^8B_1$ of $MnCH_2$, the theoretical dipole moment is +1.48 D (Mn^+C^- polarity) compared to those of isolated triplet and singlet methylene, −0.66 and −2.40 D.[118] The dipole moments of $(CO)_5Cr{=}CH(OH)$ and $(CO)_4Fe{=}CH(OH)$ are calculated to be 5.28 and 4.50 D, respectively, at the SCF level.[215]

The dipole derivatives for the metal–ligand and intraligand stretches in NiCO have been evaluated and the ratio of the two stretches shows excellent agreement with experiment.[244]

3. Electron Density

Density difference maps for the σ and π electrons of RhCO and PdCO do not show any increase of the σ electron density in the M–C bond region but an increase of the π electron density near the carbon atom.[85] σ and π density difference maps have been used to analyze the bonding in $NiCO^+$ $^2\Sigma^+$ and $TiCO^+$ $^4\Delta$.[94] Density difference maps for $Cr(CO)_6$ show a density increase in the carbon p_π orbital and in the d_σ orbital of chromium, together with a density decrease in the region of the carbon lone pair and in the d_π orbital of chromium[155] (a slightly different picture emerges from the maps of ref 238). A comparison of the maps for $V(CO)_6^-$, $Cr(CO)_6$, and $Mn(CO)_6^+$ shows that the π back-donation decreases in the order $V^- > Cr > Mn^+$.[155] Theoretical density difference maps for $(C_6H_6)Cr(CO)_3$ show a good agreement with the experimental ones.[245] A deformation density map for PdC shows the molecule to be polar with a negative charge on the carbon atom, with σ donation from palladium to carbon and π back-donation.[105] Density difference plots for $Co(CN)_6^{3-}$ show an increase of the π density on carbon due to back-bonding and an expansion of the $3d_\pi$ orbitals, together with an increase of the $3d_\sigma$ density, and the density difference maps for $Co(CN)_5(OH)^{3-}$ appear rather similar.[153,246] The difference densities between $Ni(CH_3)_2$ and the constituent atoms (d^8s^2 ^3F for Ni) indicate a charge flow from nickel to carbon with the formation of ionic nickel–methyl bonds.[111] The deformation density plot for TiH_3CH_3 shows a buildup of density in the vicinity of the carbon atom and a decrease near the titanium along the Ti–C axis.[201] Taylor and Hall have plotted atomic deformation densities for a number of metal carbenes.[218] For the Fischer-type complex $(CO)_5Mo{=}CH(OH)$ (best viewed as built from a singlet carbene) these maps show extra σ electron density localized on the carbene carbon and a decrease of electron density in the π orbital of the carbene. For the Schrock-type complex $CpCl_2Nb{=}CH_2$ (best viewed as built from a triplet carbene) the atomic deformation densities around the carbene are similar to the densities plotted for ethylene. Also, in the fragment deformation densities, the least rearrangement of electron density occurs for the Fischer complex when one substracts a singlet carbene fragment and for the Schrock complex the least rearrangement is obtained by substracting a triplet carbene. The influence of the basis set truncation on the electron deformation density has been discussed for the complex $(CO)_5Cr{=}N{=}C{=}N(CH_3)_2$.[177] An excellent agreement has been obtained between the theoretical and experimental deformation density maps for $Cl(CO)_4Cr{\equiv}CCH_3$, with the density pattern for the metal–carbon triple bond rather similar to the one obtained for the metal–carbonyl bonds.[177]

Deformation density maps have been used by Benard to study the nature of the metal–metal and metal–bridging ligand interactions in binuclear complexes. The fragment deformation density map for $Mn_2(CO)_5(PH_3)_4$ is characterized by an important electron migration from the manganese atoms toward an area covering most of the Mn–C–Mn triangle and the π region of the semibridging carbonyl ligand, a feature which is best accounted for by the electron density distribution in the HOMO of the system.[247] The density deformation map for the *trans*-$[CpFe(CO)]_2(CO)_2$ system (with two bridging carbonyls) is rather similar.[150,247] For $[Co(CO)_3]_2C_2H_2$ the deformation density distributions obtained at the SCF and CI levels are rather similar and show an excellent agreement with the maps from X-ray diffraction experiments.[248] The maps obtained for the isolobal systems $(CpNi)_2C_2H_2$ and $[Co(CO)_3]_2C_2H_2$ show the same qualitative features.[248,249] The bonding in $[(C_5H_5)_2Zr(\mu\text{-}PH_2)]_2$ has been analyzed on the basis of the deformation density maps.[144] The axial coordination of the carbonyl in $Rh_2(tcl)_4CO$ (with tcl = thiocaprolactamate) induces a weakening of the rhodium–rhodium bond as shown by the analysis of the Laplacian of the charge density.[250]

