Journal of Organometallic Chemistry, 73 (1974) 343—349
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1-(DIPHENYLPHOSPHINO)-2-(DIPHENYLARSINO)ETHANE DERIVATIVES OF GROUP VI METAL CARBONYLS

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(Received January 25th, 1974)

Summary

1-(Diphenylphosphino)-2-(diphenylarsino)ethane (dpda) reacts with hexacarbonyls of chromium, molybdenum or tungsten to form the monomeric *cis*-$[M(CO)_4(dpda)]$ and dimeric $[M(CO)_4(dpda)]_2$ (M = Cr, Mo or W) derivatives. It is concluded that these derivatives contain dpda in two different configurations. A tetrasubstituted molybdenum derivative $[Mo(CO)_2(dpda)_2]$ was obtained in very poor yield under more forcing conditions. Several mixed derivatives, viz., *cis*-$[M(CO)_3(dpda)am]$, *cis*-$[M(CO)_3(dpda)B]$, and $[M(CO)_2(dpda)B]$ (am = $C_4H_9NH_2$ or $C_6H_{11}NH_2$; B = *o*-phenanthroline or 2,2′-bipyridine) have also been synthesised.

Introduction

In our previous papers [1—3] we described the synthesis of several substituted molybdenum carbonyl derivatives containing nitrogen and sulphur donor ligands. We describe here a study of the ligand behaviour of the bidentate ligand 1-(diphenylphosphino)-2-(diphenylarsino)ethane (dpda) in the substitution reactions of chromium, molybdenum and tungsten hexacarbonyls. Although there has been considerable study of derivatives of Group VI metal carbonyls containing bidentate ligands, viz., 1,2-bis(diphenylphosphino)ethane [4], 1,2-bis(diphenyl)-arsino)ethane [5], diphenylarsinomethane [6], and its antimony analogue [7], and 2,5-dithiahexane [8], derivatives involving bidentate ligands containing two different donors are less familiar. A few examples, such as 1-(diethylphosphino)-2-(ethylthio)ethane [9], diphenyl[*o*-(methylthio)phenyl]phosphine [10] and 1-(diphenylphosphino)-2-(methylthio)ethane [11], which contain P and S donors have been investigated in the ligand exchange reactions of metal hexacarbonyls. We have used ligands containing P and As as donors. A very brief account of the reaction between chromium hexacarbonyl and dpda has appeared recently [12], but only one product, *cis*-$[Cr(CO)_4(dpda)]$, was isolated. We have studied the reaction between dpda and all the three Group VI metal carbonyls, and have isolated both monomeric *cis*-$[M(CO)_4(dpda)]$ and dimeric $[M(CO)_4(dpda)]_2$ (M = Cr, Mo or W) products. Several mixed-ligand carbonyl derivatives, containing dpda and a nitrogen donor such as butylamine, cyclohexylamine, *o*-phenanthroline or 2,2′-bipyridine, have also been prepared.

Results and discussion

dpda reacted with chromium, molybdenum and tungsten hexacarbonyls under vigorous conditions to form *cis*-$[M(CO)_4(dpda)]$ and $[M(CO)_4(dpda)]_2$ derivatives. The reactivity was in the order Mo > Cr > W. The dimeric derivatives $[M(CO)_4(dpda)]_2$ were characterized by molecular weight determinations. Both the monomeric and dimeric derivatives seem to contain dpda in two different configurations (see below). Further displacement of CO was possible only in the case of molybdenum for which the tetrasubstituted derivative $[Mo(CO)_2(dpda)_2]$ was isolated in low yield (15%). The analogous chromium and tungsten derivatives could not be prepared even on prolonged reaction at higher temperature.

Mixed *cis*-$[M(CO)_3(dpda)(am)]$ derivatives were prepared by heating equimolar mixtures of tris(amine)tricarbonylmolybdenum(0) [1] or tris(amine)tricarbonyltungsten(0) [13] derivatives and dpda in an evacuated sealed tube. The mixed derivatives with dpda and *o*-phenanthroline or 2,2′-bipyridine were obtained from the reaction between *cis*-$[M(CO)_4B]$ and dpda. The IR spectra indicated that dpda acted as a monodentate ligand in this case. We obtained a different product $[Mo(CO)_2(o\text{-phen})(dpda)]$, from the reaction between *cis*-$[Mo(CO)_4(dpda)]$ and *o*-phenanthroline; in this product the dpda is bidentate.

