Pergamon

Tetrahedron Letters, Vol. 36, No. 2, pp. 217-220, 1995
Elsevier Science Ltd
Printed in Great Britain
0040-4039/95 $9.50+0.00

0040-4039(94)02226-7

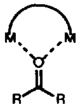
Simultaneous Coordination of 2, 6-Dimethylpyranone by 1, 8-Naphthalenediylbis(dichloroborane)

Michael Reilly and Taeboem Oh*

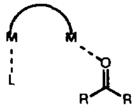
Department of Chemistry, State University of New York, Binghamton, NY 13902-6000

Abstract: We show evidence of simultaneous coordination of 2, 6-dimethylpyranone by 1, 8-naphthalenediylbis(dichloroborane) in solution.

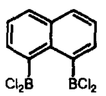
Lewis acid complexation to carbonyl compounds is known to have a dramatic effect on reactivity and selectivity in a variety of reactions.[1] One recent development has been in the area of asymmetric catalysis by Lewis acids.[2] As part of this development, Lewis acid-carbonyl group interactions have been under continuing investigation. Simultaneous coordination of a carbonyl group by two Lewis acids is a potential way to increase the organizational role played by the Lewis acid as well as doubly activate the substrate.[3,4] In a recent investigation, Wuest has shown that in an intramolecular case, where the carbonyl group was tethered by two aluminum Lewis acids, both Lewis acids simultaneously coordinated to the central ketone.[5,6] Hine has reported that the two hydroxyl groups of biphenylenediol can simultaneously hydrogen bond to a carbonyl group.[7] Kelly has also shown that biphenylenediol promotes Diels-Alder reactions.[8] Our investigation into this area is two fold. One approach consists of a bimetallic chiral Lewis acid which can simultaneously coordinate to a carbonyl group (Structure **1**). The second is that each Lewis acid plays an organizational role in coordinating a chiral ligand and a carbonyl group (Structure **2**). The subject of this paper involves the investigation of the equilibrium as shown in equation 1 and to show that structures of the type **1** and **2** are feasible.



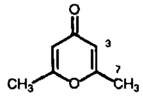
1



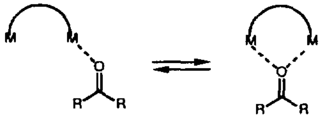
2



3



4



5 **6** (1)

For this investigation, we have chosen 1,8-naphthalenediylbis(dichloroborane)[9], **3**, and 2,6-dimethylpyranone, **4**. These compounds were chosen for their simple ^{1}H NMR spectra and their availability. There is an added advantage in that the ether oxygen of the pyranone increases the basicity of the carbonyl group. The ^{1}H NMR spectrum of a 2:1 mixture of pyranone **4** and BCl_3 show four sharp distinct signals indicating a slow equilibrium between complexed (δ 7.40 and 2.72 ppm) and non-complexed (δ 6.20 and 2.29 ppm) pyranone at room temperature. The same was true for a 2:1 mixture of the pyranone and phenylboron dichloride (complexed, δ 7.32, 2.70 ppm; non-complexed, δ 6.38 and 2.35 ppm). Next, a titration experiment was carried out with **3** and **4** and monitored by ^{1}H NMR (Figure 1). With two equivalents of ketone **4**, there is a downfield chemical shift of 0.64 ppm for H-3 and 0.13 ppm for H-7 (resonances a and c, figure 1b).

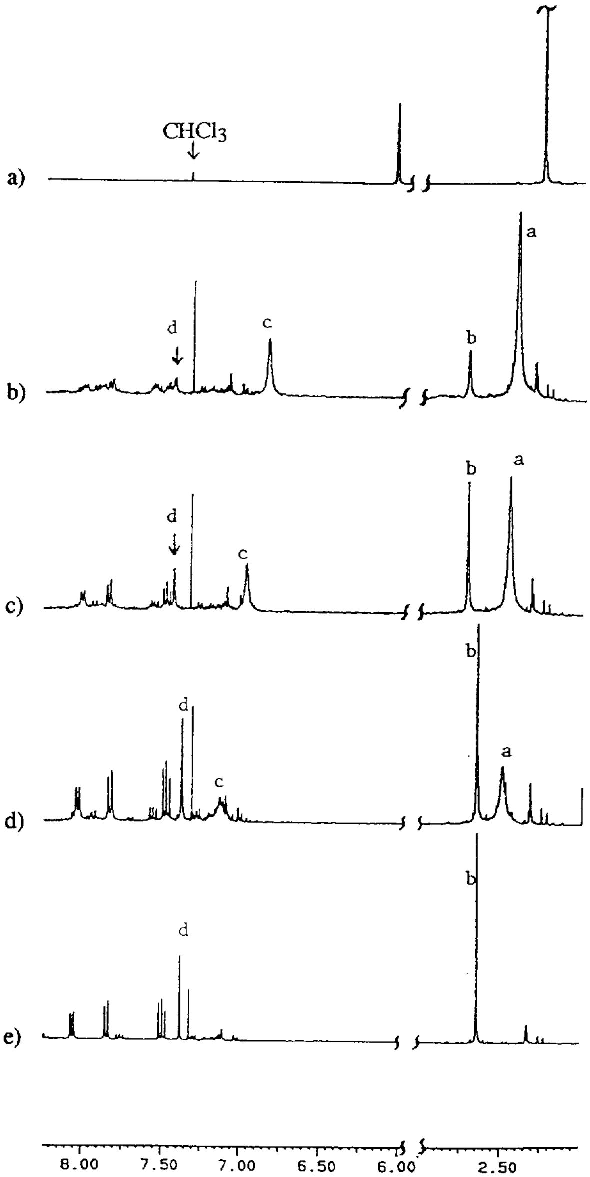
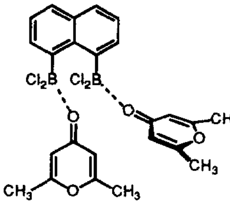