Electron densities at the iron nucleus have been calculated for the complexes $[Fe(CN)_6]^{n-}$ with $n = 3$, 4 and used to derive the isomer shift calibration constant for iron.[251] Electron densities at the iron nucleus in ferrocene and ferricinium salts have been computed in order to interpret the Mössbauer isomer shifts.[138]

4. *Miscellaneous*

The geminal H,H coupling constant in $TiCl_3CH_3$ is calculated to be 8.0 Hz larger than the coupling constant in CH_4, when the change observed experimentally is 23.7 Hz.[201]

F. Ionization Potentials and Electron Affinity

Deviations from Koopmans' theorem occur for a large number of organometallics. This was first realized for ferrocene where the lowest two ionization potentials (IP) are assigned to the metal 3d orbitals e_{2g} and a_{1g} with the highest occupied orbitals being ligand orbitals of symmetry e_{1g} and e_{1u}.[137,138] When orbital relaxation is accounted for by means of separate SCF calculations for the ionized states, the calculation predicts correctly that the order of ionization potentials should be $e_{2g} < a_{1g} < e_{1u} \approx e_{1g}$ (a consequence of the fact that there is some 6–7 eV of relaxation energy associated with ionization in the metal orbitals compared with about 0.5 eV of relaxation energy when ionization occurs in a ligand orbital).[137,138] This situation turned out to be rather general[2,252,253] and for this reason many calculations of ionization potentials were carried out by the ΔSCF method in the 1970's. In general the IP's calculated in this way were accurate within 1 or 2 eV (although the values obtained when approaching the HF limit tended to be too low by 3–4 eV due to the neglect of the correlation energy which should be larger for the neutral molecule[2,254]), and the relative order of the IP's from the metal d orbitals and from the ligand orbitals was rather well reproduced. For these reasons the ΔSCF calculations were particularly helpful for the interpretation of photoelectron spectra. The observed similarity in the spectra of $Fe(CO)_2(NO)_2$, $Co(CO)_3NO$, and $Ni(CO)_4$ was explained on the basis of such calculations.[253] IP's were also computed in this way for the systems CpNiNO,[255] $Cr(C_6H_6)_2$ and $(C_6H_6)Cr(CO)_3$,[245] $Fe(CO)_3(C_4H_6)$,[256] $(\eta^4\text{-}C_4H_4)Fe(CO)_3$,[257] and $Ni(C_4H_4)_2$.[230] The ΔSCF method has also been used for the calculation of the IP's of the metal cyanides $[Co(CN)_6]^{3-}$ [246] and $[Ni(CN)_4]^{2-}$.[4] More recently it has been extended to the calculation of the IP's of binuclear organometallics such as $Co_2(CO)_6(C_2H_2)$[258] and $Fe_2(CO)_6S_2$.[259] Core IP's have been interpreted on the basis of Koopmans' theorem.[256] An alternative to the ΔSCF calculations is a multireference CI expansion over configurations singly excited with respect to every relevant state of the $n - 1$ electron system and this method has been used to calculate the IP's of $Cr(\eta^3\text{-}C_3H_5)_3$[260] and of a number of binuclear complexes like $[Fe(\eta^5\text{-}C_5H_5)(\mu\text{-}NO)]_2$,[261] $[Co(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$, and $[Co(\eta^5\text{-}C_5H_5)(\mu\text{-}NO)]_2$.[262] A qualitative assignment of the bands in the photoelectron spectrum of *trans*-$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ has been made on the basis of a calculation for the neutral molecule.[263]

Calculations of IP's which go beyond the level of S-CI (CI restricted to monoexcitations) are scarce. A better description of the sequence of IP's of $(\eta^4\text{-}C_4H_4)Fe(CO)_3$, compared to the ΔSCF results, has been obtained from limited CI calculations but the absolute values are still off by more than 2 eV.[264] Assignment of the bands in the photoelectron spectrum of $[Fe(CO)_3]_2(\mu\text{-}Bu^tC_2Bu^t)$ was made possible through a ΔCI calculation of the IP's of $[Fe(CO)_3]_2(\mu\text{-}C_2H_2)$ but with errors as large as 2 eV (probably as a consequence of the different electronic environment of the two metal atoms[265]).[148] The lack of experimental values prevents any comparison with the IP's calculated for $Rh_2(tcl)_4CO$.[266] For the complex $(\pi\text{-}C_3H_5)_2Ni$, the ΔCI method leads to an incorrect ordering of the metal and ligand ionized states.[267] Calculation of the valence IP's of this system by a Green's function technique yields a sequence of IP's which is in rather good agreement with experiment (with absolute errors usually less than 1 eV)[268,269] although there is still some disagreement regarding the detailed assignment of the photoelectron spectrum.[270,271] The same method has been applied to the calculation of the IP's of $Ni(CN)_4{}^{2-}$, $Co(CN)_6{}^{3-}$, and $Fe(CN)_6{}^{4-}$.[267,272]

