of 460 ps. Sample lengths ranging from $d = 0.3$ to 0.7 cm yielded the same relaxation time which indicates that the thin sample approximation is valid. The relaxation time corresponds to an intervalence electron-transfer rate of 10.9×10^8 Hz. Values of 22 and 3 were obtained for ϵ_0 and ϵ_∞, respectively.

Berkooz has determined[6] the rate of intervalence electron transfer for Eu_3S_4 as a function of temperature by using Mössbauer spectroscopy. A room temperature Mössbauer spectrum of our sample has been computer simulated by using the methods outlined by Berkooz. The Mössbauer data indicate that the rate of intervalence electron transfer is 9.9×10^8 Hz, which is in good agreement with the TDR results.

The agreement between our Mössbauer and TDR results indicates that the TDR technique is a viable method for determining electron-transfer rates in mixed-valence compounds. Work is now under way to conduct variable temperature TDR and Mössbauer experiments on Eu_3S_4 and to compare these results with Berkooz's. The TDR technique should be able to provide important information concerning activation energies as well as intervalence-transfer rates for mixed-valence compounds.

Acknowledgment. We acknowledge support of this research by the National Science Foundation.

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Synthesis, Structural Characterization, and Molecular Orbital Calculations for a Titanium Lewis Acid Carbonyl Adduct

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The coordination of Lewis acids to the oxygen atom of a metal-bound carbonyl ligand is well-known.[2] The importance of this coordination in activating carbon monoxide for reduction has been suggested,[3,4] and the homogeneous reductions of CO to alkanes[4-6] and linear alcohols[7] in the presence of Lewis acids have been observed. We have been interested in the activation of CO in bimetallic systems[8] and report here the recent preparation of a Lewis acid carbonyl adduct by the in situ generation of a titanium(IV) Lewis acid.

The addition of $CpMo(CO)_3H$[9] to a toluene solution of $Cp'[C_5(CH_3)_4{=}CH_2]Ti(CH_3)$[10] [$Cp' = \eta^5\text{-}C_5(CH_3)_5$] resulted in an immediate color change from turquoise to dark red brown. Filtration and removal of solvent in vacuo gave an 80% yield of a dark red-brown powder characterized as $Cp'_2Ti(CH_3)(OC)_3MoCp$.[11] The IR spectrum of the compound taken in Nujol showed bands of medium intensity at 1927, 1918, 1849, 1830, and 1623 cm^{-1}. The absorption at 1623 cm^{-1} was indicative of a bridging carbonyl ligand, and a crystallographic determination[12] was undertaken to determine its mode of coordination.

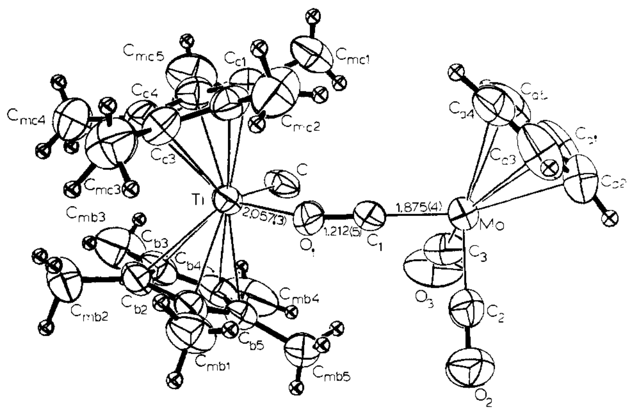

Figure 1. ORTEP drawing for $Cp'_2Ti(CH_3)(OC)_3MoCp$ (solvent molecule not shown). Bond lengths: C_1-O_1 = 1.212 (5), C_2-O_2 = 1.154 (6), C_3-O_3 = 1.150 (7), Mo-C_1 = 1.875 (4), Mo-C_2 = 1.948 (5), Mo-C_3 = 1.940 (5), Ti-O_1 = 2.057 (3), Ti-C = 1.969 (4) Å. Bond angles: Ti-O_1-C_1 = 144.3 (3), O_1-C_1-Mo = 178.8 (4)°. All hydrogen atoms, except those located on the methyl group attached to the Ti atom, were found.

