Table I. Forward Catalytic Rate Constants and Self-Exchange Barriers for Enolization

		$oxac^{2-}$			Mg(oxac)		
catalyst	pK_a^{HB}	$k_f{}^a$	ref	$\Delta G_o{}^{\ddagger b}$	$k_f{}^a$	ref	$\Delta G_o{}^{\ddagger b}$
OH^-	15.75	80	*d*	15	1.3×10^5	*d*	14
$PO_4{}^{3-}$	11.35	1.0	12	13			
DPEA	10.25	0.4	12	15			
$CO_3{}^{2-}$	9.77	0.088	12	14			
imidazole	7.2	0.062	10	14			
$HPO_4{}^{2-}$	6.7	0.014	12	13			
AcO^-	4.75	~0.005	10[c]	~13	1.1	13	14
TMEN	9.35	80	d	11	1.5×10^3	*d*	13
$HTMEN^+$	6.15	9.7	d	11	1.2×10^2	*d*	12

[a] M^{-1} s^{-1}. [b] kcal mol^{-1}. [c] Approximate value. [d] This work.

are those associated with the addition of amine to the $oxac^{2-}$ keto group.[12] Evaluations of $\Delta G°$ for catalysis by a given base were made using the pK_a^{HB} given in the table and pK_a values determined to be 13.3 for $oxac^{2-}$ and 8.0 for Mg(oxac).[14]

Those base catalysts that obey the Brønsted relationship yield values of $\Delta G_o{}^{\ddagger}$[15] lying in the range 14 ± 1 kcal mol^{-1}, while TMEN and $HTMEN^+$ show a distinctly lower apparent barrier height of 11 kcal mol^{-1}. In contrast, complexing to Mg^{II} brings about substantial increases in the rates for OH^- and AcO^- catalysis, but the $\Delta G_o{}^{\ddagger}$ values are found to remain at 14 kcal mol^{-1}. The influence of Mg^{II} on the pK_a of $oxac^{2-}$ quantitatively accounts for the rate increases. Furthermore, the value of 13 kcal mol^{-1} for the TMEN reaction with Mg(oxac) suggests that the increase in $oxac^{2-}$ acidity may cause tertiary amines to revert to the mode shown in (I).

Hydration rates are dominated by OH^- and H_2O catalysts,[11,12] but we have found weak catalysis by TMEN and $HTMEN^+$. $\Delta G_o{}^{\ddagger}$ values were calculated by using estimated hydrolysis constants pertaining to (II) of $10^{-19.7}$ M for $oxac^{2-}$ and $10^{-15.2}$ M for Mg(oxac). The results are listed in order of catalyst, observed rate constant, and $\Delta G_o{}^{\ddagger}$ (kcal/mol). $oxac^{2-}$: OH^-, 480 M^{-1} s^{-1}, 10; H_2O, 0.03 s^{-1}, complex no.; TMEN, 0.26 M^{-1} s^{-1}, 9; $HTMEN^+$, 0.16 M^{-1} s^{-1}, 7. Mg(oxac): OH^-, 1.0×10^6 M^{-1} s^{-1}, 9; H_2O, 0.6 s^{-1}, complex no.; $HTMEN^+$, 3.2 M^{-1} s^{-1}, 9. Thus, two of the rate constants for $oxac^{2-}$ and two for Mg(oxac), although spanning 7 orders of magnitude, give 9–10 kcal mol^{-1} for $\Delta G_o{}^{\ddagger}$. Discrepant results for the action of $HTMEN^+$ and H_2O on $oxac^{2-}$ are brought into mutual accord when pathways involving the conjugate bases and $H(oxac)^{-1}$ are assumed. These last pathways are expected to be slower with complexed $oxac^{2-}$ owing to a decrease in basicity, and relatively small rate increases are seen to be effected by Mg^{2+} on H_2O and $HTMEN^+$ catalysis. Indeed, the latter catalyst appears to serve as a base catalyst toward Mg(oxac).

Intrinsic barrier heights for decarboxylation were obtained from an expression that relates the barrier to the forward and backward rate constants.[18] Forward rate constants for CO_2 loss are 1.66×10^{-5} ($oxac^{2-}{}_{keto}$),[19] 0.0023 ($Mg(oxac)_{keto}$), and 0.045 s^{-1} ($Zn(oxac)_{keto}$). With the aid of recently acquired data,[20] 6.8×10^{-7} M has been assigned the equilibrium constant for $oxac^{2-} \rightleftarrows \mathbf{4} + CO_{2(aq)}$.[21] This value together with estimates of $10^{5.0}$ and $10^{7.0}$ M^{-1} for the binding constants of Mg^{2+} and Zn^{2+} to **4** enable the backward rate constants to be evaluated. The respective results for $\Delta G_o{}^{\ddagger}$ are 19, 19, and 18 kcal mol^{-1}. Thus decarboxylation represents a third example in which substantial metal ion induced changes in a reaction rate may be attributed solely to the effect on the thermodynamics of the reaction.

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Registry No. $oxac^{-2}$, 149-63-3; Mg(oxac), 65636-56-8; Zn(oxac), 88295-82-3.

