Journal of Organometallic Chemistry, 246 (1983) C53–C56
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

THE HEATS OF IODINATION OF CHROMIUM TRICARBONYL COMPLEXES OF ARENES AND CYCLOHEPTATRIENE

CARL D. HOFF
Department of Chemistry, University of Miami, Coral Gables, FL 33124 (U.S.A.)

(Received October 7th, 1982)

Summary

The heats of iodination of chromium tricarbonyl complexes of benzene, toluene, mesitylene, and cycloheptatriene have been measured by solution calorimetry in tetrahydrofuran at 25°C. The order of the Cr—ligand strength is: mesitylene > cycloheptatriene > toluene > benzene. This order differs from that determined by high temperature decomposition and iodination and is confirmed by chemical equilibration studies.

The reaction of arenechromium tricarbonyls with iodine in THF has been widely used to liberate the coordinated arene [1]. We have measured the heat given off in this reaction in order to determine the thermodynamic stability of benzene, toluene, mesitylene, and cycloheptatriene complexes of chromium tricarbonyl. The reactions studied are exemplified by those shown in eq. 1 and 2:

$$\mathrm{Arene^1Cr(CO)_3} + 3/2\ \mathrm{I_2} \xrightarrow{\mathrm{THF}} \mathrm{Arene^1} + \mathrm{CrI_3(THF)}_n + 3\ \mathrm{CO} \qquad (1)$$

$$\mathrm{Arene^2Cr(CO)_3} + 3/2\ \mathrm{I_2} \xrightarrow{\mathrm{THF}} \mathrm{Arene^2} + \mathrm{CrI_3(THF)}_n + 3\ \mathrm{CO} \qquad (2)$$

In order to determine absolute heats of formation, all relevant heats of mixing and solution must be determined. Such work is in progress, however of more importance is the difference between these measurements. Subtracting eq. 2 from eq. 1 gives directly the equation representing the substitution of one arene for another since all other terms cancel out:

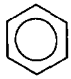
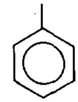
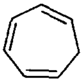
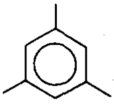
$$\mathrm{Arene^1Cr(CO)_3} + \mathrm{Arene^2} \longrightarrow \mathrm{Arene^2Cr(CO)_3} + \mathrm{Arene^1} \qquad (3)$$

0022-328X/83/$03.00

TABLE 1

HEATS OF IODINATION AND ESTIMATED ENTHALPIES FOR THE ARENE EXCHANGE:

BenzeneCr(CO)$_3$ + Arene → AreneCr(CO)$_3$ + Benzene

Ligand	Heat of iodination [a,b] (kcal/mol)		Enthalpy for arene exchange [c] (this work) (kcal/mol)	Enthalpy for arene exchange [d] (kcal/mol) [2—5]
	—40.7 —40.0 —41.5 —40.0 —40.0	—40.4 ± 0.6	0	0
	—39.3 —36.9 —40.9 —38.4 —39.6	—39.0 ± 1.5	—1.4	+0.8
	—34.0 —35.2 —33.4 —33.7	—34.1 ± 0.8	—6.3	+9.1
	—29.8 —33.3 —29.0 —31.4	—30.9 ± 1.9	—9.5	—3.6

[a] Typical reaction conditions involved addition of 0.12 g of the crystalline complex to a solution of 2.0 g of I_2 in 200 ml of rigorously dry and oxygen free THF. If the solvent is not rigorously dry a considerably more exothermic reaction occurs, due to hydration of the $CrI_3(THF)_n$ product. [b] The calorimeter used was purchased from Guild Corporation, Bethel Park, Pa., (model 400) and was installed (with some modifications) in an inert atmosphere dry box purchased from Vacuum-Atmospheres Inc., Hawthorne, California. The heats of iodination were calibrated electrically. The calorimeter system was standardized using the "TRIS" reaction [16] before establishing an inert atmosphere. [c] The enthalpy of this reaction can be viewed as a relative order of stability with benzenechromium tricarbonyl taken as reference.
[d] Data calculated using heats of formation for the complexes taken from ref. 3 and heats of formation for the ligands taken from ref. 15.

It can reasonably be assumed that solution effects are small and tend to cancel for this system*. Thus the enthalpy of arene exchange can be determined directly from the heats of iodination, and reflects the relative Cr—arene bond strength. The heats of iodination can be measured with fair accuracy by solution calorimetry, and data obtained in this study are shown in Table 1.

The enhanced stability of the Cr—arene bond upon increasing methyl substitution is in keeping with many observations in synthetic organometallic chemistry [6]. What is surprising is that the Cr—cycloheptatriene bond is stronger than the Cr—benzene and Cr—toluene bond but weaker than the Cr—mesitylene bond. Furthermore, this conclusion is in contrast to that determined by high temperature decomposition and iodination studies [2—5].

---

*Initial work indicates that this assumption is correct within experimental error [7].

