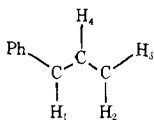


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ppm,  $\nu_B$  0.87 ppm, downfield with respect to external 85%  $\text{H}_3\text{PO}_4$  ( $^2J_{\text{P}(\text{H}_1)-\text{P}(\text{H}_2)} = 5.0$  Hz)).

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## Approaches to Homogeneous Reduction of Carbon Monoxide: Reaction of Niobium Hydrides with Coordinated CO

Sir:

There is currently intense interest in homogeneous catalysis of reactions of carbon monoxide and hydrogen ("synthesis gas"), with much of the recent activity focusing on metal clusters as potential catalysts.<sup>1,2</sup> Mechanistic considerations applied to possible pathways involving *mononuclear* catalytic sites suggest that formation of the first C-H bond may be a key step. An alternative to insertion of CO into a metal-hydrogen bond, which does not appear to be a feasible transformation,<sup>3</sup> would be nucleophilic attack by a hydride on a coordinated carbonyl. Such reactions have been found to lead to formyl,<sup>3</sup> hydroxymethyl,<sup>4</sup> and methyl<sup>5,6</sup> complexes, using boron hydride reagents. A *catalytic* process involving such a step would require a transition metal hydride capable of exhibiting hydridic character, which has been observed only for several complexes of titanium<sup>7</sup> and zirconium.<sup>8,9</sup> Examples of the reduction of CO to methane<sup>10</sup> or to alcohols<sup>11,12</sup> employing these metals have recently been reported. However, these hydrides react readily with water and alcohols, the reaction products, as well, apparently precluding their use in catalytic systems.

We have chosen to direct our attention to the next group of the periodic table, in hopes that hydride complexes would be stable to the reaction products while still maintaining some hydridic character. The complexes  $\text{Cp}_2\text{NbH}_3$  and  $\text{Cp}_2\text{NbH}(\text{CO})$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) were found to be stable to water and ethanol at room temperature but to slowly reduce

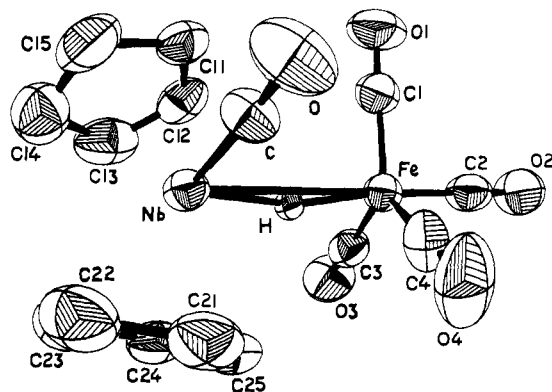


Figure 1. Molecular structure of  $(\eta^5\text{-C}_5\text{H}_5)_2(\text{CO})\text{Nb}(\mu\text{-H})\text{Fe}(\text{CO})_4$  (Cp ring hydrogens are not shown).

acetone,<sup>13</sup> suggesting that they might possess the necessary reactivity.  $\text{Cp}_2\text{NbH}(\text{CO})$  reacts slowly ( $T_{1/2} \approx 1$  day) at 140  $^\circ\text{C}$  under  $\text{H}_2$  to give an insoluble brown solid.<sup>14</sup> No new products can be detected in solution, but analysis of the gas phase<sup>15</sup> shows the presence of methane and ethane, each formed in  $\sim 2$ -5% yield (based on Nb complex consumed), plus trace amounts of propane. The origin of these products is established by labeling studies: use of  $\text{D}_2$  instead of  $\text{H}_2$  gives a roughly equal mixture of  $\text{CD}_4$  and  $\text{CHD}_3$ , while reduction of  $\text{Cp}_2\text{NbH}(\text{CO})$  gives  $^{13}\text{CH}_4$ , demonstrating that methane is produced by CO reduction. In contrast, however, the higher alkanes show no incorporation of either label, and hence are formed by a different process, most probably degradation of the Cp rings.<sup>16</sup> Use of an  $\text{H}_2$ -CO gas mixture results in no significant change in methane yield (although the ethane yield decreases, consistent with the conclusion that these are produced by different pathways).