Table I. Mulliken Gross Atomic Charges

	C	O	total
terminal	0.04	−0.09	−0.05
bridging	−0.07	−0.11	−0.18

Table II. Mulliken Populations of CO Ligand Orbitals

	3σ[15]	4σ	5σ	$1\pi_\parallel$[16]	$1\pi_\perp$	$2\pi_\parallel$	$2\pi_\perp$
terminal	2.00	2.00	1.13	2.05	2.05	0.16	0.25
bridging	2.00	1.59	1.06	1.92	2.04	0.41	0.45

The structural results are shown in Figure 1 The most interesting aspect of the structure is the coordination of the bridging carbonyl through both the carbon and the oxygen atoms. This is the first example, of a d^0 transition metal coordinating to a terminal carbonyl ligand.[13] The bonding of the bridging carbonyl ligand is explained as a Lewis acid interaction of the Ti(IV), $Cp'_2Ti(CH_3)$ moiety with the carbonyl oxygen atom. The observed lengthening of the C_1-O_1 bond and the shortening of the Mo-C_1 bond are expected upon Lewis acid coordination.[2a,b,e]

Fenske-Hall molecular orbital calculations[14] support this view. Table I shows the Mulliken gross atomic charges for the carbon and oxygen atoms of the terminal and bridging carbonyl ligands and the total charge on these ligands. The increase in negative charge in going from the terminal CO ligand (−0.05) to the bridging CO ligand (−0.18) indicates an increase in the π^* orbital

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(11) Anal. Calcd for $C_{29}H_{38}O_3MoTi$: C, 60.22; H, 6.58. Found: C, 60.77; H, 6.37. Field desorption mass spectrum molecular ion at *m/e* 572-582. NMR studies in progress.

(12) Single crystals were obtained from a saturated benzene solution. The compound crystallized as $Cp'_2Ti(CH_3)(OC)_3MoCp{\cdot}0.5C_6H_6$. Space group $P2_1/n$ with $a = 10.109$ (3), $b = 18.106$ (5), $c = 16.648$ (4) Å; $\beta = 104.21$ (2)°; Z = 4; $R = 0.043$. The structural determination was carried out at Crystalytics Co., Lincoln, NE.

(13) (a) A similar structure has been observed for a triply bridging CO in the compound $Cp_2TiCl(OC)Co_3(CO)_9$. Schmid, G; Bätzel, V.; Stutte, B. *J. Organomet. Chem.* **1976**, *113*, 67. (b) A $V^{2+}\cdots OC$ bond has been observed. Schneider, M.; Weiss, E. *Ibid.* **1976**, *121*, 365.

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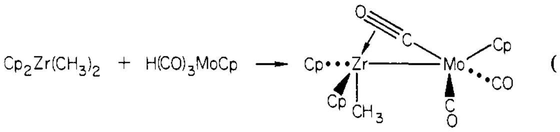
occupation. This is also illustrated in Table II, which lists the Mulliken populations in the orbitals for both kinds of CO ligands. The increase in occupancy of the π^* orbitals ($2\pi_{\parallel}$ and $2\pi_{\perp}$)[16] is due primarily to an increased bonding interaction of these orbitals with the Mo orbitals. The overlap populations (0.17 for terminal, 0.25 for bridging CO) reflect this increased π^* backbonding. In the case of the titanium atom, however, metal to π^* backbonding is negligable. The 4σ orbital is the highest σ orbital with significant oxygen character. In fact, it is almost entirely oxygen lone pair in character. This orbital is mainly responsible for the titanium–CO bond (overlap population = 0.12), although the 5σ orbital (overlap population = 0.04) and the $1\pi_{\parallel}$ orbital (overlap population = 0.03) make some contribution. It will be noted in Table II that the 4σ occupancy is less in the bridging than in the terminal carbonyl. The smaller occupancy of this orbital in the bridging carbonyl is consistent with the proposed 4+ oxidation state of the titanium atom, since the oxygen lone pair should be strongly attracted by a large charge nearby. The sizable difference between the Mulliken gross atomic charges (0.90 for Ti, 0.36 for Mo) also concurs with this assignment of the oxidation state. The $1\pi_{\parallel}$ orbital of the bridging carbonyl lies in the mirror plane and acts as a σ donor orbital to empty Ti orbitals in the same plane. Since one of these empty orbitals bisects the angle between the methyl and carbonyl ligands, more effective overlap is achieved by bending the CO ligand toward this orbital ($Ti-O_1-C_1$ = 144.3 (3)°, see Figure 1). The $1\pi_{\perp}$-titanium orbital interaction is negligible since there are no nearby titanium acceptor orbitals of appropriate symmetry.[17]

The formation of a Lewis acid adduct between $Cp'_2Ti(CH_3)$ and $(OC)_3MoCp$ indicates such structures may be observed in other systems. In particular, such an adduct may be important in the recently reported dinuclear elimination reaction of $Cp_2Zr(CH_3)_2$ and $H(CO)_3MoCp$[18] (reaction 1). The proposed



