

for 1-Li₂ would satisfy both symmetry and bonding requirements, with the C(2)-Li coupling reflecting analogous bonding to that in phenyllithium.⁷ We note that Streitwieser's calculation^{2b} restricted the lithium atoms to the plane bisecting the molecule. This structure represents one limiting form of an ensemble in which we allow the Li-C-Li plane to rotate with respect to the C-C-C plane. The other limiting form, of course, is the planar tetracoordinate carbon predicted for certain dilithio carbon derivatives.⁹ Since all such forms minimally satisfy our C₂ symmetry requirements, we can only remphasize the curious nature of bonding in organolithium compounds.

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Temperature-Independent Isotope Effects in Hydro Transfer. Do They Signify a Bent Transition State?¹

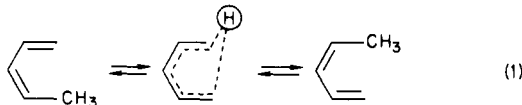
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A number of remarkable temperature-independent primary kinetic isotope effects (KIE's) for reactions involving hydro transfer have recently been reported by Kwart and his co-workers.²⁻⁴ They have contended that reactions displaying this phenomenon pass through transition states (TS's) in which the D...H...A (D = donor, A = acceptor) angle is significantly less than 180°, whilst processes having a normal temperature dependence of k_H/k_D , with $[\Delta E_a]_D^H$ ranging up to about 1.2 kcal mol⁻¹, are characterized by linear TS's having angles close to 180°.

In particular, Kwart argued that the $[\Delta E_a]_D^H$ of 1.4 kcal mol⁻¹ attending the degenerate [1,5] sigmatropic H shift of *cis*-1,3-pentadiene⁵ afforded proof of linear TS geometry, whilst the $[\Delta E_a]_D^H \approx 0$ that he found for the same process in a cyclic system resulted from enforced nonlinear TS geometry.⁶

No theoretical reasons have been advanced to rationalize this dichotomy, and for this reason we commenced model calculations at the instigation of the late Harold Kwart. The particular system investigated was the above-mentioned sigmatropic rearrangement, eq 1, but other results indicate that the findings should be generally



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Table I. Primary KIE's and Their Temperature Dependence for the Sigmatropic Rearrangement of 1,3-Pentadiene^a

angle	k_H/k_D (0 °C) for model			
	A	B	C	D
180°	9.30 (1.20)	8.38 (1.12)	4.99 (0.82)	5.72 (0.90)
150°	7.23 (1.05)	7.12 (1.04)	4.07 (0.70)	4.63 (0.68)
120°	3.84 (0.69)	3.79 (0.70)	2.30 (0.39)	2.43 (0.43)
90°	1.97 (0.34)	1.68 (0.30)	1.21 (0.05)	1.05 (0.006)

^a $n_1 = n_2 = 0.50$ in all cases. Values of $[\Delta E_a]_D^H$ in parentheses (kcal mol⁻¹).

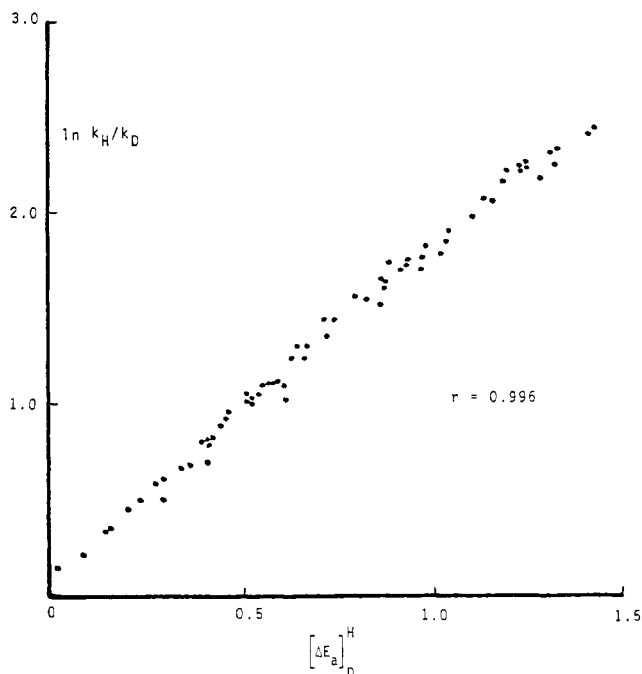
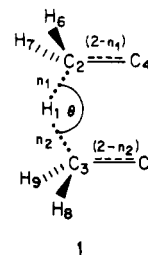