Infrared spectra

The infrared spectra of the $[M(CO)_4(dpda)]$ complexes indicated that they were *cis*-derivatives. Four C—O bands (Table 1) were observed in the IR spectrum of each complex. By comparing the CO frequencies of chromium derivative recorded in octane solution [12], it is apparent that there is no significant difference in the IR spectrum of the chromium derivative in octane [12] and that in the solid phase. Since the IR bands of most of the solvents interfere with the bands of dpda in the region 500—1600 cm^{-1}, the spectra were recorded in KBr discs. Medium strong absorptions appear around 1154, 1105 and 724 cm^{-1} in the IR spectra of dpda and the polymeric derivatives, but are absent for *cis*-$[M(CO)_4(dpda)]$ derivatives. These bands can be attributed to *trans*-CH_2 wagging, *trans*-CH_2 twisting and *trans*-CH_2 rocking modes; these band assignments are in close agreement with the CH_2 band assignments for bis(selenocyanato)ethane complexes [14]. Bands at 980 and 863 cm^{-1} which are attributable to *gauche*-CH_2 twisting and *gauche*-CH_2 rocking modes are present in the *cis*-$[M(CO)_4(dpda)]$ derivatives but absent in the spectra of $[M(CO)_4(dpda)]_2$ derivatives. It can be inferred that the diphenylphosphino- and diphenylarsino-groups present in the dpda ligand of polymeric derivatives are in *trans*-positions, while the preferred configuration is distorted (*gauche*) in case of *cis*-$[M(CO)_4(dpda)]$ derivatives. It is well known that 1,2-disubstituted ethanes exist only in the *trans*-form in the solid but in both *trans*- and *gauche*-forms in solution [15]. It is likely that dpda exists as a mixture of the two forms in solution during the reaction and

TABLE 1

CO STRETCHING FREQUENCIES OF *cis*-$[M(CO)_4(dpda)]$ AND *cis*-$[M(CO)_4(dpda)]_2$ COMPLEXES

Complex	CO bands (cm^{-1})
$[Cr(CO)_4(g\text{-}dpda)]$	2016s, 1926s, 1901s, 1882s
$[Cr(CO)_4(t\text{-}dpda)]_2$	2010s, 1930s, 1885s, 1870s
$[Mo(CO)_4(g\text{-}dpda)]$	2020s, 1932s, 1908s, 1887s
$[Mo(CO)_4(t\text{-}dpda)]_2$	2008s, 1922s, 1893s, 1862s
$[W(CO)_4(g\text{-}dpda)]$	2024s, 1924s, 1906s, 1882s
$[W(CO)_4(t\text{-}dpda)]_2$	2012s, 1922s, 1890s, 1876s

these forms coordinate to the metal atom to produce two types of derivatives, namely, *cis*-$[M(CO)_4(g\text{-}dpda)]$ and *cis*-$[M(CO)_4(t\text{-}dpda)]_2$ (*t* = *trans*, *g* = *gauche*). A slight decrease in the three carbonyl stretching frequencies in the spectra of polymeric derivatives is observed (Table 1).

Because of the limited solubility of $[Mo(CO)_2(dpda)_2]$, the IR spectrum of this compound also was recorded with a KBr disc in the C—O region; a very weak band at 1885 cm^{-1} and two strong bands at 1830 and 1760 cm^{-1} were observed. The very weak band at 1885 cm^{-1} may arise from traces of *cis*-$[Mo(CO)_4(dpda)]$, or be due to an aromatic overtone band which gained intensity from resonance interaction [16]. Other carbonyl bands fall in the same region, as observed for bis[1,2-bis(diphenylphosphino)ethane]-dicarbonylmolybdenum(0) [4] and bis[1-(diphenylphosphino)-2-(methylthio)ethane] dicarbonylmolybdenum(0) [10], these bands indicate a *cis,cis* configuration for $[Mo(CO)_2(dpda)_2]$. The spectrum in the other regions was so weak that a full assignment of the configuration of dpda in this complex could not be made.

The $[M(CO)_3(dpda)(am)]$ complexes showed three strong C—O bands (Table 2) in agreement with C_s symmetry, and these can be attributed to the A', A'' and A' modes, respectively.