Blomberg et al. have reported for NiCO an electron affinity of 0.56 eV which should be regarded as being in reasonable agreement with the experimental value of 0.80 eV, considering the known difficulty to calculate electron affinities.[97] SCF calculations have been carried out on the negative ion states of $Cr(CO)_6$ and the results compared with data obtained by electron-transmission spectroscopy.[273]

G. Nature of the Bonding

The nature of the bonding in organometallics has been the subject of much speculation and discussion, simply as a consequence of the difficulty in working backward from a physical observable to the nature of the bonding. The questions addressed are usually the following ones: (i) What is the nature of the interaction between the metal and the ligands? (ii) What is the electron distribution in the complex and how does it differ from the electron distribution in the fragments? (iii) What is the electronic state of the metal and of the ligands in the complex? Answers are based on the analysis of a number of data, including the wave function, the results of the population analysis, the electron density maps, the bond lengths, the dipole moment, the behavior of the potential energy curves, and the results of the various energy partitioning schemes.

1. *Metal Carbonyls*

The traditional view of the metal–carbonyl interaction and bonding, derived from the Chatt–Dewar–Duncanson model for the coordination of ethylene,[274,275] is that it is due to σ donation from the 5σ orbital of the carbonyl and π back-donation from the metal $d\pi$ orbital to the π^* orbital of carbonyl. Population analysis for several different carbonyls give metal and carbonyl populations which are consistent with this view.[3,4,7,8,81,82,84,85,87,89] For instance the increased π^* population of the carbonyl ligand manifests usually through a lengthening of the CO bond. σ interaction dominates at longer distances but π bonding is more efficient at shorter distances.[81,86]

However one major problem with population analysis is that the presence of diffuse functions in the basis set can cause artifactual results,[8,84,89,276] and somewhat different descriptions of the bonding have been obtained from other approaches like the constrained space orbital variation (CSOV) method. The analysis given by Bauschlicher et al. of the bonding in FeCO, NiCO, and CuCO is particularly illuminating.[90] The CSOV method is applied to SCF and CASSCF wave functions and the interaction energy is decomposed into contributions from intraunit (within the metal or the carbonyl) and interunit (between the metal and the carbonyl) charge redistributions (the starting point being the frozen orbital (FO) wave function formed by superimposing and orthogonalizing the wave functions of the free metal and free carbonyl). A general feature of the metal–carbonyl interaction is a repulsive FO interaction energy, a consequence of the Pauli repulsion largely due to the overlap of the metal valence s and carbonyl 5σ orbitals. This σ repulsion is reduced either by $4s$–$3d\sigma$ hybridization (when the $d\sigma$ and 4s orbitals are singlet coupled) or by $4s$–$4p\sigma$ hybridization (when the $d\sigma$ shell is either completely filled or empty or when the $d\sigma$ and 4s orbitals are triplet coupled). The repulsion is also reduced by mixing the spatially compact d^{n+2} configuration with $d^{n+1}s$. In all systems the metal to carbonyl π back-donation is the largest interunit contribution to the bonding and correlation increases the importance of this effect (this had been recognized early[8,9] and was later confirmed for the series of MCO carbonyls with M = Ni, Pd, Pt[84]). The π back-donation is in the order Fe > Ni > Cu, consistent with the fact that the 3d orbital grows in size as one goes to the left of the series, a factor which favors a stronger covalent bond with the $2\pi^*$ of carbonyl. When the metal $3d\sigma$ shell is doubly occupied, there is only minor σ covalent binding between the $4sp\sigma$ metal space and the carbonyl. The carbonyl σ donation increases for $3d\sigma^1$ occupation and even more when the $3d\sigma$ shell is empty. This analysis is certainly valid for the other metal carbonyls and for instance it has been found that the Sc 4s orbital in ScCO is polarized away to the opposite side of the atom.[87]

