function yielded components whose lifetimes differed by less than 2 μs, and no significant improvement over the single-exponential fits was obtained. However, following pulsed excitation at 337 nm, time resolution of the emission of A via boxcar averaging techniques reveals a structured emission at long delay times (>15 μs) with an origin at 520 nm (Figure 2), whereas time resolution of B indicates that its emission spectrum is independent of delay time. Pulsed excitation of A at 477 nm in 77 K glasses results in the same structured emission as that in Figure 2, and no further resolution of this structure is obtained by time resolution. Under these conditions, single-exponential analysis yields a 5-μs lifetime and double-exponential analysis again fails to give significant improvement to fits of the experimental data at any of the wavelengths throughout the emission spectrum. Furthermore, the same structured emission of A can be observed in its time-integrated emission spectrum under long-wavelength excitation (>460 nm) while the time-integrated emission spectrum of B is independent of excitation wavelength. The emission spectra of both A and B are independent of delay time and excitation wavelength in room temperature fluid solutions. The positions of the emission energies of both A and B were found to be dependent upon the solvent medium (blue shifts in more polar solvents). The magnitude of the luminescence lifetimes of A and B and the solvent dependence of their emission spectra are indicative of emission which originates in MLCT excited states.

Cyclic voltammetric analysis of A reveals a reversible oxidation wave at $E_{pa} = +1.32$ V vs. SCE in acetonitrile while the first oxidation wave of B is anodically shifted to $E_{pa} = +2.05$ V. The first reduction wave of A is also reversible at $E_{pc} = -1.4$ V vs. SCE while the first reduction wave of B is observed at $E_{pc} = -1.2$ V. These results are consistent with prior studies indicating that, relative to metal–nitrogen bonding in bpy species, metal–carbon bonding in ppy complexes facilitates metal oxidation.[10-13] Correlation of ΔE values ($\Delta E = E_{pa}^{ox} - E_{pc}^{red}$) for A and B (2.72 and 3.25 V, respectively) with their emission energies is consistent with a metal-centered oxidation and a bpy-centered reduction in both the optical and electrochemical processes.[14-18]

Several sources of a second emission evident in time-resolved luminescence of A should be considered. These include emission originating from impurities, such as a mixture of structural isomers or from ground-state association processes, and emission originating from a second, unequilibrated electronic excited state. The absence of evidence of impurities in TLC and NMR analyses and the adherance of solutions of A to Beer's law over the concentration range which was studied suggest that the dual emission of A is not due to impurities but rather is due to emission from unequilibrated excited states. The similarity in the lifetimes of the two emissions in the dual luminescence of A indicates contributions from a second MLCT excited state. While these two states are too similar in their lifetimes to differentiate in double-exponential fitting of their decay curves, their lifetimes are sufficiently different to show the types of changes in emission profile with time under 337-nm excitation that are illustrated in Figure 2. A MLCT state in which an electron is promoted to a π^* orbital of ppy (MLCT ppy) is expected to lie above the low-energy MLCT state in which an electron is promoted to a bpy π^* orbital (MLCT bpy) in both A and B. This type of MLCT ppy excited state may be responsible for the second component in the emission of A. The large red shift in emission from A in fluid solutions is indicative of a large distortion in the MLCT bpy excited state of A which does not

occur in B. This type of distortion may give rise to a barrier to energy transfer from the MLCT ppy to the MLCT bpy state in A which is absent in B. When this complex is excited at wavelengths longer than about 460 nm, it appears possible to preferentially excited directly into the lower energy MLCT bpy state, thereby favoring emission from this state. Studies to further characterize the two emitting states of A and the origin of the large distortion of its MLCT bpy state are in progress.

Synthesis, Structure, and Reactivity of Trimethylphosphine–Zirconocene Thioaldehyde Complexes

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Several thioaldehyde complexes of middle and late transition metals[1] have been reported. To our knowledge, however, no thioaldehyde complexes of early transition metals (groups 3–5) have been prepared. We now report a general, direct, and efficient synthesis of zirconocene thioaldehyde complexes 1 (Figure 1), which are stabilized by coordination of a trimethylphosphine ligand. These complexes have been characterized by ^{1}H, ^{13}C, and ^{31}P NMR, IR, and high-resolution mass spectrometry. In addition, complex 1a has been characterized by X-ray crystallography and elemental analysis.

Our route to compounds 1a,b (Scheme I) is related in appearance (and presumably also in mechanism) to the synthesis of zirconocene complexes of benzyne,[2a] cyclohexyne,[2b] and acyclic alkynes[2c] which we have recently reported and to the synthesis of tantalum–imine complexes reported by Bercaw.[2d] The requisite (alkylthio)(methyl)zirconocenes 2a,b are available by treatment of chloro(methyl)zirconocene[3a] with a lithium thiolate or more simply by treatment of dimethylzirconocene[3b] with 1 equiv of a thiol. Heating compounds 2a,b in the presence of trimethylphosphine leads to the formation of 1a,b in high yield.