The C—O frequencies of $[M(CO)_3(B)(dpda)]$ complexes are given in Table 3. The C—O frequencies show that dpda acts as a monodentate ligand in these cases. The lowering of C—O stretching frequencies is greater than in the $[M(CO)_3\text{-}(dpda)(am)]$ complexes. This indicates that the feeble acceptor B ligands act as bidentate and dpda as a monodentate in $[M(CO)_3(B)(dpda)]$ derivatives, since a slight increase in C—O frequencies would be expected in the other case. The three C—O stretching bands corresponded to the A', A'' and A' modes of C_s symmetry.

TABLE 2

CO STRETCHING FREQUENCIES OF $[M(CO)_3(dpda)(am)]$ COMPLEXES

Complex	CO bands (cm^{-1})	Modes
$[Mo(CO)_3(dpda)(C_6H_{11}NH_2)]$	1930s	A'
	1852s	A''
	1825s	A'
$[Mo(CO)_3(dpda)(C_4H_9NH_2)]$	1912s	A'
	1856s	A''
	1828s	A'
$[W(CO)_3(dpda)(C_4H_9NH_2)]$	1912s	A'
	1860s	A''
	1830s	A'

TABLE 3

CO STRETCHING FREQUENCIES OF [$M(CO)_3$(B)(dpda)] COMPLEXES

Complex	CO bands (cm^{-1})	Modes
[$Cr(CO)_3$(*o*-phen)(dpda)]	1904s	*A'*
	1796s	*A"*
	1782s	*A'*
[$Mo(CO)_3$(*o*-phen)(dpda)]	1910s	*A'*
	1798s	*A"*
	1778s	*A'*
[$W(CO)_3$(*o*-phen)(dpda)]	1906s	*A'*
	1792s	*A"*
	1774s	*A'*
[$Mo(CO)_3$(2,2'-bipy)(dpda)]	1912s	*A'*
	1796s	*A"*
	1776s	*A'*
[$W(CO)_3$(2,2'-bipy)(dpda)]	1906s	*A'*
	1792s	*A"*
	1778s	*A'*

For the complex [$Mo(CO)_2$ (*o*-phen)(dpda)], two strong CO bands at 1885 and 1755 cm^{-1} are consistent with a *cis,cis* configuration.

Experimental

All experiments were performed under dry nitrogen or in vacuo. Infrared spectra were measured on a Perkin—Elmer Spectrophotometer model 221. Molecular weights were determined cryoscopically. 1-(Diphenylphosphino)-2-(diphenylarsino)ethane was purchased from Strem Chemicals, Inc., U.S.A.

Preparation of [1-(diphenylphosphino)-2-(diphenylarsino)ethane] tetracarbonylchromium(0)

Hexacarbonylchromium(0) (0.2 g) and dpda (0.36 g) were refluxed together for 20 h in xylene (10 ml) under nitrogen. The colour of the mixture had become deep yellow after 7 h. After another 13 h, the mixture was cooled, the solvent was removed in vacuo, and the residue was washed four times with light petroleum (60—80°) to remove unreacted carbonyl and dpda. The yellowish white product so obtained was washed three times with diethyl ether to yield a yellow solution, leaving a white residue. A bright yellow solid was obtained on evaporating the solvent from the washings. It was recrystallised in acetone and was shown to be *cis*-[1-(diphenylphosphino)-2-(diphenylarsino)ethane] tetracarbonylchromium(0). Found: C, 58.1; H, 3.6; Cr, 8.0. $C_{30}H_{24}AsCrP$ calcd.: C, 59.4; H, 3.9; Cr, 8.5%. Yield 43.6%; m.p. 180°. It was soluble in acetone, dichloromethane, benzene, toluene and diethyl ether, and insoluble in methanol.

The white residue obtained after washing with diethyl ether was washed twice with ether then recrystallised from benzene to give an air-stable solid, m.p. 189° (dec.). The analysis was nearly the same as of the yellow derivatives. Found: C, 58.4; H, 3.5; Cr, 8.3%. The molecular weight confirmed that it was [$Cr(CO)_4$-(dpda)]$_2$ (Found: 1178. $C_{60}H_{48}As_2Cr_2O_8P_2$ calcd.: 1212.)

