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(7) (a) Spectral data for **2**: ν_{CO} (CH_3CN) 2032 (m), 1972 (vs), 1965 (sh), 1944 (s), 1918 cm^{-1} (m); ν_{NH} (CD_3CN) 3245 cm^{-1}; ^1H NMR (CD_3CN) τ 7.41 (s, 3, vs, $(C_2H_5)_4N^+$). (b) Spectral data for **3**: ν_{CO} (cyclohexane) 2088 (m–w), 2050 (s), 2022 (vs), 2014 (s), 2003 (m), 1991 (w), 1971 (w), 1964 cm^{-1} (vw); ν_{NH} (CCl_4) 3272 cm^{-1}; ν_{CN} ~1350–1510 (labeling studies are in progress to distinguish ν_{CN} from δ_{CH}); ^1H NMR ($CDCl_3$) τ 7.38 (s, 3), 36.72 (s, 1); mol wt 463 (mass spectrum, ^{56}Fe).

(8) (a) M. A. Andrews, C. B. Knobler, and H. D. Kaesz, Southern California Crystallography Meeting, May 3, 1977. Cell data: $P\bar{1}$, $a = 9.276$ (3), $b = 9.190$ (2), $c = 9.099$ (2) Å; $\alpha = 92.40$ (2), $\beta = 90.79$ (2), $\gamma = 83.45$ (3)°; $Z = 2$; $V = 770.0$ (4) $Å^3$ at −158 °C. (b) A complex containing a substitutionally isomeric form of the *C*-iminyl ligand found in **3**, namely, $H_2Os_3(CO)_9(CH{=}NCH_3)$, has recently been obtained from the reaction of $Os_3(CO)_{12}$ with trimethylamine: C. C. Yin and A. J. Deeming, *J. Organomet. Chem.*, **133**, 123 (1977).

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(10) $Fe(CO)_5$ (10 mL), NaI (11 g), and undried, reagent grade acetonitrile (300 mL) were refluxed under nitrogen for 48 h. The solvent was evaporated and the residue treated sequentially with deaerated acetone (30 mL), phosphoric acid (40 mL), and water (50 mL). The resulting precipitate was extracted with aliquots of hexane and chromatographed on silica gel. Hexane eluted complex **4** (0.45 g, 4%) and hexane–dichloromethane (80:20) eluted complex **3** (1.2 g, 11%). All complexes described in this paper are deep red. Neutral complexes are air stable for hours in hexane solution and days in the solid state.

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(12) Spectral data for **6a**: ν_{CO} (cyclohexane) 2086 (w), 2037 (s), 2028 (vs), 2015 (s), 2001 (vw), 1993 (w), 1983 (w), 1974 cm^{-1} (vw); ν_{CN} (CCl_4) 1610 cm^{-1}; ^1H NMR ($CDCl_3$) τ 6.55 (s); mol wt 463 (mass spectrum, ^{56}Fe).

(13) Complex **6b** is obtained by the same sequence of reactions as used for the preparation of **6a** except butyronitrile was employed as the solvent for the initial base disproportionation of $Fe(CO)_5$.

(14) M. A. Andrews, C. B. Knobler, and H. D. Kaesz, unpublished work. Cell data: $P2_1/m$, $a = 9.003$ (1), $b = 11.226$ (2), $c = 8.986$ (2) Å; $\beta = 101.33$ (1)°; $Z = 2$; $V = 890.6$ (3) $Å^3$.

(15) G. Gervasio and G. Ferraris, *Cryst. Struct. Commun.*, **2**, 447 (1973).

(16) Spectral data for **4a**: ν_{CO} (cyclohexane)l)089 (w),8z051 (s),8z028 (vs),i)013 (s), 2001 (m), 1995 (w), 1972 cm^{-1} (w); ν_{CN} (CCl_4) ~1325–1464 cm^{-1}; ^1H NMR ($CDCl_3$) τ 3.55 (d of q, 1, $J = 2.0$, 5.0 Hz), 7.76 (d, 3, $J = 5.0$ Hz), 28.98 (d, 1, $J = 2.0$ Hz); mol wt 463 (mass spectrum, ^{56}Fe).