One point of controversy concerns the degree of involvement of the Ni $3d^{10}$ configuration in the description of the bonding for the ground state $^1\Sigma^+$ of NiCO. The state $^1\Sigma^+$ of MCO (M = Ni, Pd, Pt) has been described initially as arising from the d^{10} ^1S state of the metal.[8,84] One reason is that this ground state can be described by one closed-shell configuration and that the only atomic state of nickel that can be described in this way is the $3d^{10}$ state. A more physical argument is that the 4s orbital of nickel is very repulsive toward the carbonyl group. Another description of the $^1\Sigma^+$ state emphasizes a strong mixing of the d^9s^1 and d^{10} configurations; examination of the CI wave function leads to a description of the ground state as a mixture of 60% Ni($3d^{10}$) and 40% Ni ($3d^94s^1$ or $3d^94p^1$).[82] On the other side Blomberg et al. consider that the ground state of NiCO corresponds mostly to the d^9s^1 configuration, since they obtain a 3d population of 9.2[81,97] (a comparable value of 8.8 for the 3d population has been reported[174]). They argue that excitation to the ^1D (d^9s) state is energetically more favorable than the use of the higher lying ^1S (d^{10}) state.[97] Bauschlicher et al. notice that the higher 3d population for the $^1\Sigma^+$ state than for the triplet states indicates that some $3d^{10}$ character mixes into the wave function but that this state is principally derived from the $3d^94s^1$ configuration.[174] The $^1\Sigma^+$ state of PtCO has a Pt atom configuration that is much closer to $5d^94s^1$ than to $5d^{10}$.[86] The stronger π back-donation observed in NiCO than in PdCO and PtCO results from the atomic ionization potentials of Pd and Pt being higher than that of Ni.[84] The lower stability of PdCO compared to NiCO and PtCO has been related to the higher ionization potential of palladium and to its reduced ability at accepting charge.[84]

In the metal carbonyl cations MCO^+, the binding mechanism is of a different nature, being essentially electrostatic as evidenced by (i) the M–C bond lengths which are large relative to those in similar neutral species; (ii) binding energies which are well represented by electrostatic formula; (iii) the Mulliken population analysis results which indicate that very little charge transfer takes place.[91,93,94,96–98] For instance, in $NiCO^+$, the bonding arises from the attraction of the ligand lone pair by the positive charge and from the charge–dipole electrostatic interaction and these effects are enhanced by the polarization of the ligand. The Ni to CO π donation is small, mainly for energetic reasons since the second ionization potential is much higher than the first one (furthermore the 4s to $3d\sigma$ promotion cannot compensate for the loss of the $3d\pi$ electrons).[93,94,97] For $NiCO^+$ the Mulliken population shows only 0.06 electron donated to the π^* orbital, which is much smaller than the 0.57 electron found for the neutral, and for $TiCO^+$ the $3d\pi$ to $2\pi^*$ donation is 0.07 electron compared to 0.52 in neutral TiCO.[94] In $CuCO^+$ π backbonding has been found to be negligible.[91] Backdonation has also been found to be unimportant in $HPdCO^+$.[277]

A rather general conclusion is that the binding in $M(CO)_n$ molecules with $n > 1$ has many similarities to the situation in the monocarbonyls.[81,243] The bonding in the monocarbonyls and dicarbonyls of Sc, Ti, and V has been described as similar to the extent that it involves $3d\pi$ to $2\pi^*$ back-donation and $4s$–5σ repulsion in both cases, with this difference that in the dicarbonyls $4s$–$4p\sigma$ hybridization is unfavorable and promotion from the 4s orbital to the more compact 3d shell is more favored than in the monocarbonyls.[243] The same types of σ and π electron transfers have been found in NiCO and $Ni(CO)_2$ and it has been concluded that the binding in the two molecules is qualitatively similar.[81]

The general mechanism of metal–ligand binding in $Fe(CO)_5$ has been discussed in refs 49 and 101. The CSOV analysis has been applied to SCF wave functions of $Fe(CO)_5$ and $Ni(CO)_4$.[276] Since the carbonyls of these complexes surround the metal, there is no possibility for the metal s charge to polarize away from the carbonyls. The strong repulsion of the ligands with the 4s orbital results in the bonding arising from the $3d^{n+2}4s^0$ occupation of the metal atom (the configuration of the Cr atom in $Cr(CO)_5$ is also close to $3d^6$ [238]). The CO to metal σ donation is large for $Fe(CO)_5$ because the 3d shell is not filled, but it is very small for $Ni(CO)_4$. The metal to CO π donation is important for both $Ni(CO)_4$ and $Fe(CO)_5$ and is increased at the CI level.[276] Increased π back-bonding upon inclusion of correlation has also been found for the tetracarbonyls $M(CO)_4$ with M = Pd, Pt,[84] for $Cr(CO)_6$,[6,238] for $Fe(CO)_5$,[49] and for a number of hydrido metal carbonyl systems.[277,278] σ donation is also increased upon the inclusion of correlation.[6,49] π back-bonding accounts for the greater stability of the cis isomer, relative to the trans one, in the disubstituted d^6 metal carbonyls $M(CO)_4L_2$ (M = Cr, Mo and L = NH_3, PH_3).[186] The stability of η^2-dihydrogen complexes $W(CO)_3(PH_3)_2(H_2)$ has been traced to the stabilization of the d orbitals by the π-acceptor carbonyl ligands, which prevents the oxidative addition from continuing on to the dihydride complex.[184]

