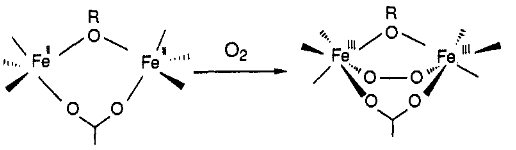

Such a μ-1,2-peroxo structure is analogous to that crystallographically characterized for $[Co_2(BPMP)(OAc)(O_2)]^{2+}$[15] and proposed for the species derived from reacting $[Fe_2(5\text{-}Me\text{-}HXTA)(OAc)_2]^-$ with H_2O_2.[16] At present, the available data do not allow us to exclude a μ-1,1-peroxo structure, but ongoing resonance Raman and EXAFS studies should aid in distinguishing between these two possibilities.

Of the four diferrous models for the iron–oxo proteins, **1** is the only complex that has been shown to bind O_2. The availability of exogenous ligand coordination sites on both iron atoms in **1** may be an important factor in promoting dioxygen binding. **1** may thus serve as a model for RRB2, in as much as RRB2 has recently been shown to have a (μ-oxo)(μ-carboxylato)diiron(III) core.[17] We are currently investigating the reactivity of the **1**–O_2 adduct when it decomposes at higher temperatures.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, bond lengths, and bond angles for $[Fe_2(N\text{-}Et\text{-}HPTB)(OBz)](BF_4)_2$ (32 pages). Ordering information is given on any current masthead page.

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Reactivity of Neutral Fe, Co, Ni, and Cu Atoms with Linear Alkanes and Alkenes in the Gas Phase[1]

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We explore the reactivity of *gas-phase, neutral* 3d-series transition-metal atoms (M) with hydrocarbons. While certain transition-metal cations (M^+) are aggressive chemicals that activate C–H and C–C bonds of alkanes,[2,3] the gas-phase chemistry of neutral transition-metal atoms remains virtually unexplored.[4,5] Cryogenic matrix isolation spectroscopy[6–8] and ab initio electronic structure calculations[9–11] on neutral metal atom complexes $M\text{–}C_2H_4$ provide another context for this work.

A hollow cathode discharge produces neutral metal atoms in a fast-flow reactor with He buffer gas. Laser-induced fluorescence (LIF) provides state-specific detection of the metal atom number density. From the linear decay of ln [M] vs hydrocarbon number density, we extract effective bimolecular rate constants[5] at 300 K in 0.8 Torr He. We studied the reactivity of $Fe(d^6s^2,{}^5D)$, $Co(d^7s^2,{}^4F)$, $Ni(d^8s^2,{}^3F)$, $Ni(d^9s,{}^3D)$, and $Cu(d^{10}s,{}^2S)$ with the linear hydrocarbons propane, *n*-butane, ethene, propene, and 1-butene. In comparison with the corresponding cations, these neutral atoms are remarkably inert. We observe no reactions with propane or *n*-butane to our detection limit (implying $k < 10^{-14}$ $cm^3{\cdot}s^{-1}$). With the exception of Co + 1-butene, which is very slow ($k = 9 \times 10^{-14}$ $cm^3{\cdot}s^{-1}$), Fe, Co, and Cu show no reaction with ethene, propene, or 1-butene.

In striking contrast, Ni reacts slowly with ethene (5.0×10^{-13} $cm^3{\cdot}s^{-1}$), moderately with propene-h_6 (1.1×10^{-11} $cm^3{\cdot}s^{-1}$) and with propene-d_6 (2.1×10^{-11} $cm^3{\cdot}s^{-1}$), and rapidly with 1-butene (1.4×10^{-10} $cm^3{\cdot}s^{-1}$). Rate constants are accurate to ±25% and precise to ±10%. The two low-energy terms[12] of Ni ($d^8s^2,{}^3F$ and $d^9s,{}^3D$) exhibit identical kinetics, suggesting rapid collisional interconversion in He. Ni reacts with C_2H_4 in 1 of 500 hard-spheres collisions, with C_3H_6 in 1 of 25 collisions, and with 1-butene in 1 of 2 collisions.[13]