The vigorous conditions required to bring about attack on CO by the niobium hydride can be ascribed, at least in part, to the low hydridic character (in comparison with group 4 hydrides). Another possible factor, however, is the character of the CO: for attack by hydride the CO should be as electrophilic as possible, but the low stretching frequency of  $\text{Cp}_2\text{NbH}(\text{CO})$  ( $\nu_{\text{CO}} 1900 \text{ cm}^{-1}$ ) suggests, on the contrary, that the CO is relatively electron rich. In contrast,  $\text{Fe}(\text{CO})_5$  (which should be more readily attacked by a hydridic reagent<sup>3</sup>) reacts rapidly with  $\text{Cp}_2\text{NbH}_3$ , even at room temperature. Evidence that hydride attack on CO takes place was obtained by monitoring the  $^1\text{H}$  NMR during the reaction;<sup>17</sup> in addition to starting material and product peaks, a new singlet at  $\delta$  14.3 appears and grows to a maximum at early stages before disappearing as the reaction goes to completion. The shift of this signal is characteristic of metal formyl complexes<sup>3</sup> and strongly suggests that an intermediate closely resembling  $(\text{HCO})\text{-Fe}(\text{CO})_4^-$  (probably strongly ion paired or even bonded through the acyl oxygen to the niobium) is involved in the reaction pathway.

Unfortunately, although the use of this mixed-metal system does appear to facilitate the attack of hydride on CO, it does not lead to reduced CO: the overall products are  $\text{H}_2$  (1 mol per Nb) and a new compound, characterized by elemental analysis, IR and NMR spectroscopy, and x-ray crystallography<sup>18</sup> as  $\text{Cp}_2(\text{CO})\text{Nb}(\mu\text{-H})\text{Fe}(\text{CO})_4$  (Figure 1). This compound may be viewed as an adduct between  $\text{Cp}_2\text{NbH}(\text{CO})$  and the unsaturated fragment  $\text{Fe}(\text{CO})_4$ , with donation through a bridging hydrogen as well as the metal-metal bond.<sup>19</sup> Even though neither of the systems examined leads to catalytic CO reduction, the postulated correlation between CO-reducing ability and the nucleophilic and electrophilic character of the metal hydride and metal carbonyl, respectively, seems to be valid, suggesting promising directions for future work in this area.

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- (15) Gas mixtures were analyzed qualitatively by mass spectrometry and gas chromatography (Porapak column) and estimated quantitatively from gas chromatographic peak intensities.
- (16) A similar degradation of Cp rings to smaller hydrocarbons has been reported in the thermal decomposition of  $\text{Cp}_2\text{Ti}(\text{CD}_3)_2$  at temperatures comparable with those employed here: H. G. Alt, F. P. Di Sanzo, M. D. Rausch, and R. C. Uden, *J. Organomet. Chem.*, **107**, 257 (1976).
- (17) Reaction followed in benzene at 20 °C, using a kinetics program for a Varian XL-100 spectrometer. Under these conditions the peak assigned to the formyl intermediate reached a maximum (~20% of total Nb concentration from peak intensity) after ~4 min and then began to decrease; the reaction was ~90% complete after 10 min.
- (18) Crystal data and refinement results: monoclinic;  $a = 7.819$  (3),  $b = 13.481$  (2),  $c = 15.135$  (2) Å;  $\beta = 97.05$  (2)°; space group  $P2_1/c$ ;  $Z = 4$ ;  $R_1 = 0.033$ ,  $R_2 = 0.042$ ; 3063 unique observed data. All atoms including hydrogen were located.
- (19) Key structural parameters: Nb-Fe, 3.318 (1), Nb-H, 1.91 (3), H-Fe, 1.61 (3) Å; Nb-H-Fe, 141 (2)°. Details of the structure will be discussed in a subsequent publication.

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## Ab Initio Calculation of the Free Energy of Liquid Water

Sir:

We report herein the first fully ab initio calculation of the free energy of a molecular liquid. The system is liquid water at 25 °C and a density of 1 g/cm<sup>3</sup>. The computational method employed is statistical thermodynamic Monte Carlo computer simulation based on an intermolecular potential function representative of quantum mechanical calculations on the water dimer.