(17) The *N*-iminyl ($-N{=}CHR$) ligand is known in terminal and double bridging forms,[16] but the triply bridging form observed for **4** is thus far unique. Somewhat related are the complexes $HM_3(CO)_{10}(C{=}NMe_2)$ (M = Fe,[19a] Ru,[19b] Os[6b]) which contain the isomeric doubling bridging $-C{=}NR_2$ ligand.

(18) M. R. Churchill and K. G. Lin, *Inorg. Chem.*, **14**, 1675 (1975), and references therein.

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(20) Spectral data for **5a**: ν_{CO} (cyclohexane) 2099 (m–w), 2060 (s), 2036 (vs), 2031 (s), 2022 (w), 2003 (s), 1985 (m), 1972 cm^{-1} (w); ^1H NMR ($CDCl_3$) τ 5.17 (q, 2, $J = 7.0$ Hz), 8.28 (t, 3, $J = 7.0$ Hz), 32.45 (s, 2); mol wt 465 (mass spectrum, ^{56}Fe).

(21) The ruthenium[22a] and osmium[22b] analogues of **5b** have been prepared previously by hydrogenation of $Ru_3(CO)_{10}(NPh)$ and by metalation of aniline with $Os_3(CO)_{12}$, respectively.

(22) (a) E. Sappa and L. Milone, *J. Organomet. Chem.*, **61**, 383 (1973); (b) C. C. Yin and A. J. Deeming, *J. Chem. Soc., Dalton Trans.*, 1013 (1974).

(23) The reduction of acetonitrile according to Scheme I is partially paralleled by the reduction of acetylene on osmium.[5] Thus, $H_2Os_3(CO)_{10}$ reacts with $RC{\equiv}CH$ to give $HOs_3(CO)_{10}(CH{=}CHR)$ which on heating gives a mixture of $H_2Os_3(CO)_9(HCCR)$ and $H_2Os_3(CO)_9(C{=}CRH)$.[5b,d] The former of these is isostructural with **3**, the latter with **4**. Importantly no evidence for interconversion could be found[5b] in contrast to our results for **3** and **4**. To our knowledge, only the latter osmium isomer (R = H) can be hydrogenated to give $H_3Os_3(CO)_9(CCH_3)$,[5c] isostructural with **5**, completing the reduction of the carbon–carbon triple bond. Similarly, we also find that isomer **4** hydrogenates much more readily than isomer **3**. The factors responsible for these differences and similarities between osmium and iron are not yet known, nor also is the feasibility of preparing the analogous acetylene-derived iron complexes.

(24) Peaks and intensities due to free aniline in the mass spectrum of **5b** (70 eV, 90 °C) compared with literature values[25] (m/e, I_{obsd}, $I_{lit.}$): 93, 100, 100; 66, 26, 33; 65, 15, 18; 39, 9, 18; 92, 11, 11; 46.5, 5, 9; 28, –, 8; 38, 3, 8.

(25) J. G. Grasselli and W. M. Ritchey, "Atlas of Spectral Data and Physical Constants for Organic Compounds", Vol. II, Chemical Rubber Co., Cleveland, Ohio, 1975, compound 1429.

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Mark A. Andrews, Herbert D. Kaesz*[26]
Department of Chemistry, University of California
Los Angeles, California 90024

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Extensive Configuration Interaction Studies of the Methylene Singlet–Triplet Separation

Sir:

For more than a decade now there have been two sets of conflicting experimental values for the $^3B_1 - {^1A_1}$ energy separation in CH_2, the simplest carbene; the "low" values[1] cluster about ~1–2 kcal/mol and the "high" values[2,3] near 8–9 kcal/mol. As if this situation were not confusing enough, a third experimental value, 19.5 ± 0.7 kcal, has recently been reported by Lineberger and co-workers[4] on the basis of their laser photodetachment study. This latest experimental value appears the most reliable, since the energy difference ΔE is obtained from a direct spectroscopic measurement.

