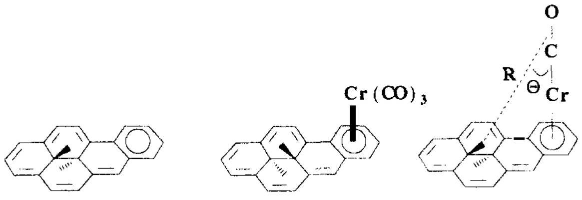
benzene ring in **4** is more aromatic than that in naphthalene, exchange of ligand between **4** and (tricarbonylchromium)-naphthalene should and did occur in ether (containing catalytic THF) to give 60% of **2** as a mixture of two isomers in a 3:1 ratio. The major isomer was separated by chromatography and fractional crystallization, mp 189–190 °C, and was shown to be **2** by a preliminary X-ray determination.[5] By NMR, the minor isomer is assigned the structure **5**. The chemical shifts found for the internal methyl protons are as follows: **2**, δ −0.87 and −0.98; **5**, δ −0.81 and −1.16. For **2**, the methyl syn to the Cr is assigned[6] the shift −0.87, and the methyl anti to the Cr is assigned the shift −0.98. The important point is that, despite the difference in positions of the two methyl groups relative to the center of anisotropy, the chemical shift difference between these methyl protons is very small. For a $Cr(CO)_3$ group, McGlinchey[7] takes the center of anisotropy of a $Cr(CO)_3$ moiety to be 3.3 Å above the Cr along the C_3 axis (see A; the three carbonyl groups have been replaced by a "supercarbonyl" along the C_3 axis), and for **2** the relevant values of R and θ for the two methyl groups are 8.49 Å, 17.18° and 5.95 Å, 54.41° for the distal and proximal methyl groups, respectively. Based on McGlinchey's results,[7] the calculated effects of the $Cr(CO)_3$ on these protons at these distances are only +0.00 and +0.16 ppm, respectively, in excellent agreement with the found difference in chemical shift for **2** of 0.11 ppm! Moreover, we have found previously that the chemical shift of the methyl protons correlates very well with the chemical shift of the distant ring proton H_d for a series of annelated annulenes;[3] in **2**, H_d has R = 8.68 Å and θ = 63.88° and thus is hardly affected by the $Cr(CO)_3$ at all. On the basis of its chemical shift of δ 6.88, we can calculate[8] the expected chemical shift of the methyl protons to be δ −0.97. Since the found values agree very closely to this and are in accord with the McGlinchey equation results, we can conclude that, in **2**, the $Cr(CO)_3$ has almost no *anisotropic* effect on the chemical shift of the methyl protons. Why then is the chemical shift of the methyls (−0.97 ppm) at lower field than those of the uncomplexed annulene **4** (−1.62 ppm)? This could be because of more bond fixation in the macrocyclic ring of **2** than of **4**, or because of removal of electron density from the macrocyclic ring in **2** by the $Cr(CO)_3$. Substantial reduction of electron density in the macrocyclic ring in **2** is not supported by π-SCF calculations[10] and is ruled out by examination of the coupling constants of **2** relative to those of **4**. If substantial removal of charge from the macrocyclic ring occurred, ^3J values in **2** would be smaller than in **4**. However, those found[11] alternate more in **2** than in **4**, consistent with *more bond fixation in the macrocyclic ring* of **2** than **4**, in agreement with the chemical shift results. The inescapable conclusion, supported by the chemical shifts of the methyl and distant protons, the increased alternation in coupling constants, and π-SCF calculations, is that a tricarbonylchromium-complexed benzene ring has more bond-fixing power, and resists bond fixation in itself more than benzene does, and is thus more "aromatic" than benzene! Using our recently developed[3] equation to estimate resonance energies of the annelating ring in annelated dimethyldihydropyrenes, we estimate that, on the basis of its bond-fixing ability, **1** thus has about 1.3 times the "resonance energy" of benzene. We are attempting to prepare other metal-complexed derivatives of **3** and **4** and thus compare them with **2**.



4 **5** **A**

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(5) Satisfactory ^{1}H and ^{13}C NMR and mass spectra and elemental analysis were obtained.

(6) Based on results of McGlinchey,[7] where protons proximal to Cr are found most deshielded.

