Table I. Stability of Anions of Alkyl-Substituted Benzenes Relative to $C_6H_6^-$ in Gas Phase and Solution[a]

Compound	ΔEA (Solution)[b]	ΔEA (Gas phase)[c]
Toluene	−0.022	0.04 ± 0.02
p-Xylene	−0.033	0.08 ± 0.02
m-Xylene	−0.059	0.09 ± 0.02
o-Xylene	−0.100	0.03 ± 0.03
tert-Butylbenzene	−0.070	0.09 ± 0.02
Isopropylbenzene	−0.055	0.07 ± 0.02
1,2,4-Trimethylbenzene		0.08 ± 0.03
1,3,5-Trimethylbenzene		0.12 ± 0.02

[a] All energies in eV. ΔEA = E.A. (substituted benzene) − E.A. (benzene), thus a negative ΔEA implies a negative ion less stable than $C_6H_6^-$. [b] Reference 6. [c] These shifts are determined with respect to an electron affinity of −1.15 eV for benzene. We estimate the absolute error in this reference value to be ±0.030. Our electron affinity is in excellent agreement with previous measurements of ref 1 and 2.

ed anions is considerably weaker than that of benzene. Space does not permit a detailed discussion of this aspect; however, it is consistent with a decrease in anion lifetime. Similar effects were observed by us in other molecules such as ethylene, butadiene, and formaldehyde under methyl substitution.[8] The interpretation is more complicated in the substituted benzenes because of the small splitting associated with the lifting of the degeneracy of the $^2E_{2u}$ electronic state. A calculation by Alper and Silbey[9] of the pseudo-Jahn-Teller effect in the toluene anion yielded a vibronic splitting of 0.033 eV. From our instrumental energy resolution, approximately 0.040 eV, and the characteristics of the transmission spectrum in benzene, we infer that the finite lifetime of the benzene anion corresponds to a spread in energy in excess of 0.040 eV. For the toluene anion, the energy spread is likely to be even greater. It is worth noting here that the effect of the finite lifetime has not been previously taken into account in the theoretical calculations.

With regard to the ordering of the two states, it has been suggested, from nodal arguments, that the antisymmetric (A) π^* orbital[10] is unperturbed through first order by the substituents in the monoalkyl- and *p*-dialkylbenzenes.[11] ESR studies[12] locate the symmetric (S) state above the A state in solution and indicate a small splitting ($\lesssim$0.1 eV) between them. It is not certain that this ordering is also correct in the gas phase. The most elaborate calculations have been parametrized with ESR data and hence incorporate solvation effects. For example, Purins and Karplus[11] in their "pure hyperconjugation model" found the S state of the anion to lie below the A state for usual values of the parameters, but since this result disagreed with the ESR results, they concluded that it was also necessary to include induction. The possibility that the S state is more stable for the gas phase substituted anions should be reconsidered as suggested by the original Purins and Karplus[11] calculation.

The shifts in electron affinity due to alkyl substitution are quite small, and it is not clear that there is a simple physical model capable of predicting the relative values. For this series of compounds, the observed shifts are likely due to the subtle contribution of several factors, including electron correlation.

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Metal Clusters in Catalysis. IV.[1] Catalytic Hydrogen Reduction of Carbon Monoxide to Alkanes

Sir:

We have advanced[1] a detailed thesis that the class of discrete metal cluster complexes are, to a first approximation, reasonable models for metal surfaces in such processes as chemisorption and heterogeneous catalysis. This thesis has been preliminarily documented in our studies of the catalytic properties of a nickel cluster,[2] $Ni_4[CNC(CH_3)_3]_7$, and of the cluster prototypes $(\eta^3\text{-}C_3H_5Fe(CO)_2L)_2$,[3] in the Roundhill et al.[4] demonstration of activity of $Rh_6(CO)_{16}$ in catalytic oxidations, and in the extremely intriguing $Os_3(CO)_{12}$ chemistry[5] with alkenes which relates[1] importantly to chemisorption phenomena. We[1] have also noted two distinctive catalytic capabilities of surfaces vis-a-vis mononuclear coordination catalysts which are catalytic reactions of aliphatic hydrocarbons[6] and the hydrogen reduction of carbon monoxide.[7] Herein we describe the catalytic hydrogen reduction of carbon monoxide to alkanes by discrete metal clusters. Observed rates were very low but the imposed reaction conditions were mild and the systems were unambiguously homogeneous.