Preparation of [1-(diphenylphosphino-2-(diphenylarsino)ethane]tetracarbonylmolybdenum(0)

Hexacarbonylmolybdenum(0) (0.2 g) and dpda (0.334 g) were refluxed for 10 h in xylene under nitrogen. Work up as for the chromium analogues gave a yellow solid (yield 50%) m.p. 165°. (Found: C, 54.6; H, 3.4; Mo, 14.2. $C_{30}H_{24}AsMoO_4P$ calcd.: C, 55.3; H, 3.6; Mo. 14.7%) and a white solid m.p. 181° (dec.) (Found: C, 54.8; H, 3.5; Mo, 14.0. Mol. wt., 1255. $C_{60}H_{48}As_2Mo_2O_8P_2$ calcd.: mol. wt., 1300).

Preparation of [1-(diphenylphosphino)-2-(diphenylarsino)ethane] tetracarbonyltungsten(0)

Similarly hexacarbonyltungsten(0) (0.2 g) and dpda (0.25 g) were refluxed for 30 h in xylene under nitrogen to give a yellow product m.p. 155°, (yield 37%) (Found: C, 47.2; H, 3.1; W, 24.0. $C_{30}H_{24}AsO_4PW$ calcd.: C, 48.7; H, 3.2; W, 24.9%) and a white product m.p. 174° (dec.) (yield 32%). (Found: C, 48.1; H, 3.2; W, 23.8. Mol. wt., 1420. $C_{60}H_{48}As_2O_8P_2W_2$ calcd.: mol. wt., 1476).

Preparation of bis[1-(diphenylphosphino)-2-(diphenylarsino)ethane] dicarbonylmolybdenum(0)

Hexacarbonylmolybdenum(0) (0.1 g) and dpda (0.35 g) were refluxed for 22 h in xylene under nitrogen, during which a reddish brown solid separated. This was filtered off and washed with petroleum ether (60—80°), ether and finally benzene to remove any unchanged reactants and the lower substituted products. It was dried in vacuo (yield 14.8%). It did not melt up to 220°, but at higher temperature decomposed without melting. (Found: C, 61.2; H, 4.1; Mo, 9.4. $C_{54}H_{48}As_2MoO_2P_2$ calcd.: C, 62.5; H, 4.6; Mo. 9.2%.) It was insoluble in almost all the common organic solvents.

Preparation of [1-(diphenylphosphino)-2-diphenylarsino)ethane](cyclohexylamine)tricarbonylmolybdenum(0)

Tris(cyclohexylamine)tricarbonylmolybdenum(0) [1] (0.2 g) and dpda (0.2 g) were heated in an evacuated sealed Pyrex tube for 5 h at 140°, during which the mixture turned yellow. The yellow solid formed was washed with 5 ml portions of diethyl ether then was extracted with benzene. Evaporation of the benzene extract gave a yellow brown solid, which was dried in vacuo (yield 43%). (Found: C, 56.8; H, 4.9; Mo, 12.7; N, 2.0. $C_{35}H_{37}AsMoNO_3P$ calcd.: C, 58.2; H, 5.1; Mo, 13.3; N, 1.9%.) It was soluble in benzene and toluene, but insoluble in light petroleum (40—60°), diethyl ether and methanol, and sparingly soluble in acetone and dichloromethane.

Preparation of [1-(diphenylphosphino)-2-(diphenylarsino)ethane] (butylamine)tricarbonylmolybdenum(0)

Similarly tris(butylamine)tricarbonylmolybdenum(0) [1] (0.2 g) and dpda (0.22 g) gave after 4 h at 140°, the expected product (yield 40%). (Found: C, 55.8; H, 4.7; Mo, 13.0; N, 1.9. $C_{33}H_{35}AsMoNO_3P$ calcd.: C, 57.0; H, 5.0; Mo, 13.8; N, 2.0%.)

Preparation of [1-(diphenylphosphino)-2-(diphenylarsino)ethane] (butylamine)-tricarbonyltungsten(0)

Similarly tris(butylamine)tricarbonyltungsten(0) [13] (0.2 g) and dpda (0.17 g) gave after 6 h at 140°, the expected product (yield 38%). (Found: C, 50.0; H, 4.2; N, 1.6; W, 22.2. $C_{35}H_{35}AsNO_3PW$ calcd.: C, 50.5; H, 4.4; N, 1.7; W, 23.5%

Preparation of o-phenanthroline[1-(diphenylphosphino)-2-(diphenylarsino)ethane tricarbonylchromium(0)