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[15] To apply the Marcus equation the rate-limiting reactions described by (I) and (II) were broken down into the following steps:

$$oxac^{2-} + B \underset{}{\overset{K_{1c}}{\rightleftarrows}} oxac^{2-}\cdots B \xrightarrow[\text{slow}]{k} (oxac)H^{3-}{}_{-1}\cdots HB^+ \overset{1/K_{2c}}{\rightleftarrows} (oxac)H^{3-}{}_{-1} + HB^+$$

Corrections to $\Delta G°$ for the free energies of forming the precursor and successor cage complexes were applied after K_{1c} and K_{2c} were evaluated using the Fuoss equation.[16] The preexponential coefficient was taken to be 0.1 to be consistent with Albery's[17] treatment of neutral species. A distance of 6 Å in the exponential term seemed to satisfactorily correct for electrostatic effects on the rates. The observed activation barrier was evaluated from the reduced constant, k/K_{1c}. The self-exchange barrier for buffer is ca. 5 kcal mol^{-1}.

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[21] $K_{111} = [\mathbf{4}][CO_2]/[\mathbf{1}] = k_fK_1K_2/k_bK_a$, where $K_1 = [pyr^-][HCO_3{}^-]/[\mathbf{1}] = 3.5 \times 10^4$;[22] $K_2 = [H^+][\mathbf{4}]/[H\mathbf{4}] = 1.0 \times 10^{-12}$, using the Taft parameters[23] to estimate the displacement from 11.1, the pK_a assigned to vinyl alcohol;[24,25] $K_a = [H^+][HCO_3{}^-]/[CO_2]_{aq} = 4 \times 10^{-7}$,[9a] pyr^- (AcO^-) → H**4**, $k_f = 5 \times 10^{-6}$ M^{-1} s^{-1};[2] H**4** (AcO^-) → pyr^-, $k_b = 0.64$ M^{-1} s^{-1}.[20]

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Aluminum Alkyls and Transition-Metal Hydrides: "Nonclassical" Adduct Structure and Catalysis of Hydrogen Migration

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An early, and now classic, demonstration of transition-metal basicity derives from the observation[1-4] that the d^2 complexes Cp_2MH_2 (M = Mo, W) react with Al_2Me_6 to form an adduct, often drawn explicitly with a dative bond (I).[5] The d^0 hydride

$$\underset{\text{I}}{Cp_2H_2W\rightarrow AlMe_3} \qquad \underset{\text{II}}{Cp_3Zr{-}H{-}AlMe_3}$$

Cp_3ZrH has been shown to have structure II.[6] We now report

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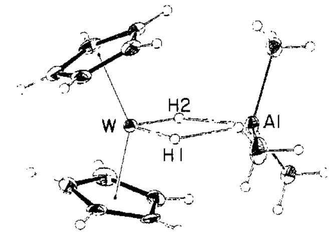


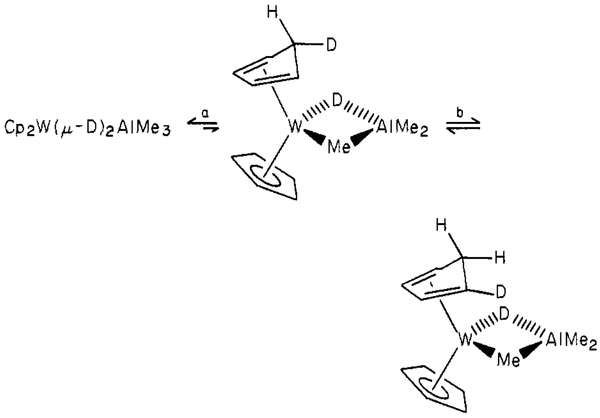
Figure 1. ORTEP drawing of $Cp_2W(\mu\text{-}H)_2AlMe_3$. Atoms W, Al, H1, and H2 lie in a crystallographic mirror plane. Selected structural parameters: W–H1 = 1.70 (5), W–H2 = 1.22 (17), Al–H1 = 1.96 (5), Al–H2 = 2.08 (16), W–Al = 3.110 (3) Å, ∠H1WH2 = 60 (7)°.

that an X-ray data set[7] collected on $Cp_2WH_2AlMe_3$ at −166 °C allows refinement of all atoms, including hydrogen (Figure 1), and reveals that the two hydride ligands interact with aluminum as well as tungsten to produce a transition-metal organometallic species with five- or six-coordinate aluminum. As detailed below the figure, both hydrides are within bonding distance of both metals.[8,9] More informative, perhaps, than bond lengths is the H–W–H angle. If the hydrides experience no bonding to aluminum, ∠HWH should increase greatly on passing from Cp_2WH_2 to $Cp_2WH_2AlMe_3$. The angle (neutron diffraction[12]) in Cp_2MoH_2 is 75.5 (3)°, while in $Cp_2WH_2AlMe_3$ it is 60 (7)°. For comparison, the relevant angle (neutron diffraction[13]) in Cp_2TaH_3 is 125.8 (5)°. Finally, we believe it is untenable to suggest that the adduct, which is stable to vacuum, owes its existence solely to a W→Al dative bond when the W–Al separation (3.110 Å) is so much greater than the sum of the covalent radii (2.71 Å). We now report that this nonclassical binding in $Cp_2W(\mu\text{-}H)_2AlMe_3$ has implications for chemical reactivity.