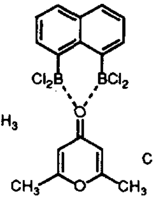
Figure 1. ^{1}H NMR spectra of 2,6-dimethylpyranone-Lewis acid complex ($CDCl_3$-CD_2Cl_2, 0.05 M in Lewis acid), a) **4**, b) 2:1, **4**:**3**, c)1.5:1, **4**:**3**, d) 1:1, **4**:**3**, e) 1:2, **4**:**3**.

There is also small set of signals arising at 7.39 and 2.70 ppm (resonances b and d). As the ratio of Lewis acid **3** is increased, the signal intensities of a and c weaken until they are completely suppressed while the signal intensities of b and d increase to completely replace resonances a and c. The resonances a and c are broad and the aromatic signals of **3** are complex (Figure 1b). The signals b and d are sharp and the corresponding aromatic signals are simple (Figure 1e). The spectrum 1d shows that there is no resonance corresponding to free pyranone **4**.

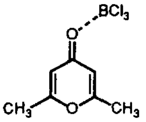
Spectrum 1b indicates that all of ketone **4** is coordinated. This suggests a complex of type **7** where two ketones are interacting with **3**. Complex **7** has several possible conformers involving each donor-acceptor bond which should result in signal broadening and complex aromatic signals. Complex **8** is a highly rigid system which should result in sharp signals for the ketone and the naphthalene protons and this is what has been observed (Figure 1e). The signals do not have sharp titration points. With two equivalents of ketone **4**, there is still a small amount of complex **8** (Figure 1b). With one equivalent of **4**, there is a significant amount of complex **7** (Figure 1d), however, with excess Lewis acid **3** the signal due to complex **7** is totally supressed.



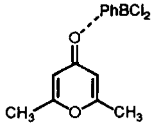
7



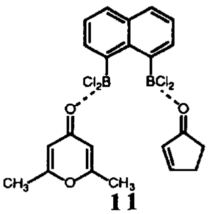
8



9



10

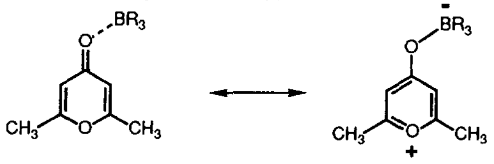


11

Low temperature ^{1}H NMR shows that the signals from complex **8** show no chemical shift changes indicating a highly rigid system. The signals from complex **7**, drifted and became sharper. A new signal arose at 2.75 ppm.

In an effort to further substantiate the existence of the structures **7**, **8**, **9**, and **10** , a comparison of the shifts of the characteristic stretching frequencies of the carbonyl and the carbon-carbon double bond was undertaken using FT-IR. The carbonyl stretch of the coordinated pyranone **7**, **8**, **9**, and **10** show a large shift (Table I). This shift indicates weakening of the carbon-oxygen double bond.[10] This is presumably caused by resonance hybrid **12** (Equation 2). Complex **8**, where both nonbonding lone pairs are coordinated, shows the largest shift and complex **7** shows the least shift. The two C=O and C=C stretches of complex **7** are indicative of the two unequivalent complexes of pyranone. Comparisons of ^{1}H NMR shifts show similar trends (Table II).[11] From the shift of the carbonyl stretch and the chemical shift, the Lewis acidity of **3**, when one boron atom coordinates to ketone **4**, is weaker than $PhBCl_2$. When the two boron atoms coordinate to the ketone simultaneously the Lewis acidity is comparable to BCl_3.