Termolecular stabilization of Ni–alkene complexes probably dominates the measured rate constants, although a contribution from bimolecular H_2 or CH_4 elimination reactions (analogous to single-collision M^+ chemistry)[2,3] is possible. H-atom abstraction by Ni is highly endothermic and therefore ruled out. The rapid increase of the Ni + alkene rate constant with alkene size is consistent with a statistical model[14] of hot $[Ni(alkene)]^*$ complex lifetimes. The observed inverse isotope effect for the Ni + propene reaction, $k(C_3D_6) = 2k(C_3H_6)$, also points to termolecular sta-

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bilization. The density of vibrational states of the deuterated complex will be larger, while the Ni–C_3H_6 and Ni–C_3D_6 bond energies will be very similar, so we would expect longer lifetimes (and greater stabilization efficiency) for the Ni + C_3D_6 reaction in a termolecular mechanism.

In an attempt to clarify the nature of the Ni + alkene products, we gently focused excimer laser pulses at 308 and 248 nm (two-photon energy of 8.1 and 10.0 eV) downstream in the flow tube and analyzed the resulting cations in a quadrupole mass spectrometer. The only photoion observed is Ni^+. It is plausible that collisionally stabilized, π-bonded Ni–alkene complexes photodissociate to Ni + alkene and that subsequent two-photon ionization of Ni produces the observed Ni^+.

The ground-state configurations[12] of Fe, Co, and Ni are $3d^{n-2}4s^2$. The $4s^2$ occupancy and the large spatial extent of 4s relative to 3d give these atoms closed-shell character at long range. Accordingly, ab initio calculations[10,11] find that $M(d^{n-2}s^2) + C_2H_4$ asymptotes produce only repulsive potentials. Substantial M–C_2H_4 binding arises only from excited-state $d^{n-1}s$ asymptotes. In Fe, Co, and Ni, the lowest energy high-spin $d^{n-1}s$ levels lie at excitation energies of 20, 10, and 0.6 kcal/mol, respectively. The lowest energy low-spin $d^{n-1}s$ levels lie at 34, 21, and 10 kcal/mol.[12]

The challenge for $d^{n-2}s^2$ reactants is to reach sufficiently short M–alkene approach distances to access attractive $d^{n-1}s$ potential surfaces before deflecting off the repulsive wall of the $d^{n-2}s^2$ surface. The attractive surfaces will often have different spin multiplicity from the reactants.[10,15] The avoided intersection between the repulsive $d^{n-2}s^2$ surface and the attractive $d^{n-1}s$ surface can produce a barrier on the lowest energy adiabatic surface whose height should be roughly proportional to the atomic excitation energy from $d^{n-2}s^2$ to $d^{n-1}s$. Thus the strength of M–alkene binding and the energy of the surface intersections combine to determine the gas-phase reactivity.

Measurement of gas-phase rate constants at 300 K with well-defined initial metal atom states can provide quantitative experimental insights into gas-phase M–alkene interactions. Assuming Arrhenius behavior $k(T) = k_{hs} \exp(-E/k_BT)$ with preexponential factor equal to the hard-spheres collision rate k_{hs} (the largest plausible value),[13] we can convert the measured reaction probabilities $P = k(300\text{ K})/k_{hs}$ to *upper bounds* E_{max} on the activation energy E using the equation $E_{max} = -k_BT \ln P$.[5b] In addition, those reactions that occur at measurable rate exhibit exponential decay of the M reactant over at least one decade. In the termolecular stabilization mechanism, this implies at least 10–15 kcal/mol of M–alkene binding energy relative to ground-state reactants, depending on the entropy change at 300 K and on the alkene number density required to effect the 10-fold decay of M atom density.[3] No reaction ($k < 10^{-14}$ cm^3·s^{-1}) implies either an activation energy in excess of 6 kcal/mol or a M–alkene binding energy less than 10–15 kcal/mol relative to ground-state reactants, or both.

