$Re(CO)_4]_2$.[15] Unlike all these reports, this paper demonstrates that CO_2 can be bound η^1 to various rhodium and iridium complexes leaving the oxygens sterically and electronically accessible. This allows such chemistry as methyl cation addition (1)[1] (which

$$Ir(CO_2)(Cl)(dmpe)_2 + CH_3FSO_3 \rightarrow [Ir(CO_2CH_3)(Cl)(dmpe)_2]FSO_3 \quad (1)$$

does not occur in Floriani's system[9]) and Lewis acid binding (2)[12c]

$$Ir(CO_2)(Cl)(dmpe)_2 + B(C_6H_5)_3 \rightarrow Ir(CO_2BPh_3)(Cl)(dmpe)_2 \quad (2)$$

to complexed CO_2. The reaction between the iridium–carbon dioxide complex and methyl triflate (1)[1] is consistent with a CO_2 structure with nucleophilic oxygen atoms. Preliminary theoretical calculations on this structure also indicate that the CO_2 ligand has significant electronegative character[16] at the oxygen atoms. All of these observations are consistent with the metallocarboxylate structure. This reaction chemistry is hopefully an important, novel addition to the "chemicals from CO_2" quest.

Acknowledgment. Dr. P. Murray-Rust, Dr. H.-Y. Chen, J. T. Corle, Jr., and L. Lardear are thanked for their assistance in this work.

Registry No. $[Rh(diars)_2]Cl$, 38337-86-9; $Rh(diars)_2(Cl)(CO_2)$, 83853-75-2; CO_2, 124-38-9.

Supplementary Material Available: A listing of fractional coordinates, thermal parameters, and all bond lengths and angles (35 pages). Ordering information is given on any current masthead page.

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Effects of Electron Correlation on the Energies of 2-Norbornyl Cation Structures. Evaluation of the Nonclassical Stabilization Energy

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The solid-state ^{13}C NMR spectrum of the 2-norbornyl cation at 5 K provides the latest evidence for the symmetrically bridged, nonclassical structure.[1] The ESCA spectrum,[2] the ^{13}C and ^{1}H chemical shifts,[3] and the perturbation isotope effects[4] all suggest that the 2-norbornyl cation has a bridged structure in stable ion media.[5]

Table I. Energy Differences (kcal/mol)

theoretical levels	2-norbornyl cations, C_1 vs. C_s forms[a] STO-3G geometries	4-21P geometries	2-norbornyl vs. 2-propyl, eq 1[b]
Hartree–Fock			
4-21P	+0.4	−0.2[c]	−13.8
6-31G	−1.0	−0.8	−11.0
4-21P+5d		+0.6	−16.0
electron correlated			
MP2/4-21P	+7.9	+2.2	−23.0
MP2/6-31G	+7.5	+2.1	−20.2
MP2/4-21P+5d		+2.4	−24.8

[a] Positive values indicate the symmetrically bridged (C_s) 2-norbornyl cation to be more stable than the partially bridged C_1 form. [b] In all cases, energies for the symmetrically bridged C_s 2-norbornyl cation were employed. [c] Identical with ref 13.

In the gas phase, experimental determinations by several groups[6] have shown that the *secondary* 2-norbornyl cation is thermodynamically much more stable than all comparable secondary aliphatic acyclic and cyclic cations and rivals *tertiary* carbocations in this respect.[7,8] This evidence, while indirect, supports the nonclassical structural assignment for the 2-norbornyl cation: the multicenter bonding associated with the bridged structure accounts for the energy lowering.

Quantitative theoretical methods provide independent means of determining both structures and energies. Earlier calculations on the 2-norbornyl cation,[9-13] while notable, were not definitive since electron correlation corrections, known from studies of smaller carbocations to favor bridged structures,[14] were not included explicitly. In this communication we report the results of our calculations including such correlation corrections.