Deuteride $(\eta^5\text{-}C_5H_5)_2WD_2$ is conveniently produced[14,15] by treatment of $(\eta^5\text{-}C_5H_5)_2WH_2$ with D^+/D_2O. Cationic $(\eta^5\text{-}C_5H_5)_2W(D,H)_3{}^+$ is an intermediate in this process, and both it and the neutral dideuteride show no evidence for isotopic scrambling between C–H and W–D over a period of hours at 25 °C in solution or solid. Adduct formation between $(\eta^5\text{-}C_5H_5)_2WD_2$ and Al_2Me_6 is completed in the time of mixing in toluene at −78 °C. The ^2H NMR spectrum (−70 °C) of this solution of the adduct held at or below −70 °C since the time of mixing (~10 min) shows the exclusive formation of $(\eta^5\text{-}C_5H_5)_2W(\mu\text{-}D)_2AlMe_3$. However, if this solution is warmed to and held at 20 °C for 10 min, the ratio of cyclopentadienyl C–D[16] and W–D intensities has already achieved its equilibrium value of ~12. Thus, isotopic scrabmling is somehow catalyzed either by $AlMe_3$ within the adduct or by external Al_2Me_6, and an equilibrium isotope effect favors deuterium on carbon in preference to the $W(\mu\text{-}D)Al$ site.

Two lines of evidence indicate that this scrambling is a unimolecular process within the intact adduct. First, if $(\eta^5\text{-}C_5H_5)_2WD_2AlMe_3$ is formed and isolated at −78 °C, the solid shows (by IR spectroscopy in fluorolube and also in KBr) a 70% approach to isotopic equilibrium in 18 h at 25 °C. In addition, it is possible to find a temperature where the spin saturation transfer technique[17-19] may be employed to directly detect hydrogen scrambling in $(\eta^5\text{-}C_5H_5)_2W(\mu\text{-}H)_2AlMe_3$. Thus, a 75 °C in toluene-d_6, complete saturation of the $W(\mu\text{-}H)_2Al$ hydrogens (-13.2 ppm) resulted in a C_5H_5 resonance (4.2 ppm) diminished 47% relative to the C_5H_5 signal in the absence of irradiation. From such experiments, a rate constant for $W(\mu\text{-}H)Al \rightarrow C_5H_5$ transfer of 0.075 (8) s^{-1} was measured.[20,21] For comparison, the value in the presence of a 15:1 mol ratio of Al_2Me_6 is 0.070 (8) s^{-1}. This independence of rate on added Al_2Me_6 excludes mechanisms involving dissociation of the adduct into $AlMe_3$ and Cp_2WH_2 as well as catalysis by attack of excess aluminum species on intact $Cp_2W(\mu\text{-}H)_2AlMe_3$.

We suggest the mechanism shown in eq 1 as the mode of



(1)

catalyzed isotopic scrambling. This involves a suprafacial 1,5-hydrogen shift (b) in the cyclopentadiene ring.[22] Also involved is a form of anchimeric assistance (a) by the alkyl group on aluminum, which rationalizes the absence of H/D exchange in the Brønsted acid adduct $Cp_2WD_3{}^+$. This $AlMe_3$-catalyzed H/D scrambling process results from the unusual bifunctionality of $AlMe_3$: Lewis acidity is necessary to first bind the pendant nucleophile (Me) to Cp_2WH_2, and nucleophilic stabilization[23] of the ring-migrated intermediate then becomes an entropically cost-free intramolecular process.

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Registry No. $Cp_2W(\mu\text{-}H)_2AlMe_3$, 12215-71-3; $Cp_2W(\mu\text{-}D)_2AlMe_3$, 88288-61-3; Cp_2WH_2, 1271-33-6; $(\eta^5\text{-}C_5H_5)_2WD_2$, 11082-26-1; Al_2Me_6, 15632-54-9.

Supplementary Material Available: Positional and thermal parameters and bond lengths and angles for $Cp_2W(\mu\text{-}H)_2AlMe_3$ (3 pages). Ordering information is given on any current masthead page.

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(8) Attempts to grow large crystals for neutron diffraction are under way in order to establish hydrogen positions with greater accuracy.

(9) For comparison, $Al(\mu\text{-}H)$ distances in the range 1.68 (2)–2.00 (10) Å have been reported by X-ray[10] and electron diffraction methods.[11]

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(21) Relaxation times (T_1) were measured at 25 °C (in the absence of site exchange) by the inversion recovery method. For C_5H_5, T_1 = 11.4 (1) s; for W (μ-H)Al, T_1 = 4.77 (3) s.

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(23) A tenfold excess of the more conventional nucleophiles PMe_2Ph and CH_3CN fails to scramble isotopes in $(\eta^5\text{-}C_5H_5)_2WD_2$ in 24 h.