

Table I. Reaction of Aldehydes **3** with Isocynoacetate **4** Catalyzed by the Chiral Ferrocenylphosphine-Gold Complex^a

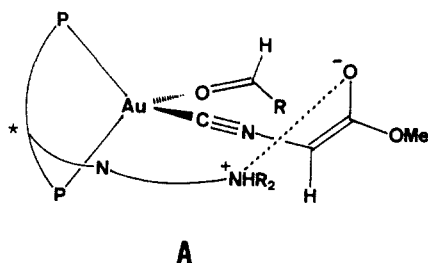
aldehyde 3	ligand 2	yield, ^b % of 5	ratio ^c of trans/cis	<i>trans</i> - 5 % ee, ^d [α] ²⁰ _D (THF) ^e	<i>cis</i> - 5 % ee ^d
PhCHO (3a)	2a	98	89/11	96 (4 <i>S</i> ,5 <i>R</i>), ^f +297°	49 ^g (4 <i>R</i> ,5 <i>R</i>) ^f
	2b	91	90/10	94 (4 <i>S</i> ,5 <i>R</i>), ^f +287°	4 (4 <i>S</i> ,5 <i>S</i>) ^h
(<i>E</i>)- <i>n</i> -PrCH=CHCHO (3b)	2a	83	81/19	84 (4 <i>S</i> ,5 <i>R</i>), ^h +230°	52 (4 <i>R</i> ,5 <i>R</i>) ^h
	2b	97	80/20	87 (4 <i>S</i> ,5 <i>R</i>), ^h +244°	0
(<i>E</i>)-MeCH=CMeCHO (3c)	2b	89	91/9	95 (4 <i>S</i> ,5 <i>R</i>), ^h +311°	31 (4 <i>R</i> ,5 <i>R</i>) ^h
MeCHO (3d)	2a	100	84/16	72 (4 <i>S</i> ,5 <i>R</i>), ⁱ +173° ⁱ	44 (4 <i>R</i> ,5 <i>R</i>) ^h
<i>i</i> -PrCHO (3e)	2a	99	98/2	92 (4 <i>S</i> ,5 <i>R</i>), ^h +250°	
<i>c</i> -HexCHO (3f)	2a	95	97/3	90 (4 <i>S</i> ,5 <i>R</i>), ^h +236°	
	2b	96	98/2	81 (4 <i>S</i> ,5 <i>R</i>), ^h +202°	
<i>t</i> -BuCHO (3g)	2a	100 ^j	100/0	97 (4 <i>S</i> ,5 <i>R</i>), ^h +265°	

^aThe reaction was carried out in dichloromethane at 25 °C for 20–40 h. **3**/**4**/catalyst = 1.1/1.0/0.01. ^bIsolated yield by distillation based on **4**. ^cDetermined by ¹H NMR analysis. ^dDetermined by ¹H NMR spectra using chiral shift reagent Eu(dcm)₃. The OCH₃ singlet of the major enantiomer of *trans*-**5** always appeared at a higher field than that of the minor one. ^e*c* 1.0–1.5. ^fThe determination of the configuration is described in the text. ^g[α]²⁰_D -80° (*c* 1.2, THF). ^hConfiguration assigned by similarity in shifts using the chiral shift reagent. ⁱLiterature rotation for optically pure (4*S*,5*R*)-**5d** is [α]¹³_D +231° (*c* 0.4, THF): Ito, Y.; Ito, I.; Hirao, T.; Saegusa, T. *Synth. Commun.* 1974, 4, 97. ^jFor 60 h with 2 mol % of the catalyst.

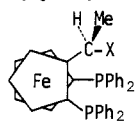
configuration of 4*S*,5*R*. Epimerization of (-)-*cis*-**5a** at C-4 with triethylamine in refluxing benzene^{8b} gave (4*S*,5*R*)-*trans*-**5a**, indicating that the configuration of (-)-*cis*-**5a** is 4*R*,5*R*.

Representative results summarized in Table I were obtained under similar conditions.¹⁶ High enantioselectivity (>90% ee) and high *trans* selectivity (>97%) were observed in the reaction of secondary and tertiary alkyl aldehydes **3e–g**, while acetaldehyde (**3d**) gave the lower selectivity. The gold catalyst was also effective for the reaction of α,β -unsaturated aldehydes **3b** and **3c** to give the corresponding oxazolines of 87% ee and 95% ee, respectively. It appears that the aldehydes with the larger substituent gave the higher enantio- and diastereoselectivity.

The high efficiency of the ferrocenylphosphine ligand **2** may be visualized by the transition state **A** where the dialkylamino



group at the end of the side chain on **2** participates in the formation of enolate of isocynoacetate coordinated with gold.¹⁷ It is probable that the participation may permit a favorable arrangement of the enolate and aldehyde on the gold(I) at the diastereomeric transition state to bring about high stereoselectivity. Use of the phosphine ligand **9**,¹⁸ which is analogous to **2a** but with 3-(diethylamino)propyl side chain, resulted in the formation of **5a** with 26% ee, indicating that the distance between the amino group and the ferrocene moiety is of crucial importance for the selectivity. The ferrocenylphosphine BPPFA (**10**)¹¹ which lacks



9: X = NMe(CH₂)₃NEt₂

10: X = NMe₂ (BPPFA)

the side chain, as well as chiraphos,¹⁹ DIOP,²⁰ and *p*-TolBINAP,²¹

(16) Satisfactory spectral and analytical data were obtained on all new compounds (see supplementary material).

(17) It has been observed that the copper-catalyzed aldol reaction is accelerated by the addition of triethylamine.^{7a}

(18) [α]²⁵_D -312° (*c* 0.69, chloroform). Prepared in a similar manner to **2b**.¹¹

(19) (*S,S*)-1,2-Bis(diphenylphosphino)butane: Fryzuk, M. D.; Bosnich, B. *J. Am. Chem. Soc.* 1977, 99, 6262.

(20) (-)-2,3-*O*-Isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)-butane: Kagan, H. B.; Dang, T. P. *J. Am. Chem. Soc.* 1972, 94, 6429.

gave almost racemic oxazolines. It should be noted that the use of gold is essential for the high selectivity, silver or copper catalyst being much less selective. This may be ascribed to the stronger affinity of gold(I) to phosphorus atoms.²² The ligand **2** can coordinate to gold with two phosphorus atoms leaving two nitrogen atoms free while silver or copper forms undesirable species by coordination of **2** with nitrogen atom(s) instead of phosphorus.²³

Supplementary Material Available: ¹H NMR data for the oxazolines **5** (1 page). Ordering information is given on any current masthead page.

(21) (*R*)-2,2'-Bis(di-*p*-tolylphosphino)-1,1'-binaphthyl: Takaya, H.; Mashima, K.; Koyano, K.; Yagi, M.; Kumobayashi, H.; Taketomi, T.; Akutagawa, S.; Noyori, R. *J. Org. Chem.* 1986, 51, 629.

(22) Pearson, R. G. *J. Chem. Ed.* 1968, 45, 581 and 643.

(23) The ³¹P and ¹H NMR spectra of the ferrocenylphosphine **2** complexed with gold(I), silver(I), or copper(I) supported the mode of the coordination, which will be fully described elsewhere.

Unusual pKs and Bond Paths of 1,3-Dilithiocyclobutane

Steven M. Bachrach

Los Alamos National Laboratory
Los Alamos, New Mexico 87545

Received April 4, 1986

The ion triplet model introduced by Streitwieser¹ interprets the stability of dianion salts in terms of the electrostatic interactions between the dianion and two bridging cations. The stability of the ion triplet is due to its four strong attractive interactions and only two weaker repulsive interactions. Streitwieser and Swanson² experimentally determined the difference between the first and second pKs of 9,9'-bifluorenyl and 2,2'-biindenyl to be less than one pK unit. They concluded that the low second pK results from the formation of a stable ion triplet. The experimental³ and calculational⁴ work by Schleyer confirms the existence of the ion triplet. In fact, Schleyer, Kos, and Kaufman⁵ have determined the disproportionation of 1,3-dilithio propane to be 19.4 kcal mol⁻¹ endothermic at the 3-21G level. This indicates that the second

(1) Streitwieser, A., Jr. *Acc. Chem. Res.* 1984, 17, 353.

(2) Streitwieser, A., Jr.; Swanson, J. T. *J. Am. Chem. Soc.* 1983, 105, 2502.

(3) Setzner, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* 1985, 24, 354.

(4) Schleyer, P. v. R. *Pure App. Chem.* 1983, 55, 355.

(5) Schleyer, P. v. R.; Kos, A. J.; Kaufman, E. *J. Am. Chem. Soc.* 1983, 105, 7617.

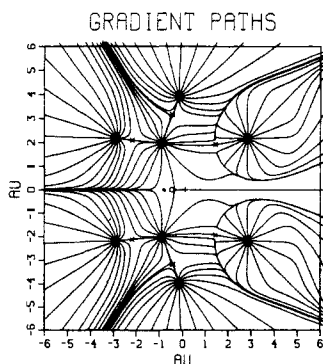
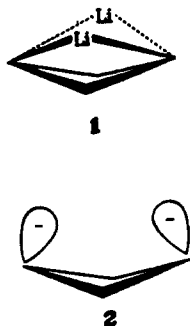


Figure 1. Gradient paths and bond paths of **1** for the plane containing the lithium and methylene carbon atoms. The lithium atoms are to the right. Bond and ring critical points are denoted by (*) and (O), respectively.

pK of propane is lower than the first. These intriguing results led us to search for other systems where the ion triplet is so stable as to result in the second pK being lower than the first.

A stable ion triplet requires the anions to be close enough together to affect adequate cation bridging but far enough apart to minimize their mutual repulsion. We chose to examine 1,3-dilithiocyclobutane (**1**). The anions are sufficiently separated



to minimize their mutual repulsion and the puckered cyclobutyl ring directs the anions above and toward the middle of the ring (see **2**). We anticipated the lithium atoms to eclipse the methylene carbons and bridge the two anions, forming a tight ion triplet. The optimized structure⁶ using the 3-21G basis set⁷ has form **1**.⁸ Using the disproportionation reaction



we find the heat of reaction to be $+7.3 \text{ kcal mol}^{-1}$ using the 3-21G basis set. This implies that the second pK of cyclobutane is 5.3 pK units lower than the first pK . Examination of this reaction at the 6-31G*//6-31G*⁹ level indicates the second pK is 4.8 pK units below the first. This larger basis set effectively eliminates superposition error¹⁰ and confirms that the result is not basis set dependent.

(6) All optimizations were carried out with GAUSSIAN-82: Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A., Carnegie-Mellon University. The CTSS version was modified by Dr. Rich Martin.

(7) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939.

(8) The geometrical parameters of **1** at 3-21G (6-31G*) in angstroms and degrees: $r_{C_1-C_2}$ 1.5970 (1.5590); r_{C_1-Li} 2.1430 (2.1394); r_{C_2-Li} 1.9840 (1.9639); r_{C_1-H} 1.0828 (1.0864); $r_{C_2-H_{eq}}$ 1.1063 (1.1129); $r_{C_2-H_{ax}}$ 1.0865 (1.0905); ring pucker angle 127.83 (128.67); $H-C_1$ -center 127.50 (128.22); $H_{eq}-C_2$ -center 159.23 (159.14); $H_{ax}-C_2$ -center 95.34 (97.20).

(9) (a) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257. (b) Dill, J. D.; Pople, J. A. *J. Chem. Phys.* **1975**, *62*, 2921. (c) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

(10) Bachrach, S. M.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 2283.

The ion triplet model is based solely on electrostatic interactions. Recent results¹¹ suggest the carbon–lithium bond is primarily ionic. In order to further confirm the ionicity, we applied Bader's topological analysis¹² to 1,3-dilithiocyclobutane. The topological method uses the value of the Laplacian of the electron density, $\nabla^2\rho$, at the bond critical point, r_c , to determine the nature of the bond. A negative value of $\nabla^2\rho(r_c)$ implies a concentration of density along the bond path and, therefore, a covalent bond.¹³ A positive value of $\nabla^2\rho(r_c)$ indicates that density is moved away from the bond critical point. This occurs when two closed-shell systems interact and the exclusion principle requires a decrease in density in the interaction region. Bader¹³ has shown that positive values of $\nabla^2\rho(r_c)$ occur for hydrogen bonds, van der Waals complexes, and ionic bonds. Cremer and Kraka¹⁴ add an additional test for determining the type of bonding using the total local energy density $H(r)$. If $H(r_c) < 0$, indicating the dominance of potential energy and, thus, the concentration of charge, the bond is covalent. For the case $H(r_c) > 0$, a situation where kinetic energy dominates, the bond is ionic, or some other closed-shell interaction.

The value¹⁵ of $\nabla^2\rho$ at the C_1 –Li critical point in 1,3-dilithiocyclobutane is $+0.1822 \text{ e}^- \text{ au}^{-5}$ which can be compared with the value of $-0.3777 \text{ e}^- \text{ au}^{-5}$ for the C–C critical point. The value of $H(r_c)$ at the C_1 –Li critical point is $+0.0039 \text{ hartrees au}^{-3}$. These results confirm the notion of an ionic carbon–lithium bond.

Each anionic carbon is connected to five bond paths: one to hydrogen, one to each neighbor ring carbon, and one to each lithium. These five paths are expected as one anticipates that lithium will bridge the two anions.

Unexpectedly, bond critical points between each lithium and its closest methylenic carbon neighbor were found. The gradient and bond paths for **1** are presented in Figure 1.¹⁶ The values of $\nabla^2\rho$ and H at these critical points are $+0.2366 \text{ e}^- \text{ au}^{-5}$ and $+0.0074 \text{ hartrees au}^{-3}$, respectively, indicating an ionic interaction. Bader has defined the existence of a bond path in a system at equilibrium to be the necessary and sufficient condition for having a chemical bond.¹⁷ Since **1** is an energy minimum,¹⁸ one is forced to conclude that five bonds, four covalent and one ionic, terminate at each methylenic carbon.

This conclusion should not be misconstrued as suggesting pentavalency. The topological method does not rigorously define valency. However, using the definition of valency as the number of shared electron pairs,¹⁹ we can describe the methylenic carbon as tetravalent but pentacoordinate. The four valencies are indicated by the four covalent bonds. The fifth coordination²⁰ arises from the ionic interaction of the lithium cation polarizing the density in the carbon basin. Additionally, the anionic carbons can be described as trivalent and pentacoordinate.

Acknowledgment. I thank Dr. James P. Ritchie for helpful discussions, Professors Bader and Schleyer for comments, and the support of a Director's Post-Doctoral Fellowship.

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(15) The author thanks Prof. Bader for a copy of EXTREME used to determine the critical points.

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(18) Vibrational frequency analysis of **1** found no imaginary frequencies.

(19) Lewis, G. N. *Valence and the Structure of Atoms and Molecules*; Chemical Catalog Co., NY, 1926.

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