Journal of Organometallic Chemistry
Elsevier Sequoia S,A., Lausanne
Printed in The Netherlands

Preliminary communication

Metal catalysed electrocyclic reactions of hexamethylDewarbenzene

C.J. ATTRIDGE and SUSAN J. MADDOCK

Imperial Chemical Industries Limited, Petrochemical & Polymer Laboratory, P.O. Box 11, The Heath, Runcorn, Cheshire (Great Britain)

(Received December 3rd, 1970)

The use of metal catalysts to overcome the principle of conservation of orbital symmetry in concerted organic reactions has aroused considerable interest recently, primarily due to theoretical work by Mango and Schachtschneider[1] and preliminary experimental studies by Pettit and his coworkers[2].

We wish to report preliminary results of a comparative study of the influence of metal catalysts on the ring opening of a cyclobutene to a butadiene. If a small ring is attached across the 3,4 carbon atoms of the cyclobutene the thermally allowed conrotatory ring opening becomes sterically very difficult[3]. This is shown by the unexpectedly high thermal stability of hexamethylDewarbenzene (HMDB) relative to hexamethylbenzene (HMB); the half life for this conversion is 2 h at 150° [4]. During the preparation of a palladium complex of HMDB, evidence of metal induced isomerisation to HMB has been observed[5] and the complex $[(HMDB)RhCl]_2$ has been shown to be active in catalytic quantities for promoting this conversion[6]. These results prompted us to take the conversion of HMDB to HMB as a convenient model system in which to investigate the influence of a range of metal species on an electrocyclic ring opening.

A convenient test reaction for catalytic activity was to heat HMDB in benzene at 65–70° with 5 mole % concentrations of catalyst for approximately 24 h. The reaction was followed by proton NMR spectroscopy and the degree of conversion estimated by integration of the respective signals of reactant and product.

The results, which are given in Table 1, indicate that complexes of metals to the right of the transition series and, in particular, second row elements, such as rhodium, palladium and silver are effective in promoting electrocyclic ring opening. There is no apparent correlation between activity and the metal d orbital configuration for the various d^{10} and d^8 systems we have studied. The inactivity of some of the catalysts may be due to the presence of bulky phosphine ligands, which hinder the approach of HMDB to the metal.

The results for silver salts indicate that the nature of the anion is important in determining activity, but further results are needed before any correlation is possible. The activity of silver fluoroborate was far greater than is suggested by the table as, in fact,

TABLE 1

$[CpFe(CO)_2]_2$ $FeCl_3$*[a] (15) $Fe_3(CO)_{12}$	$Co_2(CO)_8$ $CoCl_2$ (a)[b] $(Ph_3P)_2CoCl_2$	$NiCl_2(PPh_3)_2$ $NiCl_2$ (a) $Ni(CO)_2(PPh_3)_2$ $Ni(O)[P(Me_2CHO)_3]_4$ $NiCl_2(PhCN)_2$* (8)	CuCl $CuCl[P(OMe)_3]$ $CuCl_2$
$RuCl_3$/EtOH* (38) $Ru(CO)_3(PPh_3)_2$ $RuCl_2(PPh_3)_3$	$[RhCl(CO)_2]_2$* (25) $Rh_4(CO)_{12}$* (16) $RhCl_3$/EtOH* (16) $RhCl(PPh_3)_2$* (8) $RhH(PPh_3)_2$ $RhCl_3(MeCN)_3$* (5) $RhCl(CO)(PPh_3)_2$	$PdCl_2(PhCN)_2$* (21) $PdCl_2$/EtOH* (100) $PdBr_2$/EtOH* (100) $[Pd(C_2H_4)Cl_2]_2$* (60) Pd(10%)/Charcoal* (5)	$AgBF_4$* (100) $AgClO_4$* (100) Ag(OOCMe) $AgNO_3$ Ag/Glass fibre
	$IrCl(CO)(PPh_3)_2$ $IrCl_2(CO)(PPh_2Et_2)_2$	$[Pt(C_2H_4)Cl_2]_2$ (26) $Pt(O)(C_2H_4)(PPh_3)_2$ $PtCl_2(PhCN)_2$ Pt(5%)/Embacel	

[a] *Denotes active catalyst; % conversion is given in brackets. [b] a = anhydrous.

100% conversion was also achieved in 24 h at room temperature with a 5 mole % concentration.

A number of heterogeneous catalysts, *e.g.* silver on glass fibre, platinum on embacel, were found to be inactive. The high activity of silver fluoroborate, and the activity of some of the palladium and platinum complexes is consistent with the results of Pettit and his coworkers[2] in catalysed electrocyclic ring opening reactions of benzocyclobutene derivatives.

We are currently extending these results, by investigating more closely the influence of variations in the metal valence state, the ligands and solvent upon catalyst activity for this type of reaction.

REFERENCES

1 F.D. Mango and J.H. Schachtschneider, *J. Amer. Chem. Soc.*, 89 (1967) 2484; 91 (1969) 1030; F.D. Mango, *Tetrahedron Lett.*, (1969) 4813.
2 W. Merk and R. Pettit, *J. Amer. Chem. Soc.*, 89 (1967) 4787, 4788; R. Pettit, H. Sugahara, J. Wristers and W. Merk, *Discussions Faraday Soc.*, 47 (1969) 71.
3 R.B. Woodward and R. Hoffman, *Angew. Chem. Intern. Ed.*, 8 (1969) 802.
4 W. Schäfer and H. Hellmann, *Angew. Chem. Intern. Ed.*, 6 (1967) 518.
5 H. Dietl and P.M. Maitlis, *Chem. Commun.*, (1967) 759.
6 H.C. Volger and H. Hogeveen, *Rec. Trav. Chim.*, 86 (1967) 831; H.C. Volger and M.M.P. Gaasbeek, *ibid.*, 87 (1968) 1291.