Every ab initio theoretical study to date[5-7] has rejected the 1–2-kcal ΔE value, and all but one[8] have yielded singlet–triplet separations even larger than the old "high" value of 8–9 kcal. Among the most reliable theoretical treatments is that of Bender and co-workers,[9] whose configuration interaction (CI) calculations gave a ΔE value of 14.0 kcal. Since it appeared at the time (5 years ago) that additional refinements (e.g., basis set improvements) would lower the singlet–triplet separation, they estimated that the true ΔE value lies 1–5 kcal below the calculated 14.0 kcal. Thus, the lowest possible estimate nearly coincided with the "high" experimental value of 8–9 kcal. However, if Lineberger's experimental result[4] is the true ΔE value, this line of reasoning is incorrect and the calculated 14.0 kcal must be *increased* by ~5 kcal. In an attempt to clarify this point, it was decided to carry out state-of-the-art ab initio CI calculations. A communication by Roos[10] tackles the same problem using different theoretical methods.

Our present study begins with a "standard" set of calculations. Additional basis set and correlation effects will be evaluated relative to this standard. The standard basis was of the contracted gaussian variety,[11] labeled C(10s 6p 2d/6s 4p 2d), H(5s 1p/3s 1p). This basis is considerably larger than any to date[5-9] for which electron correlation has been variationally evaluated. This standard basis also reproduces to within 0.1 kcal the Hartree–Fock limit ΔE value[12] of 24.8 kcal/mol. Polarization function orbital exponents were optimized in the CI calculations and have the values 1.07, 0.33 (carbon d functions) and 0.95 (hydrogen p functions) for $^3B_1$ CH_2 and 1.05, 0.30 (carbon d functions) and 0.89 (hydrogen p functions) for $^1A_1$ CH_2.

The standard CI include all Slater determinants differing by one or two spin orbitals from the self-consistent field (SCF) reference configurations

$$^3B_1 \qquad 1a_1^2\, 2a_1^2\, 1b_2^2\, 3a_1\alpha\, 1b_1\alpha \tag{1}$$

$$^1A_1 \qquad 1a_1^2\, 2a_1^2\, 1b_2^2\, 3a_1^2 \tag{2}$$

Core and core-valence correlation effects were excluded by doubly occupying the $1a_1$ orbital in all determinants. This yields 4542 determinants for the $^3B_1$ state and 5359 determinants for the $^1A_1$ state when the standard 42 function basis set is employed. The CI calculations were performed on the Harris Slash Four minicomputer[13] using the BERKELEY system[14] of programs. Per point on the respective potential energy surfaces, roughly 57 and 66 min of elapsed time was required. Since the cost of time on the Harris Slash Four is only $8/hour, these computations were quite economical.

The equilibrium geometries of triplet ($\theta = 134°$, $r = 1.08$ Å) and singlet ($\theta = 102.4°$, $r = 1.11$ Å) methylene are well known[15,16] and were assumed here. The standard CI total energies were −39.06216 and −39.04065 hartrees, yielding a prediction of 13.5 kcal for ΔE ($^3B_1 - {^1A_1}$). The present variational $^3B_1$ total energy lies 31.4 kcal below the comparable result of Bender[9].

Following the "standard" calculations, a number of additional contributions to ΔE were considered.

1. Enlargement of the Carbon sp Basis. By fully contracting (except for the outer four s and three p basis functions) the 1s and 2s atomic orbitals, van Duijneveldt's much larger (13s 8p) basis[17] was adapted to the present study. However, the CI energy lowerings for the $^3B_1$ and $^1A_1$ states were only 0.17 and 0.08 kcal, respectively, and thus have little effect on ΔE ($^3B_1 - {}^1A_1$).

2. Addition of Diffuse p Functions to the Basis Set. This was done relative to a smaller (than our standard) set of 32 basis functions. Using the Raffenetti–Ruedenberg even-tempered scheme,[18] a set of p functions with $\alpha = 0.034$ was added, and this had the effect of decreasing the predicted ΔE value by 0.12 kcal.

