Journal of Organometallic Chemistry, 234 (1982) C20—C22
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

COMPLEX FORMATION BETWEEN BENZENE AND [Cr(CO)$_3$(η^6-ARENE)]

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(Received May 10th, 1982)

Summary

1/1 complex formation between benzene-d_6 and [Cr(CO)$_3$(η^6-arene)] (arene = C_6H_5R (R = H, Me, OMe, Cl), $C_{10}H_8$) has been observed by PMR spectroscopy. The equilibrium constant in the case of arene = C_6H_6 confirms earlier chemical evidence that the [Cr(CO)$_3$] unit exerts an electron-withdrawing effect upon aromatic rings which is approximately equal to that of the nitro group.

There have been many reports of the formation of charge transfer complexes between the compounds [Cr(CO)$_3$(η^6-arene)] and electron acceptors, such as tetracyanoethene and trinitrobenzene [1]. Until recently, it has been assumed that the acceptor receives metal electron density through the coordinated arene in the so-called "face-to-face" stacking arrangement. However, Kobayashi, Kobayashi and Kaizu [2] have now shown that there is a direct interaction between the metal *d*-orbitals and the acceptor with the latter sited beneath the base of the pyramid formed by the three carbonyl groups (see structure 1).

The [Cr(CO)$_3$] unit plays a role of overall electron-withdrawal from the arene in [Cr(CO)$_3$(η^6-arene)]. This characteristic has been exploited in reactions of the coordinated arene with nucleophiles and, indeed, in such reactions the [Cr(CO)$_3$] unit shows an electron withdrawing power similar in magnitude to that of the nitro group [3].

In the light of these findings we have examined the possibility that [Cr(CO)$_3$(η^6-arene)] may be able to act as an electron acceptor in charge transfer complex formation, the electron donor interacting directly with the arene ring in this case. We have chosen to study arenes as electron donors (see structure 2) and have examined the interaction of benzene-d_6 and [Cr(CO)$_3$(η^6-arene)] (arene = C_6H_6, $C_6H_5CH_3$, C_6H_5 OCH_3, C_6H_5Cl and $C_{10}H_8$) in CCl_4 by PMR spectroscopy. We are, of course, aware that aromatic solvent induced shifts

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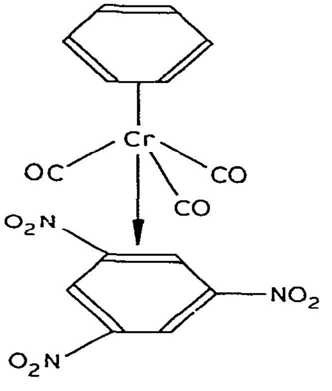

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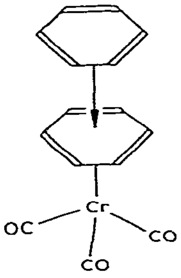

(2)

(ASIS) have been explained in terms of effects other than charge transfer complex formation [4]. However, it is now accepted that a solvent cluster model is probably most appropriate for weakly interacting systems, while strong interaction is probably best described by charge transfer [5].

The chemical shift data for the above systems were, therefore, treated by the standard method for 1/1 complex formation [6] and a typical plot of $\Delta/[D]_0$ versus Δ (Δ is the measured chemical shift) is shown in Fig. 1. Values of Δ_0 and the equilibrium constant, K, are shown in Table 1. The accuracy of the data preclude detailed discussion of substituent effects at this stage. However, it is notable that the value of the equilibrium constant in the case of $[Cr(CO)_3(\eta^6\text{-}C_6H_6)]$ ($0.126 \pm 0.009\ M^{-1}$) is almost identical to that found in this study for the nitrobenzene/benzene-d_6 system ($K = 0.13 \pm 0.01\ M^{-1}$, $\Delta_0 = -78 \pm 7$ Hz). We are thus able to confirm by spectroscopic means the previous findings that the $[Cr(CO)_3]$ unit has an electron withdrawing power upon aromatic rings approximately equal in magnitude to that of the nitro group.