Since Fe and Co ground states are unreactive, we conclude that they never reach the potential wells arising from $d^{n-1}s$ asymptotes or that the wells are not sufficiently deep. This is consistent with the minor shifts between vibrational frequencies of C_2H_4 and FeC_2H_4 in matrix IR spectra[6b] and with ab initio calculations[10a] that find a bound Fe–C_2H_4 complex lying 6 kcal/mol *above* $Fe(d^6s^2,{}^5D) + C_2H_4$. Since the $Cu(d^{10}s,{}^2S)$ ground state is well isolated from excited states, we expect no surface intersections (no potential barrier) for Cu + alkene. The absence of measurable Cu + alkene reaction implies binding energies less than 10–15 kcal/mol, consistent with a recent calculated Cu–C_2H_4 binding energy of 8 kcal/mol obtained with core pseudopotentials.[11]

NiC_2H_4 is observed in cryogenic matrices;[7] the C_2H_4 vibrational frequencies are more strongly perturbed in NiC_2H_4 than in FeC_2H_4. Only the repulsive Ni–C_2H_4 surfaces arise from the $Ni(d^8s^2,{}^3F)$ ground state. Early ab initio work[9] found a triplet NiC_2H_4 ground state (${}^3A_1$) from $Ni(d^9s,{}^3D)$. Recent calculations[10b] with more extensive basis sets find the same triplet surface to be repulsive. $Ni(d^9s,{}^1D) + C_2H_4$ gives an attractive *singlet* surface (${}^1A_1$) bound by 10 kcal/mol relative to ground-state Ni + C_2H_4.[12]

The observed extent of the $Ni(d^9s,{}^3D)$ + alkene reactions indicates Ni–alkene binding energies in excess of 10–15 kcal/mol, consistent with the recent Ni–C_2H_4 calculations.[10b] Apparently $Ni(d^9s,{}^3D) + C_2H_4$ collisions at 300 K readily access the ${}^1A_1$ potential well. The reaction efficiencies indicate very small barriers on the *adiabatic* surface which has ${}^3A_1$ character at long range and ${}^1A_1$ character at short range. Reaction probabilities of $^1/_{500}$ for Ni + ethene, $^1/_{25}$ for Ni + propene, and $^1/_2$ for Ni + 1-butene imply activation energies *not larger than* 3.5, 1.9, and 0.4 kcal/mol, respectively. For Ni + C_2H_4, the calculations[10b] find the crossing point between the ${}^3A_1$ surface and the ${}^1A_1$ surface to lie ~8 kcal/mol above $Ni(d^9s,{}^3D) + C_2H_4$, which is probably an overestimate.

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Room Temperature Generation of Reactive Intermediates $Cp^*_2Zr{=}O$ and $Cp^*_2Zr{=}S$: Trapping Reactions with Unsaturated Organic Molecules and Dative Ligands

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We provided evidence recently that the reactive intermediate $[Cp^*_2Zr{=}O]$ is generated at 160 °C by α-elimination of benzene from $Cp^*_2Zr(Ph)(OH)$.[1,2] The oxo intermediate reacts with selected alkynes, but at this elevated temperature the materials isolated presumably result from rearrangement of the initially formed alkyne addition products. We now report a novel room-temperature route to $[Cp^*_2Zr{=}O]$.[3] This reaction allows isolation of oxametallacycles that result from initial reaction of the oxo complex with alkynes and provides a means of utilizing alkyl- as well as aryl-substituted acetylenes in the reaction. In addition, we have found a mild route to the analogous sulfido complex $[Cp^*_2Zr{=}S]$. Like its oxo analogue, this material undergoes cycloaddition reactions with alkynes and nitriles; in this case, we have also been able to trap the reactive species with dative ligands.

Treatment of $Cp^*_2Zr(OH)(Cl)$ (**1**)[4] with 1 equiv of $AgOSO_2CF_3$ produces $Cp^*_2Zr(OH)(OSO_2CF_3)$ (**2**) in nearly quantitative yield by ^1H NMR (Scheme I).[5] Deprotonation of **2** with the hindered base $KN(Si(CH_3)_3)_2$ leads to the successful generation of $[Cp^*_2Zr{=}O]$ as judged by its subsequent trapping with various alkynes and nitriles. A critical example involves diphenylacetylene. The metallacycle complex **3a** was prepared recently by Hillhouse upon treatment of the zirconocene diphenylacetylene complex $Cp^*_2Zr(PhCCPh)$ with N_2O.[6] We were

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