3. Consideration of Core and Core–Valence Correlation Effects. Since this substantially increases the number of Slater determinants, the smaller 32 function basis was used. Without the $1a_1$ orbital constrained to be doubly occupied, the numbers of determinants increase from 2505 to 4891 ($^3B_1$) and 2981 to 5469 determinants ($^1A_1$). We find that these effects increase the predicted ΔE value by 0.37 kcal.

4. Additional Triplet Spin Eigenfunctions. The procedure used in our standard (and previous[9]) calculations includes only those configurations having nonzero Hamiltonian matrix elements with the respective Hartree–Fock reference configurations. However, for the $^3B_1$ state there are numerous spin eigenfunctions which do not interact[19,20] directly with the SCF configuration, but have no counterpart in the close-shell $^1A_1$ state. For example, consider the excitation

$$2a_1\,1b_2 \rightarrow ia_1\,jb_2 \qquad (3)$$

corresponding to electron configuration

$$1a_1^2\,2a_1\,1b_2\,ia_1\,jb_2\,3a_1\,1b_1 \qquad (4)$$

Only six of the Slater determinants arising from eq 4 are included in the standard CI. However a total of fifteen determinants are possible and, using the 32 function basis set, all fifteen (and the comparable determinants for all other configurations) determinants have been included. For the 32 function case, this increases the number of $^3B_1$ Slater determinants from 2505 to 4204 and also allows our wavefunction to be a pure triplet spin eigenfunction. However, the $^3B_1$ total energy changes from −39.05160 hartrees to −39.05186 hartrees, a difference of only 0.17 kcal. It is quite clear that this correlation effect does not significantly change the predicted standard ΔE value.

5. Effects of Higher Spin Orbital Excitations. These are extremely difficult to completely account for in an ab initio way, leading to approximate schemes such as the coupled electron-pair approximation (CEPA).[21] Perhaps the simplest such scheme is Davidson's approximation[22] for the correlation energy contribution due to quadruple excitations

$$\Delta E_Q = (1 - C_0^2)\Delta E_D \qquad (5)$$

where C_0 is the coefficient of the SCF configuration in the CI expansion and ΔE_D is the correlation energy due to double excitations. If in addition we assume that ΔE_D is about the same as the correlation energy due to single and double excitations, the $^3B_1$ and $^1A_1$ unlinked cluster contributions[23] are estimated to be 0.0066 and 0.0101 hartrees. This difference (2.2 kcal) lowers the predicted ΔE value from 13.5 to 11.3 kcal, our final result. These results indicate that higher excitations lower the singlet–triplet separation, as implied by the importance[12] of the second configuration $3a_1^2 \rightarrow 1b_1^2$ for the $^1A_1$ state.

In conclusion the present state-of-the-art electron correlation studies predict ΔE ($^3B_1 - {}^1A_1$) = 11.3 kcal. Theoretical considerations suggest that if any corrections need to be made to this result, they will be small. Thus, it is clear that the present, far more exhaustive study, as well as that of Roos,[10] supports the earlier theoretical work of Bender and co-workers.[9]

Finally, it cannot be overemphasized that our predicted ΔE value is what spectroscopists would call T_e, the energy difference between the *minima* of the $^3B_1$ and $^1A_1$ potential energy surfaces. However, Roos[10] has shown that the zero-point vibrational energies of the $^3B_1$ and $^1A_1$ states are nearly identical, implying that T_e is essentially the same as the observed separation T_0.

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Robert R. Lucchese
Department of Chemistry
University of California, Berkeley, California, 94720

Henry F. Schaefer III*[24]
Research School of Chemistry
Australian National University
P.O. Box 4, Canberra, A.C.T. 2600 Australia

Received February 1, 1977

Binuclear Cryptates. Synthesis and Binuclear Cation Inclusion Complexes of Bis-tren Macrobicyclic Ligands

Sir:

Macropolycyclic ligands incorporating receptor sites for two or more metal cations may form binuclear or polynuclear inclusion complexes, *polynuclear cryptates*, in which the distance and arrangement of the cations, held inside the intramolecular cavity, may be regulated via ligand design. They provide a novel entry into the study of cation interactions at short distances; at larger intercationic distances inclusion of