Journal of Organometallic Chemistry, 204 (1981) 75—78
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

ACTIVATION OF CHLOROBENZENE AS PHENYLATING AGENT BY MEANS OF A DINITROGEN-MOLYBDENUM COMPLEX

MARIO NARDELLI, CORRADO PELIZZI, GIOVANNI PREDIERI,

Istituto di Chimica Generale ed Inorganica, Università degli Studi, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Via M. D'Azeglio 85, 43100 Parma (Italy)

and GIAN PAOLO CHIUSOLI

Istituto di Chimica Organica, Università degli Studi, Via M. D'Azeglio 85, 43100 Parma (Italy)

(Received June 9th, 1980)

Summary

Bis(dinitrogen)bis[1,2-bis(diphenylphosphino)ethane]molybdenum reacts with chlorobenzene to form molybdenum chloro complexes and phenylated organic products. Benzene, biphenyl, *o*-, *m*-, *p*-chlorobiphenyl, a dihydro derivative of *o*-chlorobiphenyl, triphenylphosphine and diphenylvinylphosphine were formed. The isomer distribution of the chlorobiphenyls is close to that obtained by decomposition of 0.02 *M* benzoyl peroxide in chlorobenzene under dinitrogen. The cleavage of the Ph—Cl bond induced by the molybdenum-dinitrogen complex appears to give rise to the same homolytic reaction pattern. Phenylation of anisole and of triethyl phosphite has also been achieved with the same reagent.

Introduction

Dinitrogen complexes of the type $[M(N_2)_2(dppe)_2]$, (M = Mo, W; dppe = $Ph_2PCH_2CH_2PPh_2$), have been reported to undergo reaction with acyl [1,2] or alkyl [2,3] halides RX under mild conditions to give acyl- or alkyldiazenido complexes. In the latter case, an intermediate $[Mo(N_2)(RX)(dppe)_2]$, which undergoes homolytic cleavage of the R—X bond, has been postulated [4]. Among aryl halides, aryl bromides have been reported to give $[MoBr_2(dppe)_2]$ and diaryls under more severe conditions, whilst, to our knowledge, reactions of aryl chlorides have not been described.

As a part of a research programme aimed at producing new organometallic reagents able to cleave aromatic C—Cl bonds, we have derived from $[Mo(N_2)_2(dppe)_2]$, (I), a reagent able to react with chlorobenzene under mild conditions.

0022—328X/81/0000—0000/$02.50,

Results and discussion

The C—Cl bond cleavage was brought about simply by bubbling argon into a solution of I in chlorobenzene for 36 h at 35°C. The complex $[Mo(N_2)Cl(dppe)_2]$ * separated on addition of n-hexane (50% yield). The organic products remaining after removal of the solvent consisted mainly of *o*-, *m*-, *p*-chlorobiphenyl and of a dihydrochlorobiphenyl (22% yield based on the complex), the respective GLC peak areas being in the ratios 1 : 0.6 : 0.6 : 1. Other products were benzene, triphenylphosphine, diphenylvinylphosphine and biphenyl (all identified by gas chromatographic and spectroscopic techniques and by comparison with authentical samples). No significant reaction occurred under the same conditions without flushing with argon. This suggests that one molecule of dinitrogen has to be removed before the reaction of chlorobenzene with Mo takes place.

The same reaction took place on heating I in chlorobenzene for 2.5 h at 80°C or on refluxing it in the same solvent for 20 minutes. In the latter case, $[MoCl_2(dppe)_2]$ was precipitated in a 75% yield.

The types of products obtained in these reactions are consistent with radical pathways. The isomer distribution of the chlorobiphenyls is close to that obtained by decomposition of benzoyl peroxide in PhCl [6], when account is taken of the fact that one phenylated product corresponds to a dihydro derivative of *o*-chlorobiphenyl. A dihydro derivative of biphenyl obtained by radical decomposition of benzoyl peroxide in benzene has been reported [7], but the corresponding dihydro derivative was not noted in the reaction with PhCl in air. After carrying out the decomposition of benzoyl peroxide (0.02 *M*) in chlorobenzene under nitrogen, however, we observed the GLC peak of the dihydro derivative (M^+ 190), formed at the expense of the *o*-chlorobiphenyl peak. Thus there is a clear correspondence between the classical radical reactions and the Mo-induced reaction of chlorobenzene. Further evidence was obtained by performing experiments in the presence of other phenyl radical acceptors such as anisole. The product distribution is identical with that reported for homolytic phenylation [6].

A secondary reaction, which also probably occurs via phenyl radicals, consists of the cleavage of the dppe ligand to triphenylphosphine and diphenylvinylphosphine.

The phenylation procedure has also been extended to trialkyl phosphites. The addition of triethyl phosphite to the reaction mixture results in formation of diethyl phenylphosphonate. Preparation of the latter by the free-radical modification of the Michaelis-Arbusov reaction requires photolysis of aryl iodides [8].

