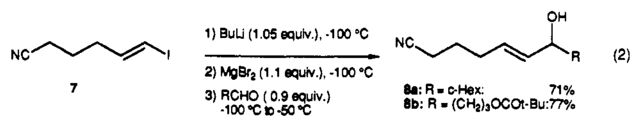

(2)

In summary, we have prepared several new classes of functionalized zinc and copper aromatic and alkenyl organometallics **3–5** which, contrary to their highly reactive organolithium precursors **2**, can be conveniently handled,[21] are relatively stable, and react chemoselectively with various classes of electrophiles with complete retention of the double bond configuration.[22] Extensions of this method allowing the preparation of other functionalized organometallics (M = Ti, Zr) are currently underway.

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Office of the Vice President for Research of The University of Michigan for generous support of this work.

Supplementary Material Available: Typical experimental procedure and listings of characterization data for all new compounds (12 pages). Ordering information is given on any current masthead page.

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(21) Typical procedure for **(2*E*,4*E*)-ethyl 8-(pivaloyloxy)-2,4-octadienoate (6i)**: A three-necked flask equipped with a thermometer, a gas inlet, and an addition funnel was charged under argon with (*E*)-5-iodo-4-pentenyl 2,2-dimethylpropanoate (0.74 g, 2.50 mmol) in a mixture of THF/ether/pentane (4:1:1; 12 mL) and cooled to −100 °C (liquid N_2, ether bath), and *n*-BuLi (2.6 mmol, 1.60 M in hexane) was added over 4 min. The resulting yellow solution was stirred for 3 min at −100 °C, and a THF (5 mL) solution of ZnI_2 (0.83 g, 2.60 mmol) was added. After the mixture was stirred for 10 min at −100 °C, a slurry of CuCN (0.23 g, 2.60 mmol) and LiCl (0.22 g, 5.2 mmol) in a mixture (10 mL) of THF and Et_2S (1:1) was added. The dark red solution was warmed to −60 °C and after 5 min was cooled back to −78 °C. Ethyl propiolate (0.20 g, 2.0 mmol) was added, and the reaction mixture was warmed to −20 °C and stirred for 2 h. After the usual workup and evaporation of the solvents, the crude residue obtained was purified by flash chromatography (hexane/ether, 19:1), yielding **6i** (360 mg, 68%) as a clear oil (100% *E,E* by GLC analysis).

(22) Presented in part at the OSCOM 6 meeting in Utrecht, The Netherlands, August 1991.

The Nature of Bonding and Stability of $(CO)_2Be{-}Be(CO)_2$: A Molecule with a Be–Be Double Bond

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Received January 21, 1992

In recent years there has been considerable interest in understanding the nature of interactions between metal atoms in polynuclear organometallic compounds where the metal atoms or ions have formally closed-shell configurations such as the d^{10} electron configuration of Cu in $[CuN_5R_2]_3$[1] (R = *p*-tosyl) and the s^2 configuration of Tl(I) or In(I) in $[(PhCH_2)_5C_5M]_2$, M = Tl or In.[2,3] An interesting feature of these molecules is that the metal–metal distances are close to the typical internuclear distance in the bulk metal, even though the metal atoms and ions have formally closed-shell configurations and hence are not expected to show metal–metal bonding. This communication reports the results of theoretical studies on the nature of the bonding and stability of $(CO)_2BeBe(CO)_2$. It is shown that as a result of hybridization the two Be atoms interact to form a double bond.

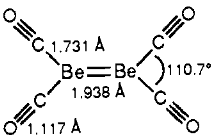
Table I. Total Energies and Dissociation Energies

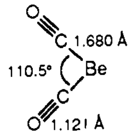
	$(CO)_2BeBe(CO)_2$			$Be(CO)_2$	
		dissoc. eng[a] (kcal/mol)			
method	tot. eng (au)	a	b	tot. eng (au)	dissoc. eng[b] (kcal/mol)
HF	−480.140 283	36.0	15.5	−240.057 902	10.4
MP2	−481.391 864	95.9	56.3	−240.651 161	19.8
MP3	−481.380 527	76.1	51.9	−240.648 986	12.2
MP4(DQ)	−481.389 015	64.1	48.4	−240.655 913	7.8
MP4(SDQ)	−481.417 629	68.3	50.0	−240.668 907	9.00

[a] Dissociation of $(CO)_2BeBe(CO)_2$ to (a) $2Be(^1S) + 4CO$ and (b) $2Be(CO)_2(^3B_1)$. [b] Dissociation of $Be(CO)_2$ to $Be(^1S) + 2CO$.