A covalent character of the metal hydride bond emerges from a study of a number of hydrido metal carbonyl systems at the CASSCF level.[278] Correlation effects in $Mn(CO)_4(NO)$ and $Co(CO)_3(NO)$ reduce the asymmetry of the charge distribution around the nitrosyl group.[279]

2. *Metal Carbides*

These molecules seem to be polar with a negative charge on the C atom, as found for PdC[105] and CrC^+ (with about 0.2 electron in excess).[106] The bonding in CrC^+ consists of a delocalized one-electron σ bond and essentially covalent π bonds.[106]

3. *Metal Cyanides*

The bonding in ScCN has been described in terms of a strongly ionic σ bonding between the Sc and C atoms.[107] In $Co(CN)_6^{3-}$ and $Ni(CN)_4^{2-}$ the metal–carbon bond is predominantly of σ character with a lack of appreciable metal–ligand π back-bonding.[4,153,246,280]

4. *Metal Carbon Dioxide Complexes*

π back-bonding has been found to be important in stabilizing the η^2 side-on complex $Ni(PH_3)_2(CO_2)$ and decreases in the order η^2 side-on $\gg$ η^1-C mode $>$ η^1 end-on. A strong electrostatic interaction between Cu(I) and the negatively charged O atom of carbon dioxide is responsible for the end-on coordination mode of $Cu(PH_3)_2(CO_2)^+$. In these systems the η^1-C mode is unfavorable due to a repulsive electrostatic interaction between the metal and the positively charged C atom.[190] The same mode becomes stable in the complex $[Co(alcn)_2(CO_2)]^-$ due to a strong charge-transfer interaction between Co and CO_2 and a weak four-electron destabilizing interaction, in spite of an unfavorable electrostatic interaction.[194] Sakaki and Dedieu proposed the following rules to predict the coordination mode of CO_2 in these complexes: (i) the most desired situation for the η^1-C mode is the presence of a HOMO mainly composed of a d_σ orbital and a low oxidation state of the metal; (ii) the best situation for the η^2 side-on mode is the presence of a $d\pi$ orbital as the HOMO and an empty $d\sigma$ orbital pointing to the CO_2 ligand.[194] Coordination of carbon dioxide with $RhCl(AsH_3)_4$ in the η^1-C mode decreases the electron population of the Rh dz^2 orbital and increases the electron population of the oxygen atoms of CO_2, mostly at the level of the HOMO, and the reactivity of CO_2 with electrophiles is enhanced.[108] The η^1-O structure of $Ni(NH_3)_2(CO_2)$ is best described as a 1,3 diradical centered on the nickel and carbon atoms.[191]

5. *Metal Alkyls*

Traditional oxidation state formalism describes the metal–methyl species in terms of M^+ interacting with CH_3^-. However the different approaches used rather favor a covalent view with the ligand neutral and a limited charge transfer (which can be either way).[51,109,113,115] The predominant bonding mechanism in the methyls and their positive ion corresponds to forming a bond either with the d or s orbitals (from either the d^n or d^ns^1 occupations) or from one of the hybrid orbitals arising from the d^ns^2 occupation after s–d or s–p hybridization.[51] In fact the bonding is often a mixture of these bonding mechanisms as shown by the example of $TiCH_3$ with a Mulliken 3d population of 2.3, which indicates that the bonding arises from a mixture of $3d^24s^2$ and $3d^34s^1$ (the degree of mixing depending to a large extent on the energy separation of the atomic asymptotes).[51] On the contrary, the bonding in $NiCH_3$ results solely from the interaction of the Ni 4s orbital with the CH_3 σ orbital.[51,109] There is an increase in the metal character of the bond moving from the early to late transition elements in each row[51] (for MCH_3^+, the charge transfer from the metal positive ion to the neutral CH_3 changes from +0.33 electron for Sc to −0.22 electron for Pd[114]). The positive ions have more d character in the bond than the neutrals and the second transition row has more d participation in the bonding than the first transition row.[51,114] Two different bonding mechanisms were reported for $CuCH_3^+$, the first one corresponding to a one-electron bond with a 3d population of 9.86, the second one arising from the $3d^94s^1$ occupation with a 3d population of 9.44.[51]

