Journal of Organometallic Chemistry, 55 (1973) 343–345
© Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

THE PREPARATION AND ISOMERISATION OF *trans*-DICARBONYLBIS-[1,2-BIS(DIPHENYLPHOSPHINO)ETHANE]MOLYBDENUM(0)

L. K. HOLDEN, A. H. MAWBY, D. C. SMITH and R. WHYMAN
Imperial Chemical Industries Ltd., Corporate Laboratory (Runcorn), P.O. Box 11, The Heath, Runcorn, Cheshire (Great Britain)
(Received November 14th, 1972)

SUMMARY

The reaction of *trans*-$Mo(N_2)_2(Dppe)_2$ ($Dppe = Ph_2PCH_2CH_2PPh_2$) with carbon monoxide gives, initially, the previously unknown *trans*-$Mo(CO)_2(Dppe)_2$, which isomerises in solution to the well-known *cis* isomer. The reaction was followed by IR spectroscopy under carbon monoxide pressure.

INTRODUCTION

The stereochemistry of complexes of the type $[ML_2(Dppe)_2]^{n+}$ ($M = Cr, Mo$; $L = N_2, CO$; $Dppe = Ph_2PCH_2CH_2PPh_2$ and $n = 0$ or 1) is of some interest. Of these compounds, only $Mo(CO)_2(Dppe)_2$ (I) has a *cis* configuration (Table 1); although $Cr(CO)_2(Dppe)_2$ was believed to exist as interconvertible *cis* and *trans* isomers[1], recent work has shown that a redox equilibrium is in fact established between *trans*-$Cr(CO)_2(Dppe)_2$ and *trans*-$[Cr(CO)_2(Dppe)_2]^+$ [2]. As yet there is no example in which both *cis* and *trans* isomers have been identified.

It is particularly interesting that while (I) has a *cis* configuration[1], the analogous dinitrogen complex, $Mo(N_2)_2(Dppe)_2$ (II), whose structure has been determined by X-ray crystallographic studies[3], occurs as the *trans* isomer. Attempts to prepare *trans*-(I), both by reduction of *trans*-$[Mo(CO)_2(Dppe)_2]^+$ [2] and by replacement of N_2 by CO in (II)[5–7] have yielded only *cis*-(I). We have found, however, that under suitable conditions *trans*-(I) may be identified as the initial product of the reaction of (II) with carbon monoxide, and that subsequent isomerisation to *cis*-(I) takes place with great facility.

TABLE 1

CONFIGURATION OF COMPLEXES $[ML_2(Dppe)_2]^{n+}$

Cis	*Ref.*	*Trans*	*Ref.*
$Mo(CO)_2(Dppe)_2$	1	$Cr(CO)_2(Dppe)_2$	2
		$[Cr(CO)_2(Dppe)_2]^+$	2
		$[Mo(CO)_2(Dppe)_2]^+$	4
		$Mo(N_2)_2(Dppe)_2$	3

RESULTS

The reaction of (II) with carbon monoxide at 50 atm pressure in tetrahydrofuran (THF) solution was followed by IR spectroscopy in a high-pressure cell[8]. The absorption at 1960 cm^{-1} due to THF was cancelled out almost entirely by balancing against a second identical cell [Fig. 1; spectrum (i)]. A THF solution of (II) was pressurised with nitrogen and spectrum (ii) was obtained, showing ν(NN) at 1976 cm^{-1}. The cell was then pressurised with carbon monoxide and stirred at ambient temperature (26–29°). The absorption at 1972 cm^{-1} disappeared over 3–4 h, to be replaced by a band at 1821 cm^{-1} [spectra (iii), (iv)]. The compound giving rise to this absorption is stable for several hours in solution under these conditions, but on warming to 50–60° the 1821 cm^{-1} band is replaced by bands at 1795 and 1859 cm^{-1} [spectra (v), (vi)]. The final spectrum is identical to that obtained from an authentic sample of *cis*-(I) under the same conditions. We attribute the absorption at 1821 cm^{-1} to *trans*-$Mo(CO)_2(Dppe)_2$, found as the initial product of the replacement of N_2 by CO in *trans*-$Mo(N_2)_2(Dppe)_2$. This reaction is not reversible. If, at the stage represented by spectrum (iv), the cell is repressurised with nitrogen, no reconversion to (II) is observed, but only slow isomerisation to *cis*-(I). There is no indication of the intermediate formation of a mixed species, $Mo(N_2)(CO)(Dppe)_2$.

