semibridging CO ligand in a rhenium cluster.

The hydride ligand was not located crystallographically. In solution, the observation of three ^{1}H NMR signals for the hydride suggests the presence of isomers differing in terms of the hydride location. If the Re1–Re3 bond distance of 3.006 (3) Å and the Re1–Re3–C32 bond angle of 113 (2)° are compared to analogous Re–Re bond lengths (average 2.984 (3) Å) and Re1–Re–C(radial) bond angles (average 107 (2)°), it seems likely that the hydride bridges the Re1–Re3 edge over the Re1–Re2–Re3 face (i.e., away from the semibridging carbonyl). A potential energy calculation[21] supports this assignment as the probable hydride site; however, these calculations suggest that a basal edge-bridging site (specifically, along the Re2–Re3 edge) and/or a face-bridging site (e.g., above the Re1–Re2–Re3 face) may be only slightly higher in energy. We note a similar distribution of sites in the structure of $Ru_5C(CO)_{13}(NO)Au(PEt_3)$:[22] two geometric forms of this molecule, μ_2-Au(PEt$_3$) (basal–apical edge-bridging) and μ_3-Au(PEt$_3$), exist in the same crystal.

Reaction of $[HRe_5C(CO)_{16}]^{2-}$ with 3 equiv of $Re_2(CO)_{10}$ in triglyme at 200 °C affords $[Re_8C(CO)_{24}]^{2-}$ quantitatively. It therefore seems reasonable that $[HRe_5C(CO)_{16}]^{2-}$ is an intermediate on the way to higher nuclearity clusters in the reductive pyrolysis of $Re_2(CO)_{10}$. Efforts to isolate other intermediates in this reaction are currently underway.

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Supplementary Material Available: Tables of atomic coordinates, thermal parameters, and bond lengths and angles for $[Et_4N]_2[HRe_5C(CO)_{16}]$ (6 pages); a listing of structure factor amplitudes for $[Et_4N]_2[HRe_5C(CO)_{16}]$ (10 pages). Ordering information is given on any current masthead page.

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CpZr(allyl)$_3$: The Molecular Structure of a π- and σ-Dynamic Allyl Transition Metal Complex

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Summary: CpZr(allyl)$_3$ (**2**), prepared by reacting CpZrCl$_3$ (**1**) with excess allylmagnesium chloride at low temperature, is characterized by rapidly occurring intramolecular allyl rearrangement and scrambling even at very low temperature in solution. In the solid state **2** features three differently bonded allyl ligands and a Cp group around zirconium in a distorted (pseudo) tetrahedral geometry (X-ray crystal structure analysis at −173 °C: space group $P2_12_12_1$; a = 8.603 (3) Å, b = 18.520 (5) Å, c = 8.033 (4) Å, Z = 4). One allyl group is σ-bonded. A slightly distorted π-allyl ligand and a η^3-allyl moiety whose bonding features are approaching those of a σ,π-allyl type complement the coordination sphere of this zirconium(IV) complex of a formal 16-electron count.

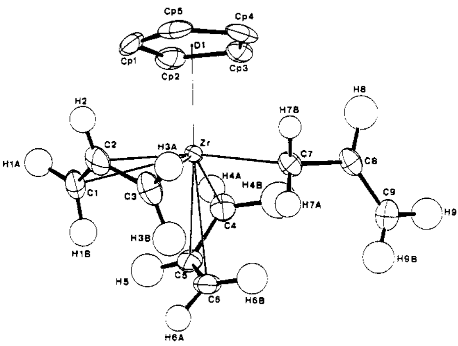

Figure 1. A view of the molecular geometry of CpZr(allyl)$_3$ (**2**) as determined by X-ray diffraction.

Allyl transition-metal complexes are of enormous practical importance as active catalysts and catalyst precursors as well as stoichiometric reagents in organic synthesis.[1] Metal allyl species have been divided into six different groups according to their IR features and NMR behavior.[2] Many representative examples of five of these groups have also been carefully examined in the solid state by X-ray diffraction.[3] To our knowledge, detailed structural information on the most interesting type, i.e. the π- and σ-dynamic allyl complexes, surprisingly, seemed to be lacking.