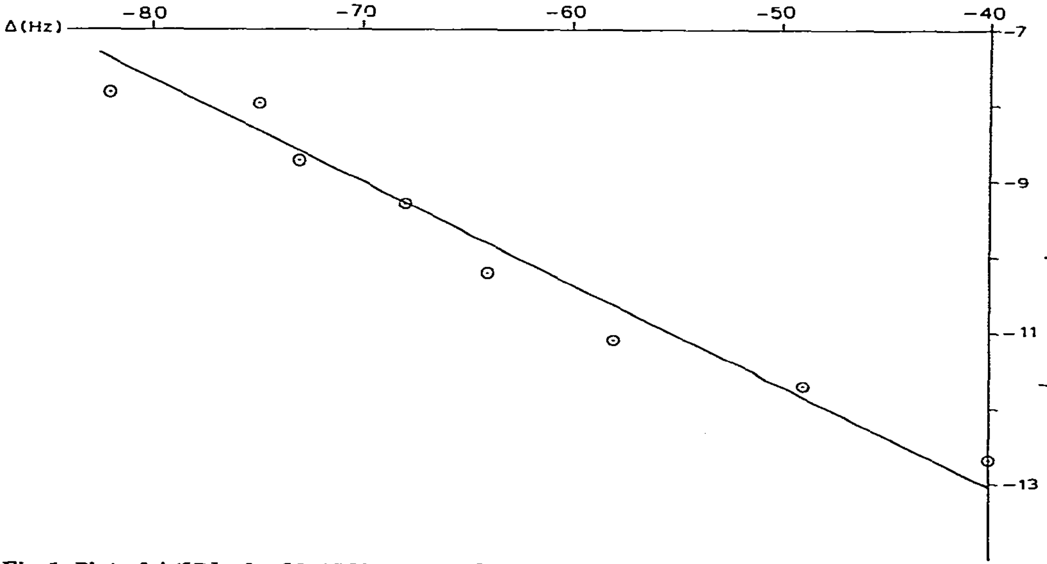

Fig. 1. Plot of $\Delta/[D]_0$ for $[Cr(CO)_3(\eta\text{-}C_6H_6)]$ and C_6D_6.

TABLE 1

STABILITY CONSTANT DATA FOR COMPLEX FORMATION BETWEEN [$Cr(CO)_3(\eta^6$-arene)] AND C_6D_6

Arene	$K (M^{-1})$	Δ_0 (Hz)
Benzene	0.126 ± 0.009	−143 ± 10
Toluene	0.163 ± 0.018	−118 ± 19
Anisole	0.164 ± 0.052	−113 ± 30
Chlorobenzene	0.146 ± 0.012	−119 ± 9
Naphthalene	0.119 ± 0.012	−122 ± 12

Furthermore, compounds of the type [$Cr(CO)_3(\eta^6$-arene)] represent relatively uncommon examples of molecules capable of displaying both electron donor and electron acceptor properties in charge-transfer complex formation.

Acknowledgement

We thank the Science and Engineering Research Council for financial support.

References

1 G. Huttner, E.O. Fischer, R.D. Carter, A.T. McPhail and G.A. Sim, J. Organometal. Chem., 6 (1966) 288; H. Kobayashi, M. Kobayashi and Y. Kaizu, Bull. Chem. Soc. Japan, 46 (1973) 3109; H. Kobayashi, M. Kobayashi and Y. Kaizu, ibid., 48 (1975) 1222.

2 H. Kobayashi, K. Kobayashi and Y. Kaizu, Inorg. Chem., 20 (1981) 4135.

3 M.F. Semmelhack, H.T. Hall, R. Farina, M. Yoshifuji, G. Clark, T. Bargar, K. Hirotsu and J. Clardy, J. Am. Chem. Soc., 101 (1979) 3535.

4 E.M. Engler and P. Lazlo, J. Am. Chem. Soc., 93 (1971) 1317.

5 M.I. Foreman, Chemical Society Specialist Periodical Report, Nuclear Magnetic Resonance Spectroscopy 3 (1974) 350.

6 R. Foster, Organic Charge-Transfer Complexes, Academic Press, London and New York (1969) 125.