We conclude that all the products observed in the present work can be accounted for in terms of the following homolytic reaction scheme

$$[Mo(N_2)_2(dppe)_2] \xrightarrow[+PhCl]{-N_2} [Mo(N_2)(PhCl)(dppe)_2] \rightarrow [Mo(N_2)Cl(dppe)_2] + Ph^{\cdot} \qquad (1)$$

---

* This formula refers to the same complex, described by different authors [3,5], that Chatt and coworkers have shown to be a 1/1 mixture of $Mo(N_2)_2(dppe)_2$ and $MoCl_2(dppe)_2$.

$$\mathrm{Ph^{\cdot} + PhCl \rightarrow \mathit{o}\text{-}, \mathit{m}\text{-}, \mathit{p}\text{-}ClC_6H_4Ph + ClC_6H_6Ph + H^{\cdot}} \tag{2}$$

$$\mathrm{Ph^{\cdot} + Ph_2PCH_2CH_2PPh_2 \rightarrow PPh_3 + PPh_2(CHCH_2) + H^{\cdot}} \tag{3}$$

$$\mathrm{Ph^{\cdot} + Ph^{\cdot} \rightarrow PhPh} \tag{4}$$

$$\mathrm{Ph^{\cdot} + H^{\cdot}\ (or\ a\ H\text{-}source) \rightarrow HPh} \tag{5}$$

$$\mathrm{Ph^{\cdot} + MeOPh \rightarrow \mathit{o}\text{-}, \mathit{m}\text{-}, \mathit{p}\text{-}MeOC_6H_4Ph + H^{\cdot}} \tag{6}$$

$$\mathrm{Ph^{\cdot} + P(OEt)_3 \rightarrow PhP(O)(OEt)_2 + C_2H_4 + H^{\cdot}} \tag{7}$$

Experimental

All reactions were carried out under dry, oxygen-free dinitrogen or argon by using standard inert atmosphere techniques. Organic solvents were reagent grade and were dried by distillation from suitable drying agents [9] under an inert atmosphere. *trans*-[$\mathrm{Mo(N_2)_2(dppe)_2}$] was prepared by the one-step method of George and Noble [10].

Infrared spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer in KBr disks. Elemental C, H, N analyses were made with a Perkin-Elmer 240 automated equipment. Gas-chromatographic analyses were performed on a Perkin-Elmer 990 instrument (SE 30 or OV 17 packed columns) or Dani 3900 (SE 52 glass-capillary column). Mass spectra were determined with a Varian CH-5 spectrometer (70 eV), connected with a Varian 2700 gas-chromatograph (OV 101 packed column).

Reactions of the complex

Argon was bubbled for 36 h in a solution of I in chlorobenzene (50 mg in 5 ml) maintained at 35°C with a water-bath ultrathermostat. Then n-hexane was added (50 ml), and the yellow-orange microcrystalline solid which separated was filtered off, washed with n-hexane and dried in vacuo (50% yield); it was identified as [$\mathrm{Mo(N_2)Cl(dppe)_2}$] [5] from its IR spectrum (310 $\mathrm{cm^{-1}}$, ν(Mo—Cl); 1966 $\mathrm{cm^{-1}}$, ν(N—N)) and elemental analysis (found: C, 64.8; H, 5.1; N, 2.5; $\mathrm{C_{52}H_{48}ClMoN_2P_4}$ calcd. C, 65.31; H, 5.06; N, 2.93%). The filtrate was reduced in volume to about 2 ml in a rotating evaporator and then analyzed by gas-chromatographic and mass-spectral methods. The following substances, in order of elution, were detected: biphenyl, *o*-chlorobiphenyl, a dihydro-*o*-chlorobiphenyl, *m*-chlorobiphenyl, *p*-chlorobiphenyl, diphenylvinylphosphine and triphenylphosphine. Their peak areas were in the ratio: 0.08 : 1 : 1 : 0.6 : 0.6 : 0.2 : 1. In the distilled fraction benzene was also detected. The yield of phenylation products of chlorobenzene was 22% based on the amount of complex taken.

The same reaction occurred at 80°C in 5 h and at 132°C in 20 minutes, without flushing with argon. In the latter case $\mathrm{MoCl_2(dppe)_2}$ was precipitated by addition of n-hexane (75% yield), and the same organic products were found in the filtrate.

When anisole (2 ml) or triethyl phosphite (1 ml) were added to the reaction mixture (132°C), the dichloro complex precipitated together with small amounts of a brown powder which was not investigated. The *o*-, *m*-, and *p*-isomers of methoxybiphenyl, in the ratio 1 : 0.5 : 0.3 (GLC peak area), and diethyl phenylphosphonate were qualitatively detected in the filtrate, along with the phenylation products of chlorobenzene.

Decomposition of benzoyl peroxide in chlorobenzene

A 0.02 *M* solution of benzoyl peroxide in chlorobenzene was maintained at 90°C under dinitrogen for 48 h with a water-bath. The solution was concentrated with a rotary evaporator to 2 ml and then subjected to gas-chromatographic and mass-spectral analysis. Biphenyl, *o*-chlorobiphenyl, the dihydrochlorobiphenyl, *m*-, *p*-chlorobiphenyl were found with the following peak area ratio 0.06 : 1 : 0.2 : 0.43 : 0.45.

References

1 J. Chatt, A.A. Diamantis, G.A. Heath, N.E. Hooper and G.J. Leigh, J. Chem. Soc. Dalton, (1977) 688.
2 M. Sato, T. Tatsumi, M. Hidai and Y. Uchida, J. Organometal. Chem., 152 (1978) 239.
3 V.W. Day, T.A. George and S.D.A. Iske, J. Amer. Chem. Soc., 97 (1975) 4127.
4 J. Chatt, R.A. Head, G.J. Leigh and C.J. Pickett, J. Chem. Soc. Dalton, (1978) 1638.
5 L.K. Atkinson, A.H. Mawby and D.C. Smith, Chem. Commun., (1971) 157.
6 W.A. Pryor, Free radicals, McGraw-Hill, New York, 1966.
7 D.H. Hey, M.J. Perkins and G.H. Williams, J. Chem. Soc., (1964) 3412.
8 J. Plumb, R. Obrycki and C.E. Griffin, J. Org. Chem., 31 (1966) 2455.
9 D.D. Perrin, W.L.F. Armarego and D.R. Perrin, Purification of Laboratory chemicals, Pergamon Press, Oxford, 1966.
10 T.A. George and M.E. Noble, Inorg. Chem., 17 (1978) 1678.