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Preliminary communication

ON THE STABILITY AND DECOMPOSITION OF η^6-(2-LITHIOCHLOROBENZENE)TRICARBONYLCHROMIUM(0)

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Summary

The decomposition of η^6-(2-lithiochlorobenzene)tricarbonylchromium(0) (I) was found to follow first order kinetics with $k_{dec} = 5.1 \times 10^{-3}$ min^{-1} at 0°C, the half life of I being 136 min at 0°C. While this dependence strongly suggests intermediacy of η^6-(benzyne)tricarbonylchromium, trapping experiments were successful in only low yield.

Coordination of a tricarbonylchromium unit to an arene enhances the kinetic acidity of the ring C—H bonds [1]. Metalation with alkyllithium reagents produces η^6-(lithioarene)tricarbonylchromium(0) complexes which have been characterized spectroscopically [1e] and have been trapped by reaction with electrophiles [1]. Parallel with directing effects observed in the metalation of uncomplexed arenes, η^6-anisole and η^6-halobenzene ligands are metalated in the *ortho* position [1]. The increased rate of deprotonation due to the $Cr(CO)_3$ unit allows direct formation of η^6-(2-lithiochlorobenzene)tricarbonylchromium(0) (I) and η^6-(2-lithiofluorobenzene)tricarbonylchromium(0) (II) in high efficiency; parallel reactions with free chlorobenzene and fluorobenzene are not possible. In addition, the trapping of I with electrophiles at −20°C [1a] suggested a thermal stability for I much higher than that of 2-lithiochlorobenzene, where decomposition within minutes at −78°C has been noted [2]. This decomposition produces 1,2-dehydrobenzene, as evidenced by characteristic in situ trapping reactions [3]. Neither the rate nor the mode of decomposition of I or II has been studied; a benzyne complex III is predicted, in a coordination mode for the benzyne ligand not previously observed [4]. Here we report efforts to define the thermal stability of I and to test for the presence of III.

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We have studied the decomposition of I, between –50°C and +33°C (ether solvent). In some cases, furan was added as a trapping agent for a benzyne complex, after lithiation appeared to be complete. For example, reaction of η^6-(chlorobenzene)tricarbonylchromium(0) with butyllithium at –35°C for 15 min, followed by addition of CO_2 gives η^6-(2-chlorobenzoic acid)tricarbonylchromium(0) in 98% yield [3a]. If the solution is allowed to warm to 0°C decomposition of I proceeds slowly; the clear orange solution turns dark brown and a solid forms. After ca. 1 h at 25°C, addition of aqueous HCl regenerates η^6-(chlorobenzene)tricarbonylchromium(0), 44% recovery. Oxidation of the remainder of the crude product with excess iodine gave a complex mixture of free arenes; the major component was identified as 2-chlorobiphenyl by GC-MS analysis, but the yield was less than 5%. Under the same conditions but in the presence of excess furan, no new product incorporating the furan unit was detected by GC-MS. Heating the solution of I with excess furan in ether at reflux for 40 min led to complete disappearance of I and formation of a complex mixture. After oxidation with excess iodine, trituration with ether, and analysis of the ether soluble material (34% recovery based on chlorobenzene), showed 13 significant components. The major components were identified as naphthalene, 1-hydroxynaphthalene, 1,4-oxo-1,4-dihydronaphthalene, and 2-chlorobiphenyl, all of which can be attributed to a benzyne intermediate. However, the inefficient and unselective trapping does not establish the presence of complex III as a major intermediate.

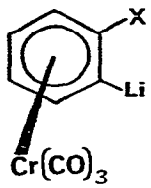
TABLE 1

MONITORING OF THE DISAPPEARANCE OF *o*-LITHIOCHLOROBENZENETRICARBONYLCHROMIUM(0)

Aliquot number	Time (min)	ln C_0/C
1	13	0.28
2	20	0.43
3	35	0.51
4	55	0.55
5	80	0.67
6	110	0.85
7	140	0.95
8	200	1.16
9	265	1.38
10	330	1.75
11	405	2.11
12	545	2.96
13	640	3.79

Careful monitoring of the decomposition of I (0.1 *M* in ether) at 0°C (±2°) showed first order dependence on the concentration of I. Aliquots of the solution were added to excess iodine and the amount of 2-chloroiodobenzene (quantitative GC analysis using 1-methylnaphthalene as internal standard) formed was taken as a measure of η^6-(2-lithiochlorobenzene)tricarbonylchromium(0) remaining (Table 1). A plot of ln C_0/C vs. time gave a slope of 5.1×10^{-3} min^{-1} with a correlation coefficient of 0.984 over the range ln C_0/C 0.28 to 3.79. The half life for I at 0°C is 136 min. The stability of I

is strongly increased compared to *o*-chlorolithiobenzene and, while the benzyne III cannot be observed directly nor trapped efficiently, the simple first order decomposition of I is consistent with the intermediacy of III.



(I, X = ce;
II, X = F)

(III)

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References

1 (a) A.N. Nesmeyanov, N.E. Kolobova, K.N. Anisimov, and Yu.V. Makarov, Bull. Akad. Sci; USSR, Div. Chem. Sci., (1968) 2538; (b) M.F. Semmelhack, J. Bisaha, and M. Czarny, J. Amer. Chem. Soc., 101 (1979) 768; (c) J. Bisaha, PhD Thesis, Cornell University, 1979; (d) R.J. Card and W.S. Trahanovsky, J. Org. Chem., 45 (1980) 2554; (e) R.J. Card and W.S. Trahanovsky, ibid., 45 (1980) 2560; (f) R.J. Card, PhD Thesis, Iowa State University, 1975.
2 O.M. Nefedov and A.I. Dyachenko, Dokl. Akad. Nauk USSR, 198 (1971) 593.
3 (a) H. Gilman and R. Gorsick, J. Amer. Chem. Soc., 78 (1956) 2217; (b) for a review, see: R.W. Hoffman, Dehydrobenzene and Cycloalkynes, Academic Press, New York, 1967, p. 43ff.
4 For a review of metal-coordinated benzyne, see: F.H. Köhler, Chemie in Unserer Zeit, 11 (1977) 190.

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AUTHOR INDEX