(7) McGlinchey, M. J.; Burns, R. C.; Hofer, R.; Top, S.; Jaouen, G. *Organometallics* **1986**, *5*, 104–109.

(8) From Haddon's[9] ring current geometry factors, the predicted sensitivity factor for the internal methyl protons relative to the external protons is 2.38. Comparison of the chemical shifts in a series[4] of annelated dihydropyrenes yields us the equation $\Delta\delta_{Me} = -2.60\Delta\delta_H - 0.029$ (ρ = 0.9998).

(9) Haddon, R. C. *Tetrahedron* **1972**, *28*, 3613–3633.

(10) Mitchell, R. H.; Williams, R. V.; Mahadevan, R.; Lai, Y.-H.; Dingle, T. W. *J. Am. Chem. Soc.* **1982**, *104*, 2571–2578. Removal of 1.5 unit charges from the benzene ring reproduces the bond orders (measured from coupling constants) found in the macrocyclic ring, without substantial removal of charge from that ring.

(11) For **4**, $J_{1,2}$ = 8.87 Hz, $J_{2,3}$ = 6.52 Hz, $J_{4,5}$ = 8.83 Hz, and $J_{11,12}$ = 6.57 Hz. For **2**, $J_{1,2}$ = 8.97 Hz, $J_{2,3}$ = 6.30 Hz, $J_{4,5}$ = 9.24 Hz, and $J_{11,12}$ = 6.53 Hz.

Can CO_2 Coordinate to a Ni(I) Complex? An ab Initio MO/SD-CI Study

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CO_2 conversion into useful substances has been an attractive object of research.[1] One of the effective attempts is electrocatalytic reduction of CO_2.[2-15] In those investigations, transition-metal CO_2 complexes have often been postulated as a key intermediate.[3a,7b,8,13-15] In this work, $Ni^IF(NH_2)_4(CO_2)$ (**1**), $[Ni^I(NH_3)_4(CO_2)]^+$ (**2**), and $[Ni^{II}F(NH_3)_4(CO_2)]^+$ (**3**) are investigated with the ab initio MO/SD-CI method. These complexes can be viewed as models of an intermediate in electrocatalytic reduction of CO_2 with Ni(cyclam)Cl_2,[7] where $(NH_3)_4$ and F are models of cyclam and Cl, respectively (note that an intermediate Ni–CO_2 complex was proposed to be a Ni^I species[7]). One important conclusion is that CO_2 can coordinate with $Ni^IF(NH_3)_4$ to form a stable η^1-CO_2 complex but not with $[Ni^I(NH_3)_4]^+$ and $[Ni^{II}F(NH_3)_4]^+$.

Spin-restricted ab initio MO/SD-CI calculations were carried out with the MELD program,[16] in which split-valence type basis sets[17] were used with the exception of minimal basis sets for N[18a] and H[18b] and a triple-ζ basis set for the Ni 3d orbital.[19] The

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(1) For instance: (a) Collin, J.-P.; Sauvage, J.-P. *Coord. Chem. Rev.* **1989**, *93*, 245. (b) Behr, A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 245. (c) Braunstein, P.; Matt, D.; Nobel, D. *Chem. Rev.* **1988**, *88*, 747. (d) Walther, D. *Coord. Chem. Rev.* **1987**, *89*, 135.

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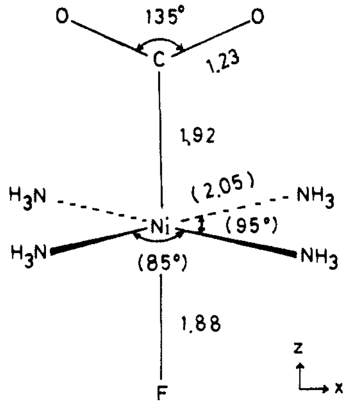

Figure 1. Optimized structure of $Ni^{I}F(NH_3)_4(\eta^1\text{-}CO_2)$. In parentheses: assumed geometrical parameters, taken from the experimental structure of a similar complex.[20]