The bonding in $Ni(CH_3)_2$ is caused by the interaction between the 4s and 4p orbitals on Ni with the methyl hybrid orbital, with eight 3d electrons localized on the metal. This bond has been described as strongly polarized with a positive charge on the metal close to unity (this polarization being increased with the addition of two water ligands).[111] On the contrary, the $M-CH_3$ bond has been described as covalent in the complexes $MH(CH_3)$ and $M(CH_3)_2$ with M = Pd or Pt, with each bond involving one electron in the CH_3 orbital and one electron in a sd hybrid orbital of the metal (the total population on the metal being close to 10 electrons).[116] This description has been extended to the complexes $M(CH_3)_2(PH_3)_2$ (M = Pd, Pt) and $Pt(H)(CH_3)(PH_3)_2$, with a $M-CH_3$ bond covalent and about 10 electrons on the metal in a configuration close to s^1d^9.[198] In the complex $Pt(CH_3)_2(Cl)_2(PH_3)_2$, the valence bond description is that of a metal in a s^2d^8 configuration, forming four covalent bonds.[198]

6. *Metal Carbenes and Metal Carbynes*

The bonding in $NiCH_2$ corresponds basically to the interaction of a 4s orbital of a Ni atom in the configuration d^9s^1 with the carbon lobe orbital of a CH_2 fragment in a state $\sigma^1\pi^1$, with only a small contribution due to the π bonding and a charge transfer of 0.5–0.6 electron from Ni to CH_2.[109,121] The ground state of $CrCH_2^+$ consists of a covalent Cr–C double bond formed by spin pairing the Cr dσ orbital (with a large amount of s character) with the CH_2 σ orbital and the Cr dπ orbital with the CH_2 π orbital.[113,120] This type of bonding has been termed "metal–methylidene" and is found also in $MnCH_2^+$ (with the σ bond made from the 4s orbital of the metal), in $FeCH_2^+$ and in $RuCH_2^+$ in its ground state (in $RuCH_2^+$ the bonding orbitals are almost entirely 4d in character).[120,123] A different type of bonding, which has been termed as "metal–carbene", is found in a cluster of low-lying excited states of $RuCH_2^+$. It involves a σ donor bond from CH_2 in its σ^2 singlet excited state to Ru^+ and a dπ–pπ back-bond from Ru^+ to CH_2, leading to a Ru–C double bond of the donor–acceptor type.[123] The excited state $^6A_1$ of $CrCH_2^+$ is also of the carbene type with a σ donor bond but practically no π back-bonding (a consequence of the single occupancy of the Cr dπ orbital).[213] The bonding in the complexes $Cl_2Ti(C_2H_4)(CH_2)$,[208] $ClRuH(CH_2)$,[123] $Cl_4M(CH_2)$, and $Cl_2M(O)(CH_2)$[242] with M = Cr, Mo corresponds to a covalent double bond of the alkylidene type. The bonding in the Fischer-type complex $(CO)_5MoCH(OH)$ has been described as forming from singlet metal and carbene fragments ("carbene-type" complex) and the bonding in the Shrock-type complex $CpCl_2Nb{=}CH_2$ as forming from triplet fragments ("alkylidene type" complex).[218] The distortion of alkylidene ligands toward $Ti^-{=}C^+$ structures in a number of substituted titanium carbenes has been related to the electron deficiency of the central metal atom and to the possible formation of a three-center M–H–C bond.[210,281]

$TiCH^+$, VCH^+, and $CrCH^+$ are all characterized by a metal–carbon triple bond, the electron distribution being similar with the σ bond polarized toward the carbon and the π bonds polarized toward M^+.[113,125] In $ScCH^+$, Sc^+ forms a double bond with CH.[115,125] In both carbynes $(CO)_5Cr{\equiv}CH^+$ and $Cl(CO)_4Cr{\equiv}CH$, the populations from the SCF wave functions correspond to a $Cr{\equiv}C$ bond which is strongly polarized, with the carbyne carbon atom negatively charged.[217] The occurrence of this negative charge has been confirmed by the CASSCF calculations for the complexes $Cl(CO)_4Cr{\equiv}CR$ (R = H, CH_3), with σ donation from the carbyne fragment and π back-donation.[177,220]