Using previous 4-21P[13] (and in some cases STO-3G[12]) optimized geometries, we have now performed single-point calculations including electron correlation corrections at the second-order Møller–Plesset (MP2) perturbation level[15] using three different basis sets, viz., 4-21P[13], 6-31G[16], and the 4-21P basis augmented by a set of five d-type polarization functions on each carbon.[17]

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Table II. Characteristic Geometrical Features

species	optimization level	distances, Å			angles, deg
		C_1–C_2	C_1–C_6	C_2–C_6	$\angle C_2$–C_1–C_6
norbornane	4-21G[a]	1.551	1.551	2.510	108.0
2-norbornyl cation (C_1), partially bridged	STO-3G[b]	1.478	1.605	2.307	96.8
	4-21P[c]	1.406	1.753	2.130	84.0
2-norbornyl cation (C_s), symmetrically bridged	STO-3G[b]	1.402	1.839	1.839	67.6
	4-21P[c]	1.384	1.940	1.940	69.1

[a] Geometry from: Van Alsenoy, C.; Scarsdale, J. N.; Schafer, L. *J. Comput. Chem.* 1982, *3*, 53–61. A slightly different version of the 4-21G basis set was used by these authors. See ref 13. The experimental and 4-31G geometries are also similar. See: Wiberg, K. *J. Am. Chem. Soc.* 1983, *105*, 1227–1233. [b] Reference 12. [c] Reference 13.

The computed total energies at different levels are given as supplementary material. The energy differences in Table I at Hartree–Fock levels between the norbornyl cation structures are small. However, when the MP2 electron correlation corrections are applied, there is an enhanced preference for the symmetrically bridged (C_s) 2-norbornyl cation at all levels of theory. The differences are larger when the STO-3G geometries[12] for the "classical" (C_1) structure are employed.

The "symmetrically bridged" 2-norbornyl cation is defined by its C_s symmetry; geometry optimization can be carried out in a straightforward manner. In contrast, the structure of the "classical" 2-norbornyl cation (C_1 point group) must be chosen arbitrarily. A truly "classical" geometry would deviate little from that of the parent hydrocarbon, norbornane (see Table II). However, even the STO-3G-optimized 2-norbornyl cation geometry is distorted from this ideal; "partially bridged" is a better description than "classical". The characteristic distances and bridgehead angle (Table II) no longer correspond to classical expectations. Optimization at 4-21P leads to further distortion away from the norbornane structure; partial bridging is even more pronounced and all geometrical features are now closer to those of the symmetrically bridged form.

It is possible to calculate geometries for partially bridged 2-nornornyl cations at STO-3G and 4-21P only because these C_1 structures are lower in energy than the C_s forms *at those levels of theory*. If d-orbital augmented basis sets were to be used (especially if electron correlation corrections were included), the symmetrically bridged (C_s) 2-norbornyl cation structure is expected to be the *only minimum*.[18] No C_1 form can be defined rigorously at higher levels of theory: neither the classical nor partially bridged cations are expected to be stationary points on the potential energy surface. The situation is illustrated by Figure 1, a plot of MP2/6-31G single-point energies at C_s (4-21P),[19] C_1 (4-21P), and C_1 (STO-3G) geometries against the C_2–C_1–C_6 angles. Parabolic extrapolation to an angle of 108.0° (the norbornane value) provides an estimate of the hypothetical "classical"–nonclassical energy difference, 15 kcal/mol, for the 2-norbornyl cation.[20]

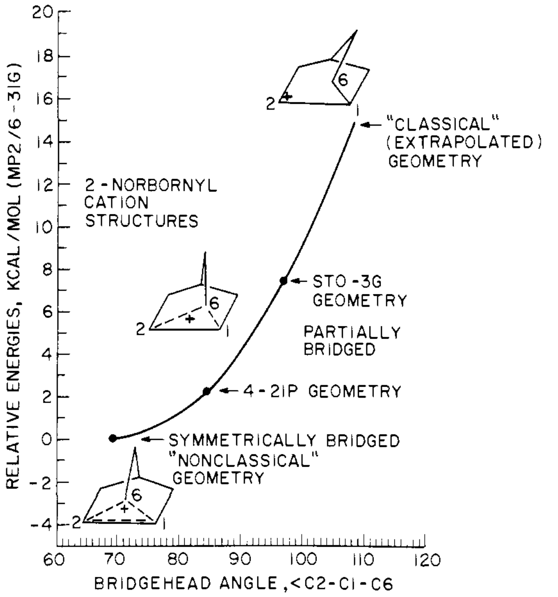
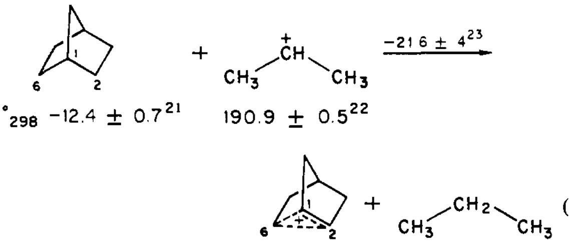