Figure 1. Relationship between the magnitude of k_H/k_D (0 °C) and the temperature dependence as expressed by $[\Delta E_a]_D^H$.

and widely applicable. To avoid complications associated with cyclic TS models, we adopted the cutoff model 1, and on the basis of various assumed geometries, we assigned force constants to coordinates which included the partial bonds by using conventional empirical formulations involving the bond orders n_1 and n_2 .⁷



Parameters varied were n_1 , n_2 , and θ , whilst many combinations of empirical formulations for the C₂...H...C₃ bending force constant and for the interaction force constants generating reaction coordinate motion were employed. Single temperature KIE's at fixed θ (90° ≤ θ ≤ 180°) displayed a dependence on n_1 and n_2 similar to that described for an earlier, simpler model.⁸ In Table I is displayed the model dependence of k_H/k_D for some cases where $n_1 = n_2 = 0.5$. Models A and B involve the generation of reaction coordinate motion by simple coupling of the C₂...H and H...C₃ stretching modes, model C includes heavy atom motion (an E2-like reaction coordinate⁹), and model D adds to this coupling of bending

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coordinates involving the nontransferring hydrogens on C₂ and C₃. Two notable facts emerge.

Firstly, single-temperature k_H/k_D values are strongly model-dependent for given θ . The practice of equating a less than maximal k_H/k_D value with a specific value of $\theta^{6,10}$ is thus invalid. Secondly, all isotope effects are temperature-dependent to some extent, even for cases where θ is small. We have investigated in total more than 1000 TS models. *In not one case is a substantial primary k_H/k_D temperature-independent.*

The plot in Figure 1, based on 68 randomly chosen models, mostly with $\theta < 180^\circ$, reveals that the magnitude of k_H/k_D at a given temperature is largely controlled by $[\Delta E_a]_D^H$, and not by A_H/A_D as alleged by Kwart.³ It follows that only KIE's very close to 1.0 will have a negligible temperature dependence in the 0-100° range.

A more direct probe involved location of the TS on the MNDO potential energy surface and the calculation of the isotopic dependence of reactant and TS vibrational frequencies. The resultant KIE's are again decidedly temperature-dependent: $[\Delta E_a]_D^H = 1.09 \text{ kcal mol}^{-1}$, $A_H/A_D = 1.06$. This is significant since the D...H...A TS angle is calculated to be 133.5° , which is in good agreement with the angle of 129.9° arising from ab initio calculations.¹¹ The MNDO KIE's are significantly lower than the experimental values,⁵ but the latter are contaminated by secondary KIE's of unknown magnitude and may well be attended by hydron tunneling.

It is clear that the observed temperature-dependent KIE's for the sigmatropic rearrangement are not incompatible with a bent TS geometry. In the wider sense, the proposed criterion of TS geometry³ appears to be without foundation. Some alternative explanations for the temperature-independent KIE's will be considered in the full paper.

Registry No. *cis*-1,3-Pentadiene, 1574-41-0; deuterium, 7782-39-0.

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Formation of Dinuclear Rhodium Dialkyl Complexes by Alkylation of a New Dinuclear Dianion and by Nucleophilic Addition of Alkylolithium Reagents across a Metal-Metal Double Bond

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We wish to report the products formed on one- and two-electron reduction of $[\text{Cp}^*\text{RhCO}]_2^{1,2}$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) and the addition

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(2) $[\text{Cp}^*\text{RhCO}]_2$ has a rich chemistry and has been utilized in the preparation of coordinately saturated dimers,³ cluster compounds,⁴ bridging carbene complexes,^{4a,5} and dimetallacycles.^{4a,6}

(3) Werner, H.; Klingert, B. *J. Organomet. Chem.* **1982**, *233*, 365.

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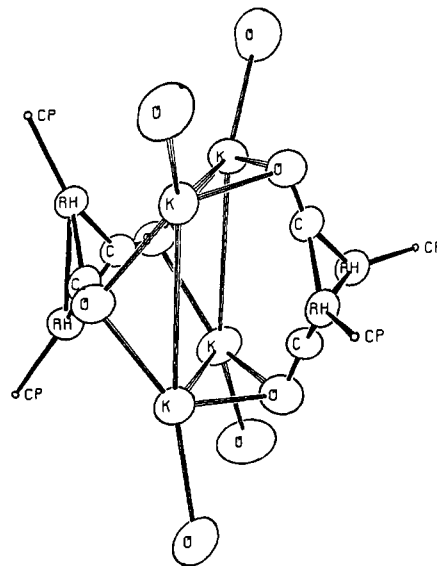


Figure 1. ORTEP diagram of $(\text{K}^+)_2[\text{Cp}^*\text{RhCO}]_2 \cdot 2\text{THF}$ showing the dimeric nature of the compound and its bonding scheme to the potassium ions (Cp* rings and the THF carbon atoms omitted for clarity). Bond distances (Å): Rh-Rh 2.606 (1) and 2.613 (1); K-K 4.205 (2), 4.040 (2), 4.162 (2), and 3.905 (3). Dihedral angles of Rh-Rh-(μ -CO) units are 122° and 125° .

of alkylolithium reagents across the formal rhodium-rhodium double bond in this molecule. To our knowledge the latter reaction is the first example of addition of an alkylolithium reagent across a metal-metal multiple bond. An X-ray diffraction study has been carried out on the potassium salt of the dianion obtained from the two-electron reduction; this complex shows a novel bonding scheme in which two dianion molecules are coordinated to a square of potassium atoms. The alkyl-substituted anions produced in the alkylolithium reactions react with organic electrophiles to provide a powerful new synthesis of dinuclear dialkyl complexes.

Treatment of neutral dimer $[\text{Cp}^*\text{RhCO}]_2$ with Na/Hg or Na/K alloy in THF was carried out at room temperature using vacuum line techniques. The navy blue solution turned forest green after stirring for 0.5-1.5 h. Slow diffusion of pentane into this solution gave $\text{K}^+[\text{Cp}^*\text{RhCO}]_2^-$. The potassium ion was also encapsulated with 2,2,2-cryptate⁷ to form $[\text{K}(\text{crypt})]^+[\text{Cp}^*\text{RhCO}]_2^-$. The IR spectrum of $[\text{K}(\text{crypt})]^+[\text{Cp}^*\text{RhCO}]_2^-$ in THF exhibited a single CO band at 1670 cm^{-1} (for comparison, neutral $[\text{Cp}^*\text{RhCO}]_2$ shows a single CO band at 1736 cm^{-1} in THF; the corresponding cobalt radical anion exhibits a single CO band at 1690 cm^{-1}). The presence of a single band indicated a planar structure in solution for the $\text{Rh}_2(\text{CO})_2$ unit similar to that observed for the isoelectronic cobalt system. ESR spectroscopy of the cryptate salt of the radical anion in 2-MeTHF showed a single broad line at room temperature ($\omega_{1/2} = 28 \text{ G}$) with $g = 2.0704$. The lack of observed coupling to the ^{103}Rh ($I = 1/2$) nuclei was not unusual due to the broadness of the line.⁸ Cyclic voltammetric measurements showed the reduction of $[\text{Cp}^*\text{RhCO}]_2$ to $[\text{Cp}^*\text{RhCO}]_2^-$ was reversible and occurred at -1.15 V relative to a Ag/AgNO₃ couple.⁹

In the analogous cobalt series, attempts to form $[\text{CpCo}(\text{CO})]_2^{2-}$ lead only to decomposition.¹⁰ In contrast, reduction of

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(7) Systematic name: 4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane. Sold as Kryptofix 2,2,2 (obtained from Fluka).

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(9) CH₃CN solution, $\text{N}(\text{C}_4\text{H}_9)_4^+\text{BF}_4^-$ supporting electrolyte.