The computations were performed using the GAUSSIAN 86 program.[4] The geometries were determined by the Hartree–Fock (HF) self-consistent (SCF) procedure with the analytical gradient method using the 6-31G*(5d) basis set.[5] The closed- and open-shell molecules were studied in the spin-restricted and spin-unrestricted HF approximations, respectively. The nature of the stationary points on the potential energy surface was determined by computing the analytical second derivatives and determining the harmonic vibrational frequencies.[6] The contribution of electron correlation effects was determined by using Moeller–Plesset perturbation theory through partial fourth order (neglecting triple substitutions)[7] at the HF geometries. Only the valence electrons were included in the perturbation theory studies.

The geometry optimizations of $(CO)_2BeBe(CO)_2$ and $Be(CO)_2$ were carried out with the constraints of D_{2h} and C_{2v} symmetries, respectively. The computed minimum energy structures are as shown:





The D_{2h} $(CO)_2BeBe(CO)_2$ species has a ^1A_g ground state, while the ground state of $Be(CO)_2$ is $^3B_1$[8] in C_{2v} symmetry. The HF harmonic vibrational frequencies computed for both of the molecules are all positive, indicating that these molecules are true potential energy minima.

The computed structure and stability of $(CO)_2BeBe(CO)_2$ are easily rationalized in terms of the type of bonding of $Be(CO)_2$, which is hence considered first. The $^3B_1$ state of $Be(CO)_2$ is stable with respect to dissociation to $Be(^1S)$ and two CO molecules. The calculated binding energies at the various levels of theory for the HF geometry of the molecule are given in Table I. The bonding between CO and Be shows the general features of the Dewar–Chatt–Duncanson[9] model of CO binding to metal atoms: σ type bonding, involving the lone pair on the carbon atom of the CO, and π back-bonding interaction between the Be 2p and CO π^*

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orbitals. Upon bonding to the two CO molecules, the Be 2s orbital mixes with its low-lying 2p orbitals to form sp^2 hybrid orbitals, two of which are used to form bonds with the carbon lone pair orbital of the CO, while the third is occupied by one of the unpaired electrons. The second unpaired electron occupies a b_1 orbital perpendicular to the plane of the molecule, which is a Be 2p type orbital that is involved in a π back-bonding interaction with the CO π^* orbital.

The $^3B_1$ state of $Be(CO)_2$ is analogous to the lowest $^3B_1$ state of methylene on the basis of the nature and type of the highest occupied orbitals. Formation of $Be_2(CO)_4$ from two $Be(CO)_2$ molecules in their $^3B_1$ states results in a Be–Be double bond. An analysis of the two highest occupied orbitals of $(CO)_2BeBe(CO)_2$ shows significant bonding between the two Be atoms. The highest occupied (b_{3u}) orbital is π bonding between the Be atoms, with each Be also involved in π back-bonding with the π^* orbitals of the CO. The second highest occupied orbital (a_g) is a σ type bonding orbital. The triplet state arising from the one-electron excitation to the π^* orbital of $(CO)_2BeBe(CO)_2$ is 16.2 kcal below the singlet state at the HF level of theory. The inclusion of electron correlation effects reverses the order of the states with the ^1A_g below the triplet state by 10.6 kcal at the MP2 level of theory.[10]

The binding energy of $(CO)_2BeBe(CO)_2$ is computed with respect to dissociation to two $Be(^1S)$ and four CO molecules as well as to two $^3B_1$ $Be(CO)_2$ fragments. The computed binding energies are given in Table I. Even at the HF level, the interaction energy between the two $Be(CO)_2$ fragments in $(CO)_2BeBe(CO)_2$ is 15.5 kcal. Note that the Be_2 molecule shows no binding at this level of theory.[11] The complete fragmentation of $(CO)_2BeBe(CO)_2$ into two Be atoms and four CO molecules requires 36.0 kcal at the HF level of theory. At the MP4(SDQ) level, the strength of the Be–Be bond in this molecule is 50.0 kcal, and the complete fragmentation requires 68.3 kcal. The contributions of electron correlation to the binding energy of both $Be(CO)_2$ and $(CO)_2BeBe(CO)_2$ are large, indicating the need to reoptimize the geometry of these molecules to include electron correlation effects.[10] This trend is consistent with other studies of CO binding to metal atoms.[12]