Figure 1. Relative energies of symmetrically and partially bridged 2-norbornyl cations. Parabolic extrapolation to $\angle C_2$–C_1–C_6 = 108.0° (the value in norbornane) provides an estimate of the "classical–nonclassical energy difference" (about 15 kcal/mol).

Since the 4-21P symmetrically bridged (C_s) and partially bridged (C_1) structures have rather similar geometries, the differential effect of electron correlation corrections are relatively small. These favor the C_s form by ≃2 kcal/mol (Table I). The STO-3G-optimized C_1 2-norbornyl cation is still partially bridged but is closer to the "classical" structure. Larger differential electron correlation effects, favoring the symmetrically bridged species by ≃8 kcal/mol, are found. A comparison of the symmetrically bridged 2-norbornyl cation and the classical 2-propyl cation is provided by eq 1. The MP2 correction again favors the



(1)

nonclassical structure; the magnitude is larger and is remarkably constant (≃9 kcal/mol). The theoretical reaction energy for eq 1 at correlated levels (Table I)[20] is in good agreement with the experimental gas-phase value (−22 ± 4 kcal/mol).[21-24]

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(17) The value for the d exponent used on carbon was 0.75. All computations were carried out on the CRAY-1 computer at Bell Laboratories with a modified version of the GAUSSIAN 80 series of programs. See: Binkley, J. S.; whiteside, R. A.; Krishnan, R.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Topiol, S.; Kahn, L. R.; Pople, J. A. *QCPE* **1981**, *13*, 406.

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(23) Although the experimental determinations of $\Delta H_f{}^\circ{}_0$ (2-norbornyl) are in good agreement,[6] these are based on $\Delta H_f{}^\circ{}_{298}$ (t-$C_4H_9{}^+$) = 163.5 kcal/mol and are subject to the uncertainties of that value.[7b,22] With $\Delta H_f{}^\circ{}_{298}$ (t-$C_4H_9{}^+$) = 166.5 kcal/mol,[7b,22] $\Delta H_f{}^\circ$ ($C_7H_{11}{}^+$) = 185 and eq 1 = −18.6 ± 2 kcal/mol.

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In the gas phase, size effects (e.g., polarization) influence the stability of charged molecules. Thus, a comparison of a $C_7H_{11}^+$ with a $C_3H_7^+$ species (eq 1) is less appropriate than that with a secondary C_7 cation.[25] E.g., for the 4-heptyl cation, Bowen and Williams[26] have suggested a correction of 6 kcal/mol. The size-corrected "extra stabilization" of the 2-norbornyl cation relative to classical secondary counterparts, 14–19 kcal/mol, agrees with that derived from Figure 1 and with many literature estimates.[5-13] The value in solution is 5–8 kcal/mol.[5,8a,27]

Conclusion. The symmetrically bridged (C_s) 2-norbornyl cation structure is expected to be the only minimum on the potential energy surface. As no minima with C_1 symmetry are found, *"classical" and partially bridged 2-norbornyl cations are not expected to exist* at least as isolated (gas phase) entities. The extra stabilization due to bridging of the C_s 2-norbornyl cation (the "classical–nonclassical energy difference") is estimated approximately in two ways to be about 15 kcal/mol.

Acknowledgment. We thank Professor Lischka and Dr. Köhler for providing the STO-3G norbornyl cation geometries and Dr. J. Chandrasekhar for suggestions. The work at Erlangen was supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft.

Registry No. 2-Norbornyl cation, 24321-81-1.

Supplementary Material Available: Table of computed total energies at different levels (1 page). Ordering information is given on any current masthead page.