The X-ray crystal structure of 1a is shown in Figure 2. Two enantiomeric, crystallographically independent, but chemically similar molecules are found in the asymmetric unit. As can be seen, the sulfur occupies the central zirconium orbital, reminiscent of the η^2-O-inside conformation seen for acyl(chloro)zirconocenes.[4] The C–S bond distances of 1.785 (11) and 1.739 (13) Å are shorter than typical C–S single bond distances of 1.805–1.825 Å,[5] indicating that while the predominant resonance form of 1a is a

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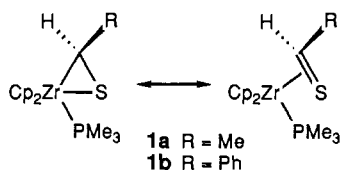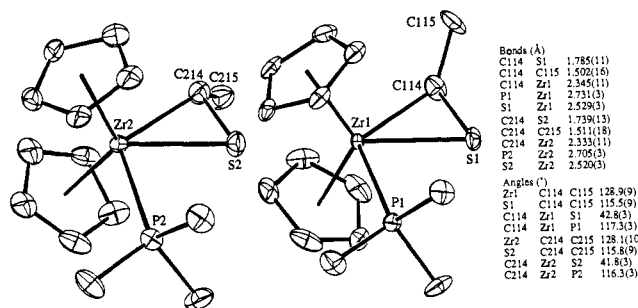
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Figure 1.

Figure 2. Molecular structure of 1a with selected bond distances and angles.

Scheme I
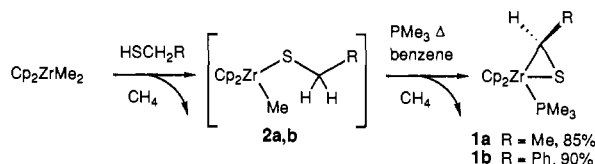
Scheme II
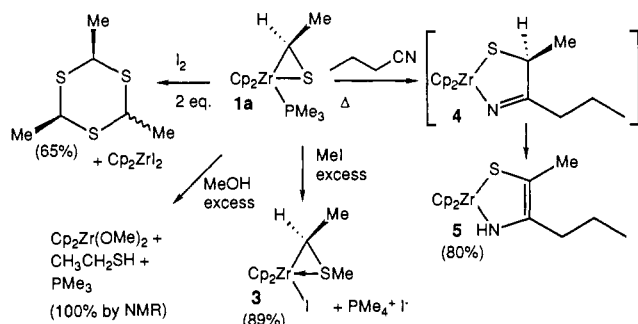
zirconium(IV) metallathiirane, there is some contribution of the zirconium(II) π-thioaldehyde form.

Compounds 1a,b are stable in benzene solution at 100 °C for an extended period of time, but they react with a variety of organic and inorganic compounds (Scheme II). For example, 1a is oxidized by iodine to yield thioacetaldehyde trimer (2,4,6-trimethyl-1,3,5-trithiane) as a mixture of α and β isomers.[6] Protonation by methanol yields ethanethiol and trimethylphosphine (quantitatively by ^{1}H NMR), along with dimethoxyzirconocene.[7] Treatment of 1a with excess methyl iodide yields the α-zirconocenyl thioether 3. 3 appears to be η^2,[8] as evidenced by the downfield chemical shift of the thiomethyl protons. In addition, the failure of the zirconium to migrate to the neighboring primary carbon is in contrast to the behavior normally manifested by alkyl(halo)zirconocenes.[9] Butyronitrile reacts with 1a to yield imine metallacycle 4 (observed by ^{1}H NMR), which tautomerizes under the reaction conditions to cleanly give enamine metallacycle 5.[10]

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We are currently investigating the reactivity of zirconocene thioaldehyde complexes toward other substrates, the use of ligands other than trimethylphosphine, and the application of our methodology for the synthesis of thioaldehyde complexes of other early transition metal systems.

Supplementary Material Available: Experimental section containing the preparation and spectroscopic characterization of compounds, along with crystallographic data and procedures, ORTEP diagrams of 1a, tables of bond distances and angles, and table of final positional and thermal parameters (6 pages); table of structure factors (14 pages). Ordering information is given on any current masthead page.

Site-Selective Observation of Nuclear Overhauser Effects in Proteins via Isotopic Labeling

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The [1]H–[1]H nuclear Overhauser effect (NOE) plays a central role in NMR studies of the conformation and dynamics of small proteins. Griffey, Redfield, and co-workers have described several powerful, one-dimensional techniques for observing specific NOEs in biological macromolecules which have been isotopically labeled at selected sites.[1,2] These experiments employ conventional NOE difference methods which are modified to make use of heteronuclear decoupling to edit the resulting one-dimensional spectra. In this paper we present a very simple, alternative method for obtaining isotopic label-edited NOE difference spectra that has several practical advantages over the previously proposed techniques.

The basic pulse sequence is shown in Figure 1a. The principle of the experiment is to invert selectively the Zeeman order of the protons directly bonded to a heteronuclear label (referred to as the labeled protons) and subsequently to allow cross-relaxation with the unlabeled protons to occur during a mixing period τ_m. The selective population inversion is achieved through the use of the bilinear rotation sequence (BIRD).[3-5] This experiment is fundamentally equivalent to the well-known transient NOE ex-

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