Identification of Diastereoisomeric Tetracarbonyl[*o*-phenylenebis(methylphenylarsine)]molybdenum Complexes by Means of ^{1}H and ^{13}C Fourier Nuclear Magnetic Resonance Spectroscopy [1]

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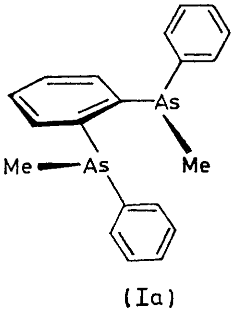
The diastereoisomers of *o*-phenylenebis(methylphenylarsine), (I), have been unambiguously identified by examining ^{13}C n.m.r. spectra of their corresponding tetracarbonylmolybdenum(0) complexes. An investigation into the nature of the triphenylphosphine-substituted complexes *fac*-[Mo(CO)$_3$(PPh$_3$)L] [L = (I)] has provided insight into the mechanism of the carbonyl-substitution reaction and an alternative means of identifying diastereoisomeric diarsines. Oxidation of the diastereoisomeric molybdenum tetracarbonyl complexes is also described. Fluxional behaviour of the seven-co-ordinate complexes [Mo(CO)$_3$(I)$_2$L] has been observed in solution and studied over the temperature range −90 to +35 °C using ^{1}H n.m.r. techniques. The stereochemistry of these complexes in solution is related to their crystal structures in the solid state.

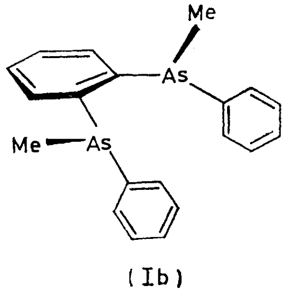
APART from any difficulties encountered in the resolution of ditertiary diarsines and related compounds, identification of the diastereoisomeric components of the dissymmetric system presents an initial obstacle which must be overcome before the enantiomers can be separated. The free diarsines have no spectroscopic property whereby identification of the diastereoisomers can be made. When both donor atoms in the bidentate molecule can be quaternised, and the substituted aliphatic diquaternary salt formed, a successful optical resolution effectively identifies the racemic component. This basic method has been employed by Bosnich and Wild [2] in identifying the diastereoisomers of 1,2-bis(methylphenylarsino)ethane. Where it is possible to doubly quaternise the ditertiary compounds and form suitable cyclic diquaternary systems, a structural assignment is possible using ^{1}H n.m.r. spectroscopy.[2-4] Another important and more general method of identification involves formation of suitable metal complexes of the diastereoisomeric compounds which allow a structural assignment to be made on the basis of a direct physical measurement. This method has been used in the work of Cheney and Shaw [5] where an examination of ^{1}H n.m.r. spectra of iodotrimethylplatinum(IV) complexes of 1,2-bis(methylphenylarsino)ethane enabled identification of each diastereoisomer of the diarsine to be made.

Recent reports [6] on ^{13}C n.m.r. spectra of transition-metal carbonyl complexes have shown that ^{13}C chemical shifts, δ(CO), of co-ordinated carbonyl groups are sensitive to changes in stereochemistry and electronic environment. We have made use of this observation and thereby unambiguously identified the diastereoisomers of the new bidentate ligand, *o*-phenylenebis(methylphenylarsine) (I), by means of its tetracarbonylmolybdenum(0) complexes.



(Ia)

racemic–(*RR*,*SS*)



(Ib)

meso–(*RS*)

RESULTS AND DISCUSSION

The ligand *o*-phenylenebis(methylphenylarsine) exists as two physically distinct diastereoisomers, (Ia) and (Ib), which can be separated by fractional crystallisation.† The work of Horner [7] showed that quaternisation of tertiary arsines occurs with retention of configuration. Only one of the two tertiary arsine moieties in each of the molecules (Ia) and (Ib) was quarternised by reaction with benzyl bromide, even under forcing conditions, and consequently the salts formed were the *threo*-(*RS*,*SR*) and *erythro*-(*RR*,*SS*) isomers (IIa) and (IIb), from the *racemic*-(*RR*,*SS*) and *meso*-(*RS*) isomers (Ia) and (Ib), respectively, both of which are potentially resolvable into enantiomers.‡ Accordingly it was not possible for us to doubly quarternise the diastereoisomers (Ia) and (Ib) with methylene or ethylene dihalides and consequently this eliminated from our considerations the identification procedure requiring formation of cyclic diquarternary systems. The method we describe here, which uses ^{13}C n.m.r. spectroscopy to

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† A detailed account of the synthesis of (I), its separation into diastereoisomers, and optical resolution is the subject of a forthcoming publication.

‡ The apparent inversion which takes place on quarternisation of the tertiary arsine groups is consistent with the specification of Cahn *et al.* for absolute configurations.[8]

[1] Presented at the Fifth Conference of the Division of Co-ordination and Metal-Organic Chemistry, Royal Australian Chemical Institute, Broadbeach Hotel, Surfers Paradise, February, 1974.

[2] B. Bosnich and S. B. Wild, *J. Amer. Chem. Soc.*, 1970, **92**, 459.

[3] L. Horner and J. P. Bercv, *Tetrahedron Letters*, 1966, 5783.

[4] E. R. H. Jones and F. G. Mann, *J. Chem. Soc.*, 1955, 401.

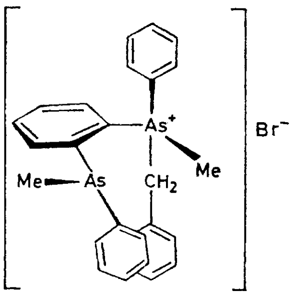
[5] A. J. Cheney and B. L. Shaw, *J. Chem. Soc.* (*A*), 1971, 3549.

[6] (*a*) L. F. Farnell, E. W. Randall, and E. Rosenberg, *Chem. Comm.*, 1971, 1078; (*b*) O. A. Gansow, B. Y. Kimura, G. R. Dobson, and R. A. Brown, *J. Amer. Chem. Soc.*, 1971, **93**, 5922; (*c*) O. A. Gansow, D. A. Schexnayder, and B. Y. Kimura, *ibid.*, 1972, **94**, 3406; (*d*) P. S. Braterman, D. W. Milne, E. W. Randall, and E. Rosenberg, *J.C.S. Dalton*, 1973, 1027; (*e*) B. E. Mann, *ibid.*, p. 2012.

[7] L. Horner and H. Fuchs, *Tetrahedron Letters*, 1963, 1573.

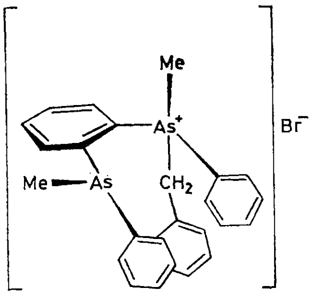
[8] R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem. Internat. Edn.*, 1966, **5**, 385.

identify the diastereoisomeric components of a dissymmetric chelating ditertiary diarsine, is believed to be of some generality since tetracarbonylmolybdenum(0) derivatives of many bidentate ligands are readily obtained and data from ^{13}C n.m.r. spectroscopy of metal carbonyl compounds are now available.



(IIa)