7. Metal Alkenes and Metal Alkynes

The bonding between a transition metal and an olefin is usually discussed in terms of the Dewar–Chatt–Duncanson (DCD) model.[274,275] In this model, bonding occurs via a simultaneous donation of electrons from the olefin π orbital to the metal and a back-donation from the metal dπ orbital to the empty π^* olefin orbital. In $Ni(C_2H_4)$, the bonding between the Ni atom in the ^1D d^9s^1 state and the π system of ethylene follows closely the DCD model, although the detailed mechanism involves considerable mixing of different configurations on nickel.[130] The interaction between the metal d^9s^1 and ethylene is repulsive due to the overlap between the 4s orbital and the π orbital of ethylene. This overlap is reduced by an sd hybridization and the process results in an unshielding of the 3d orbitals, with a donation from the π orbital and a back-donation to the π^* orbital. The charge transfer is dominated by the back-donation resulting in a negative charge of 0.18 electron on the ethylene ligand.[130] For $Fe(C_2H_4)$ the bonding in the excited states corresponding to the d^7s^1 asymptote is of the normal π-bonded type and has been analyzed in terms of sp and sd hybridization, but the interaction between ground-state iron and ethylene is not of the π-bonded type, being dominated by dispersion forces.[282] Due to the repulsion between the singly occupied 4s orbital and the π orbital of ethylene, the ground state of the copper–ethylene complex arises from a van der Waals interaction between ethylene and the copper atom in its $d^{10}s^1$ configuration, with the unpaired electron in a nonbonding 4s–4p hybridized orbital. The bonding in two $d^{10}p^1$ excited states has a significant metal to ligand charge-transfer character.[133] The interaction of ethylene with silver or gold is similar, with the gold complex being the most strongly bound in the ground state, a consequence of the relativistic effects that invert the mean radius of the atomic ns orbital with respect to the ordering of the periodic table.[134] The DCD model has also been found to describe the bonding in $Ni(C_2H_4)_2$ and $Ni(C_2H_4)_3$, with a slightly negative charge on the ethylene ligand[129,132] (the similarity of the nickel–ethylene bond in $Ni(C_2H_4)$ and $Ni(C_2H_4)_2$ has been emphasized[132]).

The complex $Cl_2Ti(CH_2)(C_2H_4)$ does not show any back-bonding from Ti into the olefin π^* orbital since it has no filled d orbitals and the olefin coordination arises solely from the donor–acceptor interaction between the olefin π-bond and partially occupied 3d orbitals on the metal.[208] In the Ni(0) complexes $NiL_2(C_2H_4)$ with L = H_2O, NH_3, PH_3 the 3d shell is filled, the donation of electrons to Ni is unimportant, and the π back-donation is the dominant contributor to the bonding.[223,224] As a result the strength of the bond is almost entirely determined by the donor strength of the Ni donor orbital, which increases with increasing orbital energy in the order $H_2O > NH_3 \gg PH_3$. The opposite situation occurs in the charged Ni(II) complexes $NiL_2(C_2H_4)^{2+}$ with the metal donor orbital having too low an energy to be effective. The bond strength is then determined by the energy of the Ni 3dσ orbital.[223] The π back-bonding in $Ni(PH_3)_2(C_2H_4)$ is enhanced by correlation effects.[78] Electrostatic factors play an important role in the interaction of ethylene with positive metal ions since the electrostatic component represents the largest stabilizing term in the energy decomposition for a number of Rh(I) and Pd(II) complexes.[175,223,226] The cis effect in $H_2RhCl(PH_3)_2(C_2H_4)$ has been explained in terms of a competition between the donative interaction from ethylene to the metal and the π donative interaction from the chlorine to the metal.[206] The bonding in bis(π-allyl)nickel and tris(π-allyl)chromium has been described in terms of donation from the ligands π orbitals to one or several metal empty d orbitals, with little back-donation[2,260] (this charge transfer being increased by correlation effects[269]).

The binding mechanism in $Ni(C_2H_2)$ is similar to the one described for $Ni(C_2H_4)$ with sd hybridization accompanied by donation and back-donation in the fashion of the DCD model.[136] On the contrary, in the complex $Pd(C_2H_2)$, the Pd atom retains the d^{10} configuration and the acetylene coordination arises solely through a small π donation from the metal to the ligand.[136] The bonding scheme in $Ni(PH_3)_2(C_2H_2)$ is similar to that of $Ni(PH_3)_2(C_2H_4)$ with the back-donative interaction being the dominant contributor.[224]

8. Metallocenes

A picture of the bonding in ferrocene follows the DCD model with a two-way donor–acceptor interaction which is increased by correlation effects.[139,228,229]