(*o*-Phenanthroline)tetracarbonylchromium(0) (0.2 g) and dpda (0.25 g) were refluxed for 3 h in benzene under nitrogen, during which the mixture turned viole and pink crystals began to separate. The solid was filtered off and washed with ligh petroleum (40—60°) and finally with benzene to remove unreacted ligand and (*o*-phenanthroline)tetracarbonylchromium(0). The residue was dried in vacuo (yield 70%). It decomposed above 220° (without melting). (Found: C, 63.2; H, 4.1; Cr, 6.2; N, 3.3. $C_{41}H_{32}AsCrN_2O_3P$ calcd.: C, 64.9; H, 4.2; Cr, 6.8; N, 3.6%.) It was soluble in acetone, dichloromethane and insoluble in light petroleum(40—60°), ether and benzene. It was air stable.

Preparation of o-phenanthroline[1-(diphenylphosphino)-2-(diphenylarsino)ethane] tricarbonylmolybdenum(0)

(*o*-Phenanthroline)tetracarbonylmolybdenum(0) (0.2 g) and dpda (0.25 g) were refluxed for 2 h in benzene under nitrogen. The product was isolated in the same way as its chromium analogue (yield 60%) (Found: C, 60.2; H, 3.8; Mo, 10.8; N, 3.4. $C_{41}H_{32}AsMoN_2O_3P$ calcd.: C, 61.3; H, 3.9; Mo, 11.9; N, 3.4%.)

Preparation of o-phenanthroline[1-(diphenylphosphino)-2-(diphenylarsino)ethane] tricarbonyltungsten(0)

(*o*-Phenanthroline)tetracarbonyltungsten(0) (0.2 g) and dpda (0.2 g) were refluxed for 3½ h in benzene under nitrogen. The procedure used for isolation of the chromium analogue (yield 50%) gave the expected product (Found: C, 54.8; H, 3.2; N, 3.0; W, 19.4. $C_{41}H_{32}AsN_2O_3PW$ calcd.: C, 55.2; H, 3.4; N, 3.1; W, 20.6%.)

Preparation of 2,2'-bipyridine[1-(diphenylphosphino)-2-(diphenylarsino)ethane]-tricarbonylmolybdenum(0)

(2,2'-Bipy)tetracarbonylmolybdenum(0) (0.2 g) and dpda (0.25 g) were refluxed for 2 h in benzene under nitrogen. The product was isolated as above (yield 68%). (Found: C, 59.8; H, 4.0; Mo, 11.4; N, 3.5. $C_{39}H_{32}AsMoN_2O_3P$ calcd.: C, 60.1; H, 4.1; Mo, 12.3; N, 3.6%.)

Preparation of 2,2'-bipyridine[1-(diphenylphosphino)-2-(diphenylarsino)ethane]-tricarbonyltungsten(0)

(2,2'-Bipy)tetracarbonyltungsten(0) (0.2 g) and dpda (0.2 g) were refluxed for 4 h in benzene under nitrogen. The product was isolated as above (yield 56%). (Found: C, 53.2; H, 3.5; N, 3.2; W, 20.1. $C_{39}H_{32}AsN_2O_3PW$ calcd.: C, 54.0; H, 3.6; N, 3.2; W, 21.2%.)

Preparation of o-phenanthroline[1-(diphenylphosphino)-2-(diphenylarsino)ethane]-dicarbonylmolybdenum(0)

cis-[1-(Diphenylphosphino)-2-(diphenylarsino)ethane]tetracarbonylmolybdenum(0) (0.2 g) and *o*-phenanthroline (0.06 g) were refluxed for 8 h in toluene (15 ml) under nitrogen, during which a dark brown solid began to separate. The solid was filtered off, and washed first with light petroleum (40—60°) and then with benzene. The residue was dried in vacuo (yield 54.4%). (Found: C, 61.2; H, 3.2; Mo, 11.2; N, 3.0. $C_{40}H_{32}AsMoO_2N_2P$ calcd.: C, 62.0; H, 4.1; Mo, 12.4; N, 3.6%.) It was soluble in acetone and dichloromethane and insoluble in light petroleum (40—60°), diethyl ether and benzene, and was stable in air.

Acknowledgement

We thank the Council of Scientific and Industrial Research, New Delhi, for a research grant to A.K.S.. A gift of hexacarbonylmolybdenum(0) from the Climax Molybdenum Co., U.S.A., is also gratefully acknowledged.

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