Reduction of carbon monoxide by hydrogen to alcohols or alkanes is a highly favorable thermodynamic process, yet practical operation of this reaction with heterogeneous catalysts as in methanol production or the Fischer–Tropsch process requires rather extreme operating conditions[7] (200–400° and 10–200 atm of pressure). If such conditions are truly required, many of the traditional homogeneous coordination or organometallic catalysts would be excluded on stability grounds. There is, however, a mechanistic constraint that may severely limit a mononuclear complex as a catalyst in the $CO\text{-}H_2$ reaction. Well established mechanistic features of the hydroformylation reaction[8] suggest that a mononuclear catalyst might take CO and H_2 to CH_2O[9] although there is no evidence for direct formation of formylmetal complexes.[10] No precedent[11] exists in homogeneous catalysis for a reaction mode that would convert a formylmetal species to CH_3OH, and furthermore, formation of CH_4 would seem to require a second metal center for scission of the carbon-oxygen bond. In metal clusters (and metal surfaces), there is the possibility of a $\mu_2(\eta^2)$-CO bonding mode wherein conversion, through hydrogen atom transfer, to CH_3OH or CH_4, could be readily achieved. We have demonstrated a $\mu_2(\eta^2)$-bonding mode for isocyanides[2] in $Ni_4(CNR)_7$ complexes, μ_4-acetylene bonding situations are established for metal clusters,[12] and we describe[13] in another paper a simple $\mu_3(\eta^2)$-acetylene bonding mode at three edge sites in $Ni_4(CNR)_4(RC{\equiv}CR)_3$ which is isostructural with $Ni_4(CO)_4(CF_3C{\equiv}CCF_3)_3$.[14] We suggest that a $\mu_x(\eta^2)$-ligand bonding will prove to be an important phenomenon in metal clusters and will extend to other molecules with triple bonds, such as CO and N_2, at least in reaction intermediates in catalysis.

We find that $Os_3(CO)_{12}$ and $Ir_4(CO)_{12}$ catalyze the hydrogen reduction of carbon monoxide to give methane. Reaction conditions were quite mild: 140° and ~2 atm of pressure. These catalytic reactions were effected[15] in sealed glass tubes so that homogeneity of the reaction system could be monitored under reaction conditions; there was *no* evidence for the presence of solids at reaction temperatures. Selectivity was a distinctive feature of the osmium and iridium cluster catalyzed reactions in that only methane was detected. Analysis of reaction products was based on high resolution mass spectrometric analysis; with D_2 and CO as reactants, only D_2O and CD_4 were detected. Reaction rates under these mild conditions were explicably low (~1% conversion in 3-5 days with 3-5 catalyst turnovers), but we consider such reaction condition constraints essential to mechanistic studies of this important reduction reaction and to a constant definitive survey of reaction homogeneity. An elevation of reaction rates by a factor of at least 100 is necessary for mechanistic features to be effectively probed. Substitution of carbonyl groups in $Ir_4(CO)_{12}$ by triphenylphosphine[16] did increase the methane production rate but selectivity was lost because ethane and propane were formed in addition to the methane. Most significant was the result with trimethyl phosphite[17,18] as a substituent ligand where rates were at least threefold higher than in the triphenylphosphine-$Ir_4(CO)_{12}$ system and where selectivity to methane was maintained. Similar results were observed with the osmium cluster. Reduction of CO pressure seemed to lead to a rate increase in methane formation which would be consistent with a mechanism in which the key intermediate is a highly unsaturated carbonyl cluster (wherein there could be an η^2-CO ligand). Hydrogenation of $Ir_4(CO)_{12}$ or $Os_3(CO)_{12}$ in a nitrogen atmosphere gave no ammonia; methane production was relatively fast but this system was not homogeneous since either an insoluble cluster or metal was formed as the reduction proceeded.

A careful search was made for alcohols and alkenes in these reaction mixtures using both H_2-CO and D_2-CO reactant combinations. In none of these catalytic reactions was methanol or an alkene detected as a product. A set[19] of patents has described the catalytic conversion of CO and H_2 to methanol, ethylene glycol, and propylene glycol, at 220° and 30 atm with rhodium catalysts; $Rh_6(CO)_{16}$ was specifically cited as a catalyst. These patents claim that *no* hydrocarbons are formed in the rhodium catalyzed reactions. Hence, either rather striking selectivity may be found in clusters or large changes in reaction conditions may effect correspondingly large changes in reaction modes for this reduction reaction.

It should be noted that we have examined a large number of classic mononuclear coordination catalysts in the H_2-CO reaction with a wide range of solvents and have found none to be active, but of course, our examination of this class has not been exhaustive. One apparent exception was η^3-$C_3H_5Mn(CO)_4$ which has given evidence of CH_4 formation although results have ***not been consistent***. In this reaction, there was a rather fast cleavage of the allyl group; cluster formation may follow the cleavage reaction but the manganese product isolated at the end of the reaction was $HMn(CO)_5$.

We are now seeking a higher rate in this homogeneous catalytic hydrogen reduction of carbon monoxide, through substitution of the metal carbonyl clusters with phosphines and phosphites, to facilitate a mechanistic study of this important reaction under homogenous conditions.

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(17) A 1:1 molar ratio of $(CH_3O)_3P$ to $Ir_4(CO)_{12}$ was used.[16]

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An Intramolecular Model for the Enzymatic Insertion of Coenzyme B_{12} into Unactivated Carbon-Hydrogen Bonds

Sir:

Extensive work[1] on the biochemical reactions catalyzed by coenzyme B_{12}, such as the isomerization of methylmalonyl CoA to succinyl CoA, has led to a unified picture of the mechanisms involved. First, coenzyme B_{12} inserts into