Trans-(I) may be isolated from the above reaction, and may also be prepared by passing carbon monoxide through a solution of (II) at atmospheric pressure for a

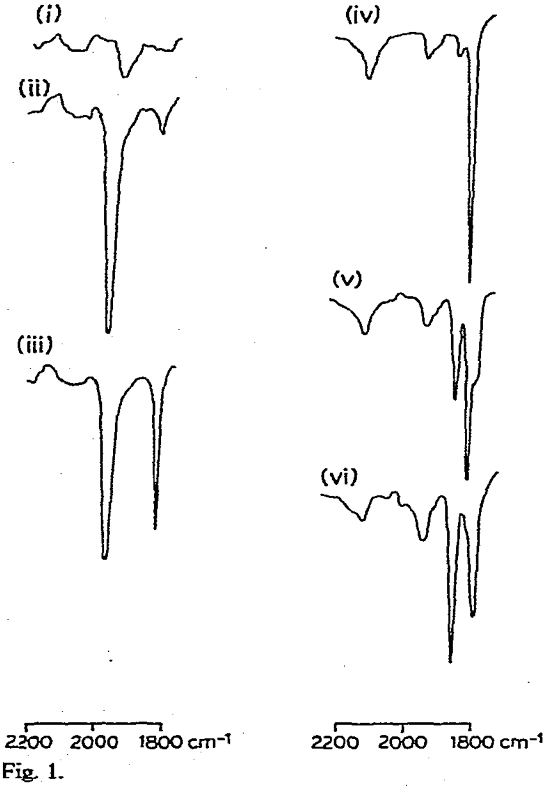

Fig. 1.

limited time, although in neither case was the product quite free from (II) or *cis*-(I). Optimum yields were obtained at atmospheric pressure with reaction times of 5 h (ambient temperature) or 24 h (0°)*. Yellow-orange *trans*-$Mo(CO)_2(Dppe)_2$ is stable in the solid state, but isomerises rapidly in solution. Isomerisation takes place too quickly to allow dipole moment measurements to be made in either benzene or dioxane.

DISCUSSION

The balance of steric and electronic factors in complexes of the type $[ML_2(Dppe)_2]^{n+}$ must be very fine. Thus for steric reasons a complex containing two bulky chelating ligands would be expected to adopt a *trans* configuration, while two monodentate ligands with strong π-acceptor properties would be expected to occupy *cis* positions. In (I), the π-acceptor properties of the carbonyl ligands apparently dominate, causing the *cis* configuration to be preferred. In the dinitrogen complex back donation from the metal is less significant and the sterically favoured *trans* configuration is adopted. Oxidation to Mo^I in $[Mo(CO)_2(Dppe)_2]^+$ simultaneously increases steric crowding by reducing the radius of the metal ion, and decreases back-bonding potential, and hence the *trans* configuration is again found.

The relative stability of *trans*-(I) in solution under pressure of CO contrasts with the rapid isomerisation at atmospheric pressure. This suggests that the isomerisation may involve dissociation of CO to form a 5-coordinate intermediate, $Mo(CO)(Dppe)_2$, with subsequent recombination in the *cis* position.

EXPERIMENTAL

trans-Dicarbonylbis[1,2-bis(diphenylphosphino)ethane]molybdenum(0)

A slow stream of carbon monoxide was passed through a stirred solution of *trans*-bis(dinitrogen)bis[1,2-bis(diphenylphosphino)ethane]molybdenum(0)[9] (150 mg) in dry tetrahydrofuran (25 ml) at ambient temperature with the exclusion of light. After 5 h, the solution was evaporated to dryness at or below room temperature. No further purification was possible without causing isomerisation of the product. (Found C; 68.8, H; 5.3, N; 0.4. $C_{54}H_{48}MoO_2P_4$ calcd.: C; 68.4, H; 5.1, N; 0.0%.)

ACKNOWLEDGEMENT

The authors thank F. W. S. Gaffney for experimental assistance.

REFERENCES

1 J. Chatt and H. R. Watson, *J. Chem. Soc.*, (1961) 4980.
2 P. F. Crossing and M. R. Snow, *J. Chem. Soc. A*, (1971) 610.
3 T. Uchida, Y. Uchida, M. Hidai and T. Kodama, *Bull. Chem. Soc. Jap.*, 44 (1971) 2883.
4 J. Lewis and R. Whyman, *J. Chem. Soc.*, (1965) 5486.
5 M. Hidai, K. Tominari and Y. Uchida, *J. Amer. Chem. Soc.*, 94 (1972) 110.
6 T. A. George and C. D. Seibold, *Inorg. Nucl. Chem. Lett.*, 8 (1972) 468.
7 D. J. Darensbourg, *Inorg. Nucl. Chem. Lett.*, 8 (1972) 529.
8 W. Rigby, R. Whyman and K. Wilding, *J. Phys. Sci. Instr.*, 3 (1970) 572.
9 L. K. Atkinson, A. H. Mawby and D. C. Smith, *Chem. Commun.*, (1971) 157.

---

* Hidai *et al.* passed CO through a benzene solution of (II) under ambient conditions for 4 days. This period is sufficient for complete isomerisation of *trans*-(I) under these conditions and hence only *cis*-(I) was observed.