(1)

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structure of **1** is based on IR and ^{13}C NMR data. The IR spectrum shows a strong band at 1545 cm^{-1} which is assigned to the bridging carbonyl ligand shown in (1). The ^{13}C NMR spectrum at room temperature has a single carbonyl peak at δ 236.1, while two peaks at δ 245.4 and 232.5 (relative intensity 1:2) are observed when the spectrum is recorded at −80 °C. We propose that a Zr Lewis acid adduct[19] analogous to the Ti adduct reported in this paper is also consistent with these data. In view of this possibility a crystallographic investigation of the Zr system would be of interest.

Finally, this reaction demonstrates a novel method of generating an open coordination site on a transition-metal complex. Further studies to extend the scope of this reaction to other transition-metal hydrides and carbenes, as well as studies on the reactivity of the Ti–Mo system, are under way.

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Supplementary Material Available: A listing of positional and thermal parameters derived from full-matrix least-squares refinements (5 pages). Ordering information is given on any current masthead page.

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[16] C_s symmetry was imposed on the molecule so that the C(methyl), Ti, O_1, C_1, and Mo atoms lie in a mirror plane along with the centroid of the molybdenum cyclopentadienyl ring. The 2p atomic orbitals which form the basis for $1\pi_{\parallel}$ and $2\pi_{\parallel}$ are parallel to the mirror plane; those for $1\pi_{\perp}$ and $2\pi_{\perp}$ are perpendicular to the aforementioned 2p orbitals and the C–O internuclear axis.

[17] An interesting comparison was made with a system in which the $Cp_2Ti(CH_3)$ moiety used in the calculations was replaced with a group having no d orbitals, viz., the H_3O^+ ion. The H_3O^+ oxygen and one of its hydrogen atoms were oriented collinearly with the C–O ligand axis, giving distances of 1.579 and 2.59 Å, respectively, from the hydrogen and oxygen atoms to the carbonyl oxygen. The negative charge on the CO oxygen atom increased substantially (from −0.11 to −0.35), and the C–O bond strength increased slightly, as measured by overlap populations (from 0.59 to 0.62).

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Gas-Phase Hydrogen–Deuterium Exchange Reactions in Carbanions: Exchange of Vinyl and Aryl Protons by D_2O

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In previous papers[1,2] we showed how gas-phase hydrogen–deuterium exchange reactions between carbanions and deuterated reagents such as D_2O, CH_3OD, and CF_3CH_2OD can be used to determine ion structures, bracket carbanion basicities, and probe ion–molecule reaction mechanisms. Hunt and Sethi recently demonstrated the utility of H–D exchange in negative chemical ionization mass spectrometry (NCIMS) in which the number of hydrogen atoms of various types can be counted directly in a mass spectrometer.[3] Using ion cyclotron resonance spectroscopy, Nibbering and co-workers have applied H–D exchange to the solution of a variety of ion structural problems.[4] In view of the large number of potential applications of gas-phase H–D exchange, it is important to understand the full range of its utility as well as its possible pitfalls. We wish to report that under the proper conditions D_2O can serve as an exchange reagent for hydrogens which are much less acidic than water; as a result, in certain carbanions aryl and vinyl hydrogens can be observed to exchange with D_2O. Such exchanges give rise to many new possible applications for the technique, especially as a tool for investigating relative acidities of types of hydrogens which have not been previously studied. At the same time, they may add unexpected complications to the routine use of the technique with NCIMS.

Using our flowing afterglow apparatus,[5] we have previously examined the exchange characteristics of a wide variety of organic anions. Three types of behavior were delineated, depending upon the base strength of the carbanion relative to that of the conjugate base of the exchange reagent. These are illustrated below for reactions with D_2O and are as follows: proton transfer for anions which are stronger bases than OD^- (eq 1), H–D exchange for

$$\underset{(398)}{C_6H_5^-} \xrightarrow{D_2O} \underset{(391)}{OD^-} \tag{1}$$

$$\underset{(372)}{\bar{C}H_2CN} \xrightarrow{D_2O} \bar{C}D_2CN \tag{2}$$

$$\underset{(369)}{\bar{C}H_2COCH_3} \xrightarrow{D_2O} \text{no exchange} \tag{3}$$

carbanions which are up to about 20 kcal/mol less basic than OD^- (eq 2), and no observable exchange for still weaker bases (eq 3) [proton affinities (PA), in kcal/mol, shown in parentheses].[6] By

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