CpZr(allyl)$_3$ (**2**)[4] was prepared by treating a suspension of CpZrCl$_3$ (**1**)[5] in ether with excess (4 equiv) allylmagnesium chloride at −40 °C. After low-temperature workup (<−35 °C), large, dark red crystals of **2** were obtained by crystallization from pentane at −80 °C. The CpZr(allyl)$_3$ thus obtained is thermally rather sensitive; it slowly decomposes at temperatures above −10 °C even in the solid state. In solution **2** exhibits two different types of allyl ligands as judged by IR spectroscopy [alkane solvent: ν 1595 cm^{-1} (η^1-allyl); 1535 cm^{-1} (η^3-allyl)]. These rapidly equilibrate on the NMR time scale [toluene-d_8: ^{1}H (60 MHz, −78 °C) δ 5.10 (s, 5 H, Cp), 5.27 (m, 3 H), 2.95 (d, 12 H, dynamic allyl); ^{13}C (100.6 MHz, −30 °C) δ 106.4 (Cp), 135.3 (allyl-CH), 71.9 (allyl-CH$_2$)]. At temperatures

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0276-7333/87/2306-2620$01.50/0

below −90 °C in toluene (<−130 °C in diethyl ether) solution substantial line broadening of the ^1H (400 MHz) and ^{13}C (100.6 MHz) NMR CH_2 resonances of **2** due to decreasing exchange rates is observed. However, for this compound both the intraligand syn/anti allyl hydrogen scrambling and intramolecular π-/σ-allyl exchange are taking place so rapidly that up to now **2** has eluded structural characterization on the basis of its "static" low-temperature-limiting NMR spectra.

The molecular structure of **2** was determined by X-ray diffraction at −173 °C.[6] The zirconium atom is coordinated to a η^5-cyclopentadienyl ligand and three differently bonded allyl groups arranged around the central metal in a pseudo tetrahedral geometry. One position is occupied by a σ-allyl group [Zr–C(7) = 2.375 (3) Å, C(7)–C(8) = 1.461 (5) Å, C(8)–C(9) = 1.332 (5) Å; Zr–C(7)–C(8) = 107.9 (2)°]. The remaining tetrahedral bonding sites are used to coordinate two η^3-allyl moieties. To a first approximation one of these appears to be an ordinary π-allyl ligand [C(4)–C(5) = 1.387 (5) Å, C(5)–C(6) = 1.382 (5) Å; C(4)–C(5)–C(6) = 123.9 (3)°] which is only slightly distorted by an "unsymmetrical" coordination to the Cp–Zr unit [C(4) positioned cis and the C(5)–C(6) vector positioned trans to Cp; Zr–C(4) = 2.405 (4) Å, Zr–C(5) = 2.525 (3) Å, Zr–C(6) = 2.549 (3) Å]. The bonding features of the η^3-allyl ligand "all-cis" to Cp are substantially different. Increasing zirconium-to-carbon distances [Zr–C(1) = 2.442 (4) Å, Zr–C(2) = 2.523 (3) Å, Zr–C(3) = 2.624 (3) Å] and decreasing carbon to carbon bond lengths [C(1)–C(2) = 1.412 (5) Å, C(2)–C(3) = 1.371 (6) Å] indicate a pronounced distortion toward an unsymmetrical σ,π-type (η^3-allyl)-metal complex structure.[7] The observed hydrogen positions in the X-ray crystal structure analysis disclose additional systematic distortions of the η^3-allyl ligands. Relative to the C(4),C(5),C(6) plane the "meso" hydrogen H(5) is tilted substantially toward the zirconium center (0.24 (4) Å). This is not an uncommon structural feature for a (π-allyl)metal complex,[8] nor is the slight pyramidalization at C(4) (H(4)-syn coplanar, H(4)-anti turned away from the metal by 0.47 (4) Å). However, a substantial twisting at C(6) appears noteworthy. This distortion places H(6)-syn 0.15 (3) Å out of the allyl carbon plane toward the metal and places H(6)-anti by 0.34 (4) Å in the opposite direction. Similar effects are observed for the hydrogen atoms at the C(1), C(2), and C(3) of the allyl group (distortions: H(2), +0.19 (4) Å; H(1)-syn in plane; H(1)-anti, −0.43 (4) Å; H(3)-syn, +0.17 (3) Å; H(3)-anti, −0.30 (4) Å). In a formal way this type of an allyl ligand distortion observed in the solid-state structure of **2** might be regarded as modeling an intermediate stage along the reaction coordinate of the η^3–η^1 interconversion,[4] although this case is corresponding to a geometry being located rather close to the π-bonded isomer. This ground-state structural feature could possibly help to explain the extremely low activation barrier of the intramolecular allyl isomerization and interconversion. On the basis of the solid-state structure of **2** one might even speculate that the rearrangement of the three allyl ligands is not occurring independently but possibly in a "concerted" fashion.