9. Binuclear Complexes

For these systems, one key question is the nature of the interaction holding the mononuclear fragments together. To what extent does the bonding result from a direct metal–metal bond or from three-center bonds through the bridging ligands? For instance, in the complex $[(\eta^5\text{-}C_5H_5)Zr(\mu\text{-}PH_2)]_2$, the populations obtained for the natural orbitals σ and σ^* are characteristic of a relatively strong metal–metal bond in spite of the metal–metal distance of 3.65 Å, a result which is made possible by an expansion of the 4*d* orbital.[144] On the other side, it has been concluded from the electronic configuration and the Mulliken population analysis that there is no direct Fe–Fe bond in $Fe_2(CO)_9$, the iron atoms being held together through three-center Fe–C–O–Fe bonds. This is achieved through donation from the bridging CO σ orbitals into the empty $d\pi$ orbital of the iron atoms and back-donation from the Fe $d\pi^*$ filled orbital into the bridging CO $2\pi^*$ orbitals.[149] A similar description of the bonding has been given for the complexes $[(\eta^5\text{-}C_5H_5)Fe(CO)(\mu\text{-}CO)]_2$ and $Fe_3(CO)_{12}$, with a lack of direct bonding between the carbonyl-bridged iron atoms.[150] In $[Fe_2(CO)_6(\mu\text{-}C_2H_2)]$ the metal–metal interaction does not involve any direct coupling between the metal d electrons but is insured through back-donation to the semibridging carbonyl and to the acetylene ligand.[148] In the complex $Mn_2(CO)_5(PH_3)_4$, donation occurs from the Mn $d\pi$ filled orbital into the $2\pi^*$ orbital of the semibridging carbonyl ligand.[247] In the binuclear clusters $[M(\eta^5\text{-}C_5H_5)(\mu\text{-}NO)]_2$ with M = Fe, Co and $[Co(\eta^5\text{-}C_5H_5)(\mu\text{-}CO)]_2$, the low-lying π^* orbitals of the bridging ligands interact with the metal d orbitals of the proper symmetry to form molecular orbitals delocalized over four centers.[145,261,262] The situation is intermediate in a number of divanadium complexes such as $[(\eta^5\text{-}C_5H_5)V]_2(C_8H_8)$ and $[(\eta^5\text{-}C_5H_5)V(\mu\text{-}C_4H_8)]_2$. The V–V bond involves two contributions of distinct nature, one coming from a weak double bond and the other one originating from delocalized interactions through the bridging ligands.[141,142]

IV. Concluding Remarks

It is now well established that the Hartree–Fock approximation is frequently in error for organometallics. When low levels of theory often give a qualitative description of the bonding for first-row chemistry, a high level of theory is usually required for organometallics. Several factors seem to be responsible for these correlation effects, some being specific of organometallics and some not:

(i) Hartree–Fock calculations favor the states of higher multiplicity (or correlation effects are greater for closed-shell states). This well-documented effect, not specific of organometallics, affects particularly the calculation of excitation energies.[5,108]

(ii) Organometallics should be rather sensitive to the atomic correlation effects since the transition-metal atom has many low-lying excited states. Correlation is essential in reproducing the atomic energy level splittings in the transition-metal atoms, for instance Hartree–Fock calculations place the ^3D d^9s^1 state of Ni 1.27 eV above the ^3F d^8s^2 state, whereas experimentally these states are essentially degenerate.[77] A correct description of these energy splittings is essential in order to compute correctly dissociation energies and excitation energies.

(iii) A near-degeneracy effect plays an important role in the description of the binding of simple closed-shell ligands (like carbon monoxide and ethylene) to transition metals and is a consequence of the hybridization between the 4s orbital and a singly occupied 3d orbital. When the metal is strongly perturbed by a ligand, the hybrid pointing away from the ligand tends to be doubly occupied with the other hybrid empty. However correlation effects result in the occupations of these hybrids being nonintegral.[81]

(iv) The spatial extent of the metal *n*d orbitals is small and as a consequence the Hartree–Fock orbitals tend to be localized on the metal or on the ligands, yielding a description of the metal–ligand bonding which is too ionic.[120,228,229,279] This is usually remedied through nondynamical (or near-degeneracy) correlation effects which increase the covalent character of the metal–ligand bond. In the carbon monoxide and ethylene complexes, the most important CASSCF or CI contribution is usually of the type $d_\pi^2 \rightarrow \pi^{*2}$ which increases the charge transfer corresponding to π back-bonding.[6,8,9,49,78,81,90,168,228,229,238,277,279]

(v) The role of dynamical correlation effects in organometallics is at present rather unclear.[49]

Will ab initio calculations on organometallics ever become black-box calculations as they are now for some organic systems? There is no reason to be unduly optimistic on this point. Reasonably accurate calculations on organometallics require extended basis sets. The Hartree–Fock approximation has given a qualitative picture that is satisfactory only for a limited number of specific problems.[192,198,206] Of the various theoretical methods for dealing with electron correlation, brute-force CI requires comparatively fewer subjective decisions but the results of limited CI calculations have been often disappointing. MCSCF and CASSCF methods are computationally much more laborious. The usual perturbation expansion which is based on one Slater determinant is inappropriate when no single configuration accounts for an overwhelming portion of the correlated wavefunction, a situation which is not exceptional.[6,279]

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