Journal of Organometallic Chemistry, 77 (1974) 45—48

COMPLEXES OF METAL IONS WITH PHOSPHORUS OR ARSENIC CONTAINING LIGANDS

XVII. PHOTOCHEMICALLY INDUCED SUBSTITUTION IN GROUP VI METAL CARBONYLS WITH DITERTIARY PHOSPHINES AND ARSINES

S.S. SANDHU and A.K. MEHTA
Chemistry Department, Guru Nanak University, Amritsar (India)
(Received April 2nd, 1974)

Summary

The bidentate ligands 1,2-bis(diphenylphosphine/arsine)ethane and 1,4-bis-(diphenylphosphine/arsine)butane react with Group VI metal hexacarbonyls under ultraviolet irradiation to form compounds of the type $M(CO)_4LL$ and $M(CO)_2(LL)_2$. The infrared spectra of the complexes indicate that there is an octahedral disposition of ligands around the metal atom. The interaction constants have been calculated.

Introduction

Complexes of Group VI metal hexacarbonyls with ligands having donor atoms such as nitrogen, phosphorus, arsenic, antimony sulphur etc., have been described [1—4]. The chelates of metal hexacarbonyls with 1,2-bis(diphenylphosphine/arsine)ethane having five membered ring [3] and bridged complexes of the type $M_2(CO)_6L_3$ [4] and $M_2(CO)_{10}L$ [5] have been obtained by thermal methods. In view of lack of information on them in the literature, the complexes of the Group VI metal hexacarbonyls with 1,2-bis(diphenylphosphine)-ethane DPE; 1,2-bis(diphenylarsine)ethane DAE; 1,4-bis(diphenylphosphine)butane DPB and 1,4-bis(diphenylarsine)butane DAB have been prepared by the ultraviolet irradiation method.

Experimental

The ligands DPE, DAE, DPB and DAB were prepared by known methods [6]. Chromium, molybdenum and tungsten hexacarbonyls were obtained (99.9% pure) from Alfa Inorganics. The complexes were prepared by exposing an equimolar solution of metal hexacarbonyl and ditertiary phosphine or arsine in an evacuated pyrex tube to ultraviolet light for 50 h. The solution was then filtered and the solvent distilled off under reduced pressure.

(*a*). The tetrasubstituted complexes were obtained by washing the product with hot absolute alcohol followed by drying in vacuo.

(*b*) The disubstituted complexes were isolated by dissolving the product in methylene chloride and allowing the solution to evaporate slowly in a desiccator. The product was washed with petroleum ether and crystallised from absolute alcohol.

Infrared spectra of the complexes were recorded on Perkin—Elmer model 337 in Nujol mull using sodium chloride plates in the 4000-650 cm^{-1} region. The molar conductance of millimolar solutions of the complexes were measured in nitrobenzene with a Toshniwal Conductivity bridge CLOI/OI. Estimation of C, H and P was carried out by the Australian Microanalytical Service, Melbourne.

Results and discussion

The stoichiometries of the complexes were established by elemental analyses, which indicated that there were two types of complexes (*a*) $M(CO)_4(LL)$ and (*b*) $M(CO)_2(LL)_2$, where M is Cr, Mo or W and LL is a bidentate ligand (Table 1). The infrared spectra of all the complexes were recorded in the range 4000-650 cm^{-1}. In the spectra of the ligands DPE and DPB, the band at 1092 cm^{-1} has been assigned to P—C(aromatic) stretch [7]. However, the bands at 1070 and 1068 cm^{-1} have been assigned to As—C(aromatic) stretch in the spectra of ligands DAE and DAB respectively [8]. On complex formation the rise in stretching frequency by 8—15 cm^{-1} and 10—15 cm^{-1} in the P—C(aromatic) and As—C(aromatic) stretches respectively is indicative of the coordination of the donor atoms (phosphorus or arsenic) to the metal atom. Our complexes gave two or four absorption bands in the 2100—1860 cm^{-1} region, and these are

TABLE 1

ANALYSES AND PHYSICAL PROPERTIES OF COMPLEXES

Complex	Colour	M.p. (°C)	Molar conductance (ohm^{-1} cm^{2} mole^{-1})	Analysis found (calcd.) (%)		
				C	H	P
$Cr(CO)_4DPB$	Light green	150—154	1.6	63.96 (65.08)	4.8 (4.7)	10.2 (10.5)
$Cr(CO)_2(DAE)_2$	Yellow	150	6.1	60.79 (60.0)	4.9 (4.4)	
$Cr(CO)_2(DAB)_2$	Green	140	2.7	59.75 (61.1)	4.6 (4.9)	
$Mo(CO)_4DPB$	Light yellow	172—174	1.7	60.80 (61.5)	4.37 (4.6)	9.7 (10.2)
$Mo(CO)_4DAE$	Yellow	174	1.1	51.50 (52.0)	3.58 (3.4)	
$Mo(CO)_2(DPE)_2$	Yellow	170	5.0	68.6 (68.2)	5.6 (5.9)	
$Mo(CO)_2(DAB)_2$	Yellow	140—144	3.3	58.92 (58 90)	4.6 (4.7)	
$W(CO)_4DPE$	Light yellow	140—142	1.5	51.43 (51.8)	3.69 (3.4)	8.7 (8.9)
$W(CO)_4DPB$	Light yellow	138—140	1.4	51.93 (53.2)	3.94 (4.0)	
$W(CO)_4DAE$	Light greenish yellow	130—132	1.3	45.76 (46.05)	3.27 (3.0)	
$W(CO)_4DAB$	Light yellow	118	1.1	48.1 (47.4)	3.98 (3.4)	