Acknowledgment. Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Dr. R. Benn and Dr. A. Rufinska for many low-temperature NMR spectra.

Supplementary Material Available: Tables of crystal data, atomic coordiniates, thermal parameters, and selected interatomic distances and angles for **2** (5 pages); a listing of observed and calculated structure factors for **2** (12 pages). Ordering information is given on any current masthead page.

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(6) Crystallographic data for **2**: $C_{14}H_{20}Zr$, M_r 279.5; crystal size 0.31 × 0.30 × 0.02 mm; orthorhombic, space group $P2_12_12_1$; a = 8.603 (3) Å, b = 18.520 (5) Å, c = 8.033 (4) Å; V = 1279.8 Å^3; Z = 4; T = −173 °C; d_{calcd} = 1.45 g cm^{-3}; graphite-monochromated Mo Kα radiation, λ = 0.71069 Å; μ = 8.13 cm^{-1}; no absorption correction has been applied; hydrogen atoms were located in the difference fourier map and refined isotropically; all non-hydrogen atoms were refined anisotropically; the absolute configuration was determined by a Hamilton test of the R factor ratio of both enantiomers (significance $\alpha \gg 99.5$ %); Nonius CAD-4 (Ω–2θ scan technique with scan speeds varying from 1.0 to 10.0° min^{-1}, depending on the standard deviation to intensity ratio of a preliminary 10° min^{-1} scan; the time taken to measure the background was half that taken to measure the peak; Ω-scan range ($a + 0.35 \tan \theta$), where a was twice the average width of the Ω-scans of several low-angle reflections; horizontal detector aperture ($3.0 + 1.05 \tan \theta$) mm and vertical aperture 4.0 mm); reflections measured, 7894 ($\pm h,+k,+l$, $1° < \theta < 30°$); reflections unique, 3804 (R_{av} = 0.028); reflections observed, 3174 ($I \geq 2\sigma(I)$); number of variables, 216; R = 0.029, R_w = 0.028 ($w = 1/\sigma^2(F_o)$); goodness of fit, 1.16; maximum shift/error in the final cycle, 0.1; final difference Fourier, 0.78 e Å^{-3} (close to Zr).

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Actinide-to-Transition Metal Bonds. Synthesis, Characterization, and Properties of Metal–Metal Bonded Systems Having the Tris(cyclopentadienyl)actinide Fragment

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Summary: Reaction of Cp_3AnCl complexes (Cp = η^5-C_5H_5; An = Th, U) and $(CH_3C_5H_4)_3ThCl$ with $CpM(CO)_2Na$ (M = Fe, Ru) yields the corresponding metal–metal bonded compounds $Cp_3An{-}M(Cp)(CO)_2$ and $(CH_3C_5H_4)_3Th{-}M(Cp)(CO)_2$. Electron-releasing tendencies follow the order $Cp_3U{-} > Cp_3Th{-} \gg [(CH_3)_5C_5]_2Th(X){-}$ (X = Cl, I, CH_3). Evidence for hindered rotation about the metal–metal bonds and facile cleavage by alcohols and ketones is presented.

We recently described[1] the synthesis and properties of $Cp'_2Th(X)Ru(Cp)(CO)_2$ complexes (Cp′ = η^5-$(CH_3)_5C_5$; Cp = η^5-C_5H_5; X = Cl, I, CH_3) which contain unsupported actinide-to-transition metal bonds.[2-4] The scope of ac-

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