At the HF level of theory the BeBe distance in $(CO)_2BeBe(CO)_2$ is only 1.938 Å, which is considerably shorter than the experimental bond distance of 2.45 Å in Be_2,[13] the shortest Be–Be distance of 2.226 Å in Be metal,[14] and the Be–Be bond length of 2.124 Å in HBeBeH at the same level of theory.[15] The computed harmonic vibrational frequency for the Be–Be stretch for this molecule of 942 cm^{-1} is more than 4 times larger than the experimental value of the vibrational frequency of Be_2 at 223 cm^{-1} and is also larger than the Be–Be stretching frequency of 645 cm^{-1} in HBeBeH at the same level of theory. The barrier for rotation about the Be–Be bond, computed at the HF geometry of the ground state by the GVB method[16] correlating only the pair of electrons in the π bond, is 6.70 kcal. The computed properties of the Be–Be bond, bond distance, bond energy, vibrational stretching frequency, and barrier to rotation, all lend support to the idea of a double bond between the Be atoms in this molecule.

The nature of the bonding and the stability of $(CO)_2BeBe(CO)_2$ demonstrate that it is indeed possible to form strong double bonds between Be atoms. The bonding in this molecule where two formally s^2 closed subshells interact arises from the mixing of the empty p orbitals with the occupied s orbitals, i.e., hybridization. A ligand field of D_{2h} symmetry is shown to induce strong bonding between two Be atoms which are weakly bound in the Be_2 molecule.

Acknowledgment. It is a pleasure to acknowledge Profs. K. D. Jordan, L. C. Allen, and J. M. Schulman and Dr. V. Balaji for many insightful discussions and Ms. D. M. Corsi for critical comments on the manuscript.

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Proton Affinities of the 20 Common α-Amino Acids[†]

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Received December 27, 1991

We report the first measurement of the gas-phase basicities ($-\Delta G$ of protonation) of all of the 20 common α-amino acids, from which we can derive their proton affinities ($-\Delta H$ of protonation). The basicities are determined by observing the occurrence or nonoccurrence of reaction 1, and its reverse reaction, in which A represents an amino acid, B a reference base, and AH^+ and BH^+ their respective protonated forms. The observation of proton

$$A + BH^+ \rightarrow AH^+ + B \qquad (1)$$

transfer between the protonated molecule of a base and an amino acid implies a negative free energy for reaction 1. The reverse reaction is observed if the free energy of reaction 1 is positive.

The α-amino acids are low-volatility compounds and thus are difficult subjects for the type of gas-phase equilibrium experiments generally utilized to measure gas-phase basicity or proton affinity.[1] To date, values of the proton affinity of only 6 of the 20 common α-amino acids have been published.[2,3] Meot-Ner et al. used high-pressure mass spectrometry to measure the gas-phase basicity of six amino acids (glycine, alanine, valine, leucine, phenylalanine, and proline), and they also used variable-temperature studies to directly measure the enthalpy of the proton-transfer reaction and thus the proton affinities of three of the amino acids.[2] Locke and McIver measured the gas-phase basicities of glycine and alanine with ion cyclotron resonance spectrometry.[3] In these studies, for the cases where enthalpies were not measured directly, proton affinity values were obtained from the gas-phase basicity data by estimating the entropy of the reaction, which was found to be a small or negligible correction.

In this study, we use Fourier transform ion cyclotron resonance spectrometry to observe the reaction of laser-desorbed, neutral amino acid molecules with a series of protonated reference bases, as in reaction 1. With this technique, called laser desorption/chemical ionization (LD/CI), low-volatility or nonvolatile compounds can be utilized as the neutral partner in studies of ion–molecule reactions.[4] The reverse of reaction 1 is examined by forming a protonated molecule of an amino acid by matrix-assisted laser desorption of the amino acid,[5] followed by reaction with a

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[*] Author to whom correspondence should be addressed.

[†] Dedicated to Professor Fred W. McLafferty on the occasion of his retirement.

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