TABLE 2

INFRARED SPECTRAL DATA

Complex	P—C(ar)	As—C(ar)	Shift (cm^{-1}) P—C(ar)	Shift (cm^{-1}) As—C(ar)	C—O stretching frequencies (cm^{-1})
$Cr(CO)_4DPB$	1100		+ 8		1990, 1860
$Cr(CO)_2(DAE)_2$		1085		+15	1845, 1790
$Cr(CO)_2(DAB)_2$		1080		+12	2000, 1910
$Mo(CO)_4DPB$	1105		+13		2010, 1900
$Mo(CO)_4DAE$		1080		+10	2010, 1950, 1920, 1880
$Mo(CO)_2(DPE)_2$	1100		+ 8		1870, 1800
$Mo(CO)_2(DAB)_2$		1080		+12	2000, 1870
$W(CO)_4DPE$	1105		+13		2005, 1910, 1880[a]
$W(CO)_4DPB$	1100		+ 8		2000, 1930, 1885[a]
$W(CO)_4DAE$		1080		+10	2000, 1935, 1910, 1870
$W(CO)_4DAB$		1080		+12	2000, 1920, 1870[a]

[a] Broad band, P—C(ar) 1092 cm^{-1} in DPE and DPB. As—C(ar) 1070 and 1068 cm^{-1} in DAE and DAB, respectively.

assigned to carbon monoxide groups (Table 2). The complexes in which two or four carbon monoxide groups are replaced are of the C_{2v} class; for this type of complex four infrared active carbonyl stretching modes are expected ($\tau = 2A_1 + B_1 + B_2$). The vibrations are combination of two pairs: (*a*), symmetric A_1 and antisymmetric B_2 modes of *trans* carbonyls group; (*b*), symmetric A_1 and antisymmetric B_2 of two *cis* carbonyls. There will be some interaction between these modes, and this will be greater in the case of A_1 modes which will be quite close to each other. For the assignments of modes Orgel [8] used intensity criteria. However, Cotton and Kraihanzel [9] have given a simple model for the assignments of infrared active carbonyl stretching frequencies of simple and substituted metal carbonyls of Group VI. This model is applicable only where the environment around the metal atom is octahedral.

The interaction constants (k_i, k_1 and k_2) for the four complexes of tung-

TABLE 3

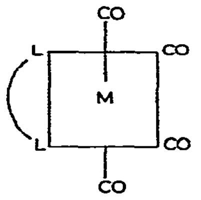
INTERACTION CONSTANTS

Complex	Calculated interaction constants (mdynes/Å) k_i	k_1	k_2	Max. Error in k_i calculated	Calculated value for the broad band
For $W(CO)_4$ L—L complexes (A)					
$W(CO)_4DPE$	0.288	14.6	15.23	0.13	1870 cm^{-1}
$W(CO)_4DPB$	0.22	14.54	15.51	0.12	
$W(CO)_4DAB$	0.26	14 37	15.39	0.14	
$W(CO)_4DAE$	0.211	14.32	15.56	0.11	
For $M(CO)_2(L—L)_2$ complexes (B)					
$Cr(CO)_2(DAE)_2$	0.41	13.35			
$Cr(CO)_2(DAB)_2$	0.72	15.44			
$Mo(CO)_2(DPE)_2$	0.51	13.59			
$Mo(CO)_2(DAB)_2$	1.03	15.13			

sten have been calculated and are shown in Table 3. The interaction constants are smaller than those in the literature. One of the reasons for the lower value of k_i may be the precision of the instrument. The maximum possible error in k_i is shown in Table 3, and indicates that the data are markedly more precise than those obtained earlier. The exact position of the broad band observed near 1880 cm^{-1} is calculated to be 1870 cm^{-1}. The broadness of the observed band may be due to

calculated to be 1870 cm^{-1}. The broadness of the observed band may be due to

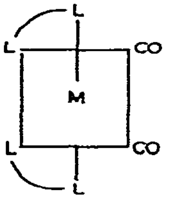
mixing of B_1 and B_2 modes. However, it was not possible to derive the relative position of two pairs of bands. The most probable structure for the complexes in which two 'CO' groups have been replaced is given below (A).



(A)

Interaction constants have also been calculated for the complexes in which four CO groups have been replaced by bidentate ligands, and are shown in Table 3.

On the basis of the calculated interaction constants and the symmetry of the complex, structure B is probable for these complexes. However, the interaction constants obtained in case of the complexes of DAB are higher.



(B)

Acknowledgement

We thank the Council of Scientific and Industrial Research, New Delhi for the award of Junior Fellowship to one of us (AKM).

References

1 G.R. Dobson, I.W. Stolz and R.K. Sheline, Advan. Inorg. Chem. Radiochem., 8 (1966) 1.
2 H. Schuman, O. Stelzer and W. Gick, Angew. Chem., Int. Ed. Engl., 8 (1968) 271.
3 J. Chatt and H.R. Watson, J. Chem. Soc., (1961) 4980.
4 F. Zingates, F. Canziani and R. Ugo, Gazz. Chim. Ital., 92 (1962) 761.
5 H. Werner, R. Prinz, E. Bundschuh and K. Deckelmann, Angew. Chem., Int. Ed. Engl, 5 (1966) 606.
6 J. Chatt and F.A. Hart., J. Chem. Soc., (1961) 1378.
7 S.S. Sandhu and R S. Sandhu., Ind. J. Chem., 9 (1971) 482.
8 S.S. Sandhu and S.S. Parmar Chem. Commun., (1968) 1335.
9 L.E. Orgel., Inorg. Chem., 1 (1962) 25.
10 F.A. Cotton and I.S. Kraihanzel, J. Amer. Chem. Soc., 84 (1962) 4432.