460 ± 30 (calcd 420).
(13) The major products are $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ and a new organozirconium complex tentatively assigned the empirical formula $\{(\eta^5\text{-}C_5Me_5)[C_5\text{-}(CH_3)_3(CH_2)_2]Zr\}_n$ (NMR).
(14) (a) Unfortunately, 2-methylpropane suffers severe fragmentation upon ionization even at low energies, loss of CH_3 being the primary process. Comparison of the relative intensities of the parent ion and the next two lower mass ions gave fairly reliable results; however, supplementation of these mass spectral data with infrared spectra was necessary. The characteristic IR bands used were as follows. **2a**: $\delta(CH_3)$ 1480, 1380, 1335 cm^{-1}; $\nu(C–C)$ 1180 cm^{-1}. **2b**: $\nu(C–D)$ 2145 cm^{-1}; $\delta(CH_3)$ 1475, 1380 cm^{-1}; $\nu(C–C)$ 1235, 1225 cm^{-1}. **2c**: $\nu(C–D)$ 2180, 2160 cm^{-1}; $\delta(CH_3)$ 1470, 1385 cm^{-1}; $\nu(C–C)$ 1295, 1220 cm^{-1}. **2d**: $\nu(C–D)$ 2165 cm^{-1}; $\delta(CH_3)$ 1470, 1385 cm^{-1}; $\nu(C–C)$ 1285, 1155 cm^{-1}. (b) According to Scheme I the observed ratio of $k(H)/k(D)$ is a composite of a kinetic deuterium isotope effect for **3 → 4** and a thermodynamic deuterium isotope effect for the fast pre-equilibrium step **1 ⇌ 3**.
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(19) Although β-H abstraction from the isobutyl group of intermediate **10** could conceivably lead to isobutylene and an ethyl hydride derivative, no evidence of this reaction is observed. We attribute the much greater preference for β-H abstraction from the ethyl group to steric factors which disfavor coordination of the bulky olefin isobutylene in the coordination of the sphere of the alkyl hydride (as would be required for generation of the ethyl hydride). This argument is supported by the observation that isobutylene does not promote reductive elimination of isobutane from **1**.[9]
(20) P. T. Wolczanski and J. E. Bercaw, manuscript in preparation.
(21) Gell and Schwartz have postulated that reaction of the closely related alkyl hydride complex, $(\eta^5\text{-}C_5H_5)_2Zr(H)(CH_2C_6H_{11})$, with H_2 proceeds via a fundamentally different mechanism involving hydride abstraction from H_2 by the formal Zr(IV) center.[7] Elimination of methylcyclohexane is postulated to occur in a subsequent step by electrophilic attack of H^+ on the resulting five-coordinate intermediate. A faster, competitive attack of H^+ on this intermediate to regenerate H_2 was postulated to account for the observed incorporation of deuterium into the hydride position of the alkyl hydride upon exposure to D_2. We find no such exchange when **1a** is exposed to D_2. Thus treatment of a toluene solution of **1a** with a 5 M excess of D_2 (1 atm) at -15 °C for 3 min led to a 3:1 mixture of **1a** and $(\eta^5\text{-}C_5Me_5)_2Zr(H)_n(D)_{2-n}$ ($n = 0$, 1, or 2). Analyses of the residual gas phase by mass spectrometry and the resulting mixture of the two organozirconium compounds by ^1H NMR indicated no detectable exchange of deuterium with the hydride position of residual **1a**.
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On the Existence of Colorless Europium(IV)

Sir:

Recently, Firor and Seff[1] presented crystallographic evidence for the novel oxidation state europium(IV) in zeolites. Obviously, it is interesting to determine the local symmetry, the coordination number N, and the preponderant electron configuration[2] defining the oxidation state in noncatenated transition-group (and other) atoms. However, here is a case where visible spectra can be used to render the conclusion highly improbable. First of all, it is well known[3,4] that the difference, 3.6 eV, between the ionization energies[1] of gaseous Eu^{3+} and Pr^{3+} for the greatest part is conserved in the standard oxidation potential, E^0, of Eu(III)/Eu(IV) and Pr(III)/Pr(IV) (estimated from the refined spin-pairing theory for the aqua ions, +6.4 and +3.4 V, respectively). This constitutes a major distinction from the other transition groups[2] where such differences can be highly attenuated. It is always conceivable that a new type of ligand may be found, such as the bidentate phosphine[5] stabilizing Fe(IV), Ni(IV), and Cu(III) by unexpectedly effective covalent bonding. However, it is excluded that $4f^5$ Eu(IV) could be *colorless*. Traces of Pr(IV) and

Tb(IV) in mixed oxides provide strong colors, such as purple ThO_2, chamois CeO_2 and orange Y_2O_3, and it can be easily extrapolated from the observed positions[6] of electron-transfer bands[7,8] that the strong transitions of Eu(IV) surrounded by oxygen-containing ligands would start in the far-infrared and probably would correspond to lower minimum energy of the potential surface[6] producing spontaneous redox reactions. It has previously been pointed out[9] that such strong colors might be a helpful indicator for ephemeral formation of quadrivalent intermediates (say, at low temperature) in solution. Though the positions of electron-transfer bands to a certain extent[6] depend on the distances to the ligating atoms, they are not exceedingly sensitive to changes of the coordination number, N, and, for instance, $M\{N[Si(CH_3)_3]_2\}_3$ having $N = 3$ shows the same colors[3] (orange for M = Eu and yellow for M = Yb) as $M[S_2CN(C_4H_9)_2]_4^-$ with $N = 8$.

A closer analysis of the crystallographic data[1] shows some similarity with the classical case[10] of $Cr(NH_3)_3(O_2)_2$ originally described as a chromium(II) superoxo complex (based on the intraligand oxygen-oxygen distance) but now recognized as Cr(IV) and peroxo ligands. A review of a large number of Eu(III)-oxygen internuclear distances[11] shows a remarkably large dispersion (e.g., 2.29 Å in EuOCl and six distances between 2.31 and 2.37 in Å $Eu(dpm)_3(py)_2$ with $N = 8$ compared with B-type Sm_2O_3 where the average Sm–O distance, 2.46 Å, is the mean value of lengths scattered from 2.25 to above 2.7 Å). It may be argued that the oxidized zeolite[1] has the low $N = 4$ predisposing to shorter distances. Anyhow, the values 2.28 and 2.13 ± 0.04 Å cannot prove the presence of Eu(IV). The situation is rather different in the product obtained by reaction with chlorine where the lower of the two Eu–Cl distances ($N = 5$), 2.06 and 2.31 Å, is exorbitantly shorter than 2.835 and 2.919 Å observed[11] in $EuCl_3$ ($N = 9$). Nevertheless, the lack of color strongly suggests an alternative explanation involving Eu(III).

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Homogeneous Catalysis of the Water Gas Shift Reaction Using a Platinum Chloride–Tin Chloride System

Sir:

The water gas shift reaction

$$H_2O + CO \rightleftharpoons H_2 + CO_2 \qquad \Delta G°_{298} = -4.76 \text{ kcal/mol} \tag{1}$$