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Theoretical Structure of the $B_2H_7^-$ Anion

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The X-ray structure of $[(Ph_3P)_2N]^+B_2H_7^-\cdot CH_2Cl_2$ indicated a bent B–H–B three-center two-electron bond (∠BHB = 136 ± 4°) for the $B_2H_7^-$ anion and C_s symmetry.[1] Earlier theoretical studies on isolated $B_2H_7^-$ correctly predicted that double- or triple-bridged alternatives would be less stable, but indicated that a *linear* single B–H–B bridge should be favored.[2-4] The bent experimental $B_2H_7^-$ structure (**1**) also contrasts with the results of an X-ray structure of the related $(CH_3)_3Al\text{-}H\text{-}Al(CH_3)_3^-$ anion[6] and with theoretical calculations on $H_3Al\text{-}H\text{-}AlH_3^-$,[7] which all indicate *linear* Al–H–Al bridging to be preferred. Shore, Bau, et al. recognized that the conformation of $B_2H_7^-$ "might be sensitive to crystal lattice effects" and further X-ray and neutron diffraction experiments are being carried out.

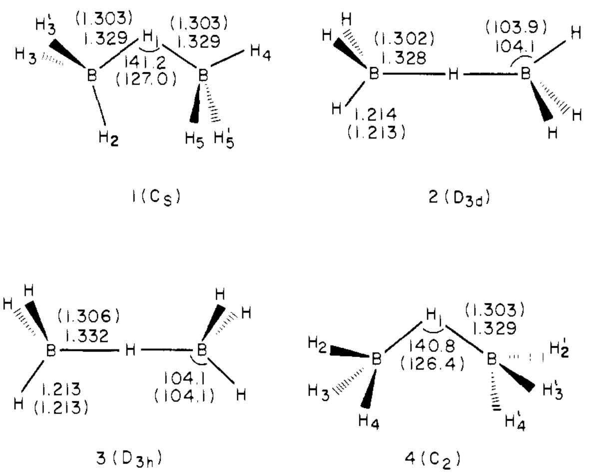

Figure 1. The various structures for $B_2H_7^-$ considered in this study. Some geometrical parameters optimized at HF/6-31G* (MP2/6-31G*) levels are shown. The remaining geometrical parameters are specified in the footnote to Table I.

As our previous ab initio calculations on $B_2H_7^-$, like those in the literature,[2-4] appeared to favor a linear D_{3d} structure, **2** (the D_{3h} from **3** is only slightly less stable),[5] we were intrigued by the apparent discrepancy with experiment. For example, when the experimental geometry **1** was taken as the starting point for optimization with the split valence 3-21G basis set,[8] no bent minimum was found and **2** resulted. However, our prior experience with the isoelectronic $C_2H_7^+$ cation indicated such structural details to be extremely sensitive to the level of theory employed.[9] Larger basis sets with polarization functions and especially corrections for the effects of electron correlation favor bent over linear C–H–C bridges. Thus, definitive studies on $B_2H_7^-$ need a similar degree of sophistication, which was not employed in the prior theoretical investigations.[2-5] We now report the results of such an examination which confirms *bent* B–H–B structures to be favored.

Starting again with the experimental geometry of **1**, optimization was carried out at two higher levels. We first employed the 6-31G* basis set,[10] which has d-type polarization functions on boron. A bent structure (see Figure 1) with a $B\text{-}H_1\text{-}B$ angle of 141.2° was found with C_s symmetry (**1**). However, **1** had one negative eigenvalue of the force constant matrix and was a transition structure rather than a local minimum. Although having almost identical energy, a minimum, **4**, with C_2 symmetry, was located. At this level, the potential energy surface was very flat and the energies of **1** and **4** were less than a kcal/mol more stable than those of the linear alternatives, **2** and **3** (Table I). These forms had more than one negative eigenvalue of the force constant matrix[14] suggesting that they are higher order saddle points.

The next geometry optimization was carried out at the MP2/6-31G* level which includes corrections for electron correlation using second-order Møller–Plesset perturbation theory.[11] As in the case of $C_2H_7^+$,[9] this caused a further bending of the molecule. A $B\text{-}H_1\text{-}B$ angle of 126.4° resulted for **4** (C_2). At this optimized MP2/6-31G* level, the energetic advantage of **4** over the linear D_{3d} (**2**) and D_{3h} (**3**) forms was still low, ≃2 kcal/mol. The structures of **2** and **3** reoptimized at the MP2 level underwent only minor changes.

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