Table I. Relative Stabilities and CO_2 Binding Energies of $Ni^{I}F(NH_3)_4(\eta^1\text{-}CO_2)$ (**1**), $[Ni^{I}(NH_3)_4(\eta^1\text{-}CO_2)]^+$ (**2**), and $[Ni^{II}(NH_3)_4(\eta^1\text{-}CO_2)]^+$ (**3**)[a]

complex	state	rel energy (kcal/mol), HF	binding energy[b] (kcal/mol)	
			HF	SD-CI[c]
1	$^2A_2$ $(d_{z^2}{}^2d_{xy}{}^1)$	0	22[d]	48[e]
	$^2A_1$ $(d_{z^2}{}^1d_{xy}{}^2)$	27		
2	$^2A_2$ $(d_{z^2}{}^2d_{xy}{}^1)$	0	−44[f]	−14[g]
	$^2A_1$ $(d_{z^2}{}^1d_{xy}{}^2)$	62		
3	$^1A_1$ $(d_{z^2}{}^2d_{xy}{}^0)$	0	−80[h]	−29[i]
	$^1A_1$ $(d_{z^2}{}^0d_{xy}{}^2)$	44		
	$^3A_2$ $(d_{z^2}{}^1d_{xy}{}^1)$	−51	−96[j]	−21[k]

[a] Geometries of **2** and **3** are assumed to be the same as in **1**. [b] $E_t[R(\text{Ni–CO}_2) = 50$ Å$] - E_t$(optimized structure). [c] After Davidson's correction.[25] [d] $E_t = -2016.4174$ hartrees. [e] $E_t = -2017.4063$ hartrees. [f] $E_t = -1916.8916$ hartrees. [g] $E_t = -1917.7618$ hartrees. [h] $E_t = -2016.1397$ hartrees. [i] $E_t = -2017.1327$ hartrees. [j] $E_t = -2016.2202$ hartrees. [k] $E_t = -2017.1658$ hartrees.

Ni–CO_2 part was optimized independently at the Hartree–Fock (HF) level by using parabolic fitting of total energies, while the Ni–NH_3 distance was taken from an experimental structure of $Ni(cyclam)(NO_3)_2$,[20] together with the experimental geometry of free NH_3.[21] Only in the optimization, a basis set for F was changed to a minimal one to shorten computation time.[22] SD-CI calculations were carried out with all core orbitals excluded from an active space and virtual orbitals transformed to K orbitals,[23] after all single–double excited configurations were screened by perturbation selection.[24]

Two electronic states are conceivable in a η^1-C coordinated Ni(I)–CO_2 complex which takes either a square-pyramidal or a pseudooctahedral structure (the η^2-side-on mode is unstable, vide infra); one is the $^2A_2$ $(d_{z^2}{}^2d_{xy}{}^1)$ and the other is the $^2A_1$ $(d_{z^2}{}^1d_{xy}{}^2)$ (all other d orbitals are doubly occupied; see Figure 1 for the coordinate system). In **1** and **2**, the $^2A_2$ state was calculated to be much more stable than the $^2A_1$ state at the HF level (see Table I), probably because a strongly antibonding orbital between a Ni d_{xy} orbital and NH_3 lone pairs is doubly occupied in the $^2A_1$ state. Thus, in the $^2A_2$ state of **1**, several orientations of CO_2 were examined. In the most stable orientation, CO_2 was staggered to the Ni–NH_3 bond. Although the electrostatic attraction between CO_2 and the N^-–H^+ bond of cyclam has been proposed to favor the CO_2 coordination to Ni,[7b] the most stable orientation does not involve such an electrostatic attraction between $O^{\delta-}$ of CO_2 and $H^{\delta+}$ of NH_3.[26] The Ni–CO_2 part of $Ni^{I}F(NH_3)_4(CO_2)$ was optimized in this orientation. The optimized structure of the Ni–CO_2 part (Figure 1) resembles very much the Co–CO_2 part of a typical η^1-C coordinated CO_2 complex, K[Co(*n*-Pr-salen)-(CO_2)].[27] The binding energy of CO_2 coordination is larger in **1** than in $Ni(PH_3)_2(\eta^2\text{-}CO_2)$[28] and $RhCl(AsH_3)_4(\eta^1\text{-}CO_2)$.[29] This means that the CO_2 coordination in **1** is rather strong (although all these complexes were calculated with split-valence type basis sets, the basis sets used in refs 28 and 29 differ from those used in this work, which means that only a qualitative comparison is possible).

In **2**, the CO_2 binding energy is significantly negative at both HF and SD-CI levels (Table I: the Ni–CO_2 geometry of **2** was assumed to be the same as in **1**). Furthermore, both HF and SD-CI calculations indicate that CO_2 dissociates from Ni with no barrier.[30] Thus, we might conclude that CO_2 coordination would not be stable in **2**. **3** was also briefly examined, in which its structure was assumed to be the same as **1**. The most stable $^3A_2$ $(d_{z^2}{}^1d_{xy}{}^1)$ and the next most stable $^1A_1$ $(d_{z^2}{}^2d_{xy}{}^0)$ states were calculated with the SD-CI method. For these two electronic states, however, considerably negative binding energy was obtained at both the HF and SD-CI levels (Table I). From this result, CO_2 coordination to Ni(II) seems impossible.

The η^2-side-on CO_2 complex of **1**[31] has two possible electronic states, $^2A'$ $(d_{z^2}{}^1d_{xy}{}^2)$ and $^2A''$ $(d_{z^2}{}^2d_{xy}{}^1)$. Both states were calculated to be significantly unstable; $^2A'$ is 74 kcal/mol unstable and $^2A''$ is 152 kcal/mol unstable, compared to the η^1-C coordination mode.[32] In $Ni^{I}F(NH_3)_4$, the dπ orbitals are much more stable in energy than the d_{z^2} orbital. Therefore, the η^2-side-on mode is unstable in **1**.[33]

The reason why only **1** forms a stable η^1-CO_2 complex is that, in **1**, the F^- ligand pushes up the d_{z^2} orbital energy and neutralizes the positive charge of Ni(I),[34] which allows a strong Ni → CO_2 charge transfer and stabilizes the CO_2 coordination.[28,29,33] Furthermore, the charge neutralization by F^- coordination would decrease the charge–dipole repulsion between the distorted CO_2 and Ni(I). On the other hand, **2** does not have the F^- ligand, and **3** is a positively charged Ni(II) complex. As a result, **1** forms a stable η^1-CO_2 complex unlike **2** and **3**. The great charge transfer of **1** increases the negative charge on the O atom (−0.58*e* in **1**, −0.45*e* in **2**, −0.36*e* in **3**, and −0.33 in the free CO_2), which would facilitate protonation to the coordinated CO_2. This result supports the reaction mechanism proposed by Sauvage et al.[7b]

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(19) $\zeta = 0.10$, which was determined with the even-tempered criterion, was added.

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(22) The Ni–F distance optimized with a minimal basis set of F would be slightly shorter than that optimized with a better basis set. However, the significantly large stability of **1** would be kept semiquantitatively even if the Ni–F distance is optimized with a better basis set.

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(24) (a) Langhoff, S. R.; Davidson, E. R. *Int. J. Quantum Chem.* **1974**, *8*, 61. (b) The threshold of energy contribution was 200 μhartrees. This value seems rather large; remaining SD excitations which undergo a variational CI calculation include about 85% of estimated SD excitation energy. However, a threshold of 100 μhartrees needs too large a memory space and too much computational time. The influence of threshold, which was examined in **3** taking the $^1A_1$ state, is negligibly small; the binding energy is −29.1 kcal/mol at 100 μhartrees, −28.6 kcal/mol at 150 μhartrees, and −28.9 kcal/mol at 200 μhartrees.

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(30) The Ni–C distance is lengthened from 1.92 to 2.22 Å, then CO_2 distortion is decreased, and again the Ni–C distance is lengthened to 2.52 A. All these geometry changes result in energy stabilization, and the final structure [R(Ni–C) = 2.52 Å, ∠OCO = 180.0°] is calculated to be more unstable than the infinite separation.

(31) The structure of the η^2-side-on complex was assumed. The Ni–C distance and the geometry of the CO_2 part were taken to be the same as in **1**. The C=O bond was placed perpendicular to the *z* axis, staggered to the Ni–N bond.

(32) SD-CI calculations were not carried out because this mode is significantly unstable, compared to the η^1-C mode.

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