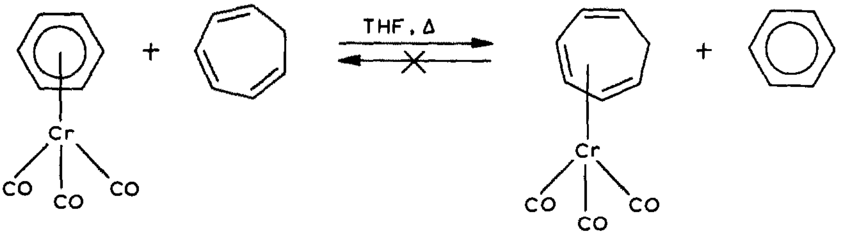
Cycloheptatrienechromium tricarbonyl is relatively labile [8] and has been reported to undergo substitution with various reagents as shown below in eq. 4:

$$\text{cyclo-}C_7H_8Cr(CO)_3 + 3\,L \rightarrow L_3Cr(CO)_3 + \text{cyclo-}C_7H_8 \qquad (4)$$

L = PR_3, RNC, mesitylene, etc.)

While mesitylene has been shown to substitute for cycloheptatriene, no mention has been made of this reaction taking place for benzene or toluene [8]. It is relevant to note that the major product from the reaction of $Cr(CO)_6$ with phenylcycloheptatriene (which could coordinate through either the arene or cycloheptatriene) coordinates the substituted cycloheptatriene unit rather than the arene [9—11]. These observations are in keeping with the relative order of stability determined in our work, however they are not definitive.

In order to establish this point, competition experiments have been done under conditions similar to those used by Strohmeier and coworkers studying the kinetics of arene substitution [12—14]. For example, heating benzenechromium tricarbonyl in THF in the presence of a tenfold excess of both benzene and cycloheptatriene in sealed tubes (90°C for 14 days, or 135°C for 20 h) results in near complete conversion of benzenechromium tricarbonyl to the cycloheptatriene complex as shown in eq. 5.



(5)

Starting from cycloheptatrienechromium tricarbonyl does not lead to production of benzenechromium tricarbonyl under equivalent conditions. Since the cycloheptatriene complex has been shown to be more labile to substitution [12—14], this provides strong support for our work. Observations using other arenes are consistent with the order of stabilities measured by solution calorimetry.

The temperature/time curves provide information about the kinetics of iodination of these complexes. The relative rates under equivalent conditions are: cycloheptatriene > benzene ≈ toluene > mesitylene. Thus while the cycloheptatriene complex enjoys considerable thermodynamic stability, it is kinetically the most reactive.

This work indicates that, at least for the chromium complexes studied, conclusions drawn from high temperature methods may be subject to the same limitations associated with static bomb calorimetry of organometallic compounds [15]. Further thermodynamic studies on these and related compounds are in progress.

Acknowledgements. The author acknowledges support of this work through grants from the Petroleum Research Fund administered by the American Chemical Society and by the Research Corporation. It is also a pleasure to thank Dr. John Connolly of the University of Missouri-Kansas City for the loan of calorimetry equipment, and Dr. Cecil Criss of the University of Miami for helpful discussions.

References

1 M.F. Semmelhack, in D. Seyferth (Ed.), J. Organometal. Chem. Libr., 1, Elsevier, Amsterdam, 1976, p. 361—395.
2 J.A. Connor, Topics Curr. Chem., 71 (1977) 71.
3 J.A. Connor, H.A. Skinner, and Y. Virmani, J. Chem. Soc. Faraday I, 69 (1973) 1218.
4 F.A. Adedeji, D.L.S. Brown, J.A. Connor, M.L. Leung, M. Paz-Andrade, and H.A. Skinner, J. Organometal Chem., 97 (1975) 221.
5 D.L.S. Brown, J.A. Connor, C.P. Demain, M.L. Leung, J.A. Martinho-Simoes, H.A. Skinner, and M.T.Z. Moattar, J. Organometal. Chem., 142 (1977) 321.
6 W.E. Silverthorn, Adv. Organometal. Chem., 13 (1975) 48.
7 C.D. Hoff, unpublished results.
8 R.P.A. Sneeden, Organochromium Compounds, Academic Press, New York, 1975.
9 E.W. Abel, M.A. Bennett, R. Burton, and G. Wilkinson, J. Chem. Soc., (1958) 4559.
10 J.D. Munro and P.L. Pauson, J. Chem. Soc., (1961) 3475.
11 P.E. Baikie and O.S. Mills, J. Chem. Soc. A., (1968) 2704.
12 W. Strohmeier and H. Mittnacht, Chem. Ber., 93 (1960) 2085.
13 W. Strohmeier and H. Mittnacht, Z. Phys. Chem., 29 (1961) 339.
14 W. Strohmeier and E.H. Staricco, Z. Phys. Chem., 38 (1963) 315.
15 J.D. Cox and G. Pilcher, Thermochemistry of Organic and Organometallic Compounds, Academic Press, New York, 1970.
16 E.J. Prosen and M.V. Kilday, J. Res. National Bureau of Standards, 77A (1973) 581.