Ab initio theoretical calculations of the thermodynamic internal energy and average quantities such as radial distribution functions have been reported for liquid water from several laboratories. Computer simulations based on the analytical potential function developed by Matsuoka, Clementi, and Yoshimine<sup>1</sup> and representative of moderately large ab initio intermolecular configuration interaction calculations are found to produce oxygen-oxygen radial distribution functions in close accord with experiment at 25 °C.<sup>2,3</sup> The calculated internal energy,  $-8.58 \pm 0.06$  kcal/mol, may be compared with the corresponding observed value of  $-9.9$  kcal/mol.<sup>4</sup> The discrepancy of 1.3<sub>2</sub> kcal/mol is ascribed to the assumption of

pairwise additivity in the configurational energy calculations and limitations in the intermolecular potential function due to truncation errors in the configuration interaction basis set and truncation errors in the orbital basis set expansion in the quantum mechanical data base of pairwise interaction energies. A detailed theoretical analysis of the structure of liquid water using Monte Carlo computer simulation based on this function has been contributed previously from this laboratory.<sup>3</sup>

The ensemble average expression for free energy is not convenient for computational procedures owing to the ill-conditioned nature of the integrand and concomitant convergence problems.<sup>5</sup> The various possible computational approaches to free energy considered to date have been recently reviewed by Valleau and Torrie,<sup>6</sup> who have discussed the theoretical or computational limitations of each method. The procedure used herein follows Kirkwood,<sup>7,8</sup> wherein the Helmholtz configurational free energy  $A$  is given by

$$A = \int_0^1 U(\xi) d\xi \quad (1)$$

Here the integrand  $U(\xi)$  can be expressed as an ensemble average,

$$U(\xi) = \int \dots \int E(\mathbf{X}^N) P(\mathbf{X}^N/\xi) d\mathbf{X}^N \quad (2)$$

where  $E(\mathbf{X}^N)$  is the configurational energy and  $P(\mathbf{X}^N, \xi)$  is the probability of observing the system in configuration  $\mathbf{X}^N$ , conditional upon the auxiliary parameter  $\xi$ ,

$$P(\mathbf{X}^N/\xi) = \frac{\exp[-\beta E(\mathbf{X}^N, \xi)]}{\int \dots \int \exp[-\beta E(\mathbf{X}^N, \xi)] d\mathbf{X}^N} \quad (3)$$

with  $\beta$  representing  $(kT)^{-1}$ . When the auxiliary parameter serves to couple the system according to the expression

$$E(\mathbf{X}^N, \xi) = \xi E(\mathbf{X}^N) \quad (4)$$

the free energy is defined with respect to an ideal gas reference state of liquid density and is equivalent to the general class of "thermodynamic integrations" for free energy,<sup>6</sup> the main disadvantages of which stem from problems in the integration over  $\xi$ . The simple extra computational effort required may be complicated by convergence problems for small  $\xi$  and possible discontinuities in  $U(\xi)$ .

In view of the central importance of liquid water in the chemistry and physics of liquids we have proceeded with Monte Carlo calculations of the free energy of liquid water based on eq 1-4 despite the problems outlined above. The computational labor may be kept down by keeping the number of particles explicitly considered to a minimum and effecting the integration over  $\xi$  by a low order numerical quadrature.

The  $U(\xi)$  in this calculation were determined by canonical ensemble Monte Carlo Metropolis<sup>10</sup> computer simulation on 64 molecules treated under periodic boundary conditions in the minimum image convention.<sup>11</sup> A spherical cutoff at half the cell edge was applied to the potential function. In previous studies it has been found that simulations based on 64 particles give essentially the same results for internal energy as those with 0(125) particles,<sup>2,3</sup> the number used when further detail is required on structure. Convergence criteria and statistical error bounds were established using control functions.<sup>12</sup> Convergence to the correct result was established for  $N = 125$  by carrying out two independent calculations on the worst case ( $\xi = 1$ ), one beginning from an initial configuration near the minimum of energy for the ensemble and one beginning at a very high energy configuration. The calculation converged to the same result well within the quoted error bounds, and agreed with the results of Clementi et al. obtained from an independent computer program and different initial guess. Thus we feel we have not encountered any practical nonergodicities.

The Monte Carlo calculations of  $U(\xi)$  involved surprisingly few difficulties. The  $U(\xi)$  for each of the 8 points converged