The ^{13}C resonance of the carbonyl carbon of pyranone, complex **7**, and complex **8** were observed at



12

(2)

TABLE I. IR absorption of C=O and C=C (cm^{-1})

Entry	Complex	C=O	C=C	C=C
1	**6**	1664.5	1613.7	1597.0
2	**7**	1498.0	1645.9	1558.0
		1495.8	1633.7	
3	**8**	1492.8	1646.9	1552.7
4	**9**	1499.2	1648.0	1555.8
5	**10**	1506.0	1650.3	1557.7

TABLE II. Chemical Shift Comparisons

Entry	Complex	H-2(δ)	H-7(δ)
1	**6**	6.05	2.24
2	**7**	6.83	2.42
3	**8**	7.43	2.66
4	**9**	7.40	2.72
5	**10**	7.34	2.70

180.2, 180.4, and 178.0 ppm respectively. There is a 0.2 ppm shift downfield for the carbonyl peak of complex **7**. The 2.2 ppm upfield shift of complex **8**, again, is indicative of resonane hybrid **11**. It should be noted that the 178.0 ppm indicates that complex **8** exhibits a carbonyl moiety. These chemical shifts are consistent with the literature value in a bidentate coordination of an intramolecular system.[5]

As noted earlier, a second equivalent of pyranone prevents the formation of complex **8**. Addition of cyclopentenone, a weaker Lewis base than pyranone, also prevents the formation of complex **8**. The ^1H NMR chemical shift of cyclopentenone and pyranone indicates that each are coordinated to one boron Lewis acid (Structure **11**). However, Lewis bases weaker than cyclopentenone do not prevent the formation of **8**. For example, addition of one equivalent of tetrahydrofuran shows complex **8** still exists and there was no indication of coordination to tetrahydrofuran.

The work presented here is consistent with simultaneous coordination of a carbonyl group with a boron Lewis acid. There are no sharp titration points and the fact that the equilibrium can be manipulated between complex **7** and **8** show that simultaneous coordination of carbonyl groups can be enthalpically feasible. The 1, 8-Naphthalenediylbis(dichloroborane) can also coordinate to two different Lewis bases. This behavior has several implications including the potential use of these type of Lewis acids to play a role in organizing two substrates.

REFERENCES AND NOTES

1. For review of this area, see: Shambayati, S.; Schreiber, S. L. In *Comprehensive Organic Synthesis: Selectivity, Strategy & Efficiency in Modern Organic Chemistry*", B. M. Trost, I. Fleming and L. A. Paquette, Eds., Pergamon Press, New York, 1991, Vol 1, Chapter 1.10, p.283-324.
2. For reviews, see: a) Kagan, H. B.; Riant, O. *Chem. Rev.* **1992**, *92*, 1007-1019. b) Narasaka, K. *Synthesis* **1991**, 1-11. c) Oh, T.; Reilly, M. *Org. Prep. Proced. Int.*, **1994**, 26, 129-158.
3. Beauchamp, A. L.; Olivier, M. J.; Wuest, J. D.; Zacharie, B. *J. Am. Chem. Soc.* **1986**, *108*, 73-77.
4. For a theoretical study of formaldehyde complexed to two equivalents of borane, see: Lepage, T. J.; Wiberg, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 6642-6650.
5. Sharma, V.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **1992**, *114*, 7931-7933.
6. For related complexes, see: a) Adams, R. D.; Chen, G.; Chen, L.; Wu, W.; Yin, J. *J. Am. Chem. Soc.* **1991**, *113*, 9406-9408. b) Waymouth, R. W.; Potter, K. S.; Schaefer, W. P.; Grubbs, R. H. *Organometallics* **1990**, *9*, 2843-2846. c) Erker, G.; Dorf, U.; Czisch, P.; Petersen, J. L. *Organometallics* **1986**, *5*, 668-676. d) Adams, H.; Bailey, N. A.; Gauntlett, J. T.; Winter, M. J. *J. Chem. Soc., Chem. Commun.* **1984**, 1360-1361.
7. a) Hine, J.; Anh, K. *J. Org. Chem.* **1987**, *52*, 2083-2086. b) Hine, J.; Anh, K. *J. Org. Chem.* **1987**, *52*, 2089-2091.
8. Kelly, T. R.; Meghani, P.; Ekkundi, V. *Tetrahedron Lett.* **1990**, *31*, 3381-3384.
9. Katz, H. E. *Organometallics* **1987**, *6*, 1134-1136. b) Katz, H. E. *J. Org. Chem.* **1985**, *50*, 2575-2576.
10. a) reference 5. b) Vedejs, E.; Erdman, D. E.; Powell, D. R. *J. Org. Chem.* **1993**, *58*, 2840-2845.
11. a) Childs, R. F.; Mulholland, D. L.; Nixon, A. *Can. J. Chem.* **1982**, *60*, 801-808. b) Laszlo, P.; Teston, M. *J. Am. Chem. Soc.* **1990**, *112*, 8750-8754.

(*Received in USA* 4 *October* 1994; *revised* 2 *November* 1994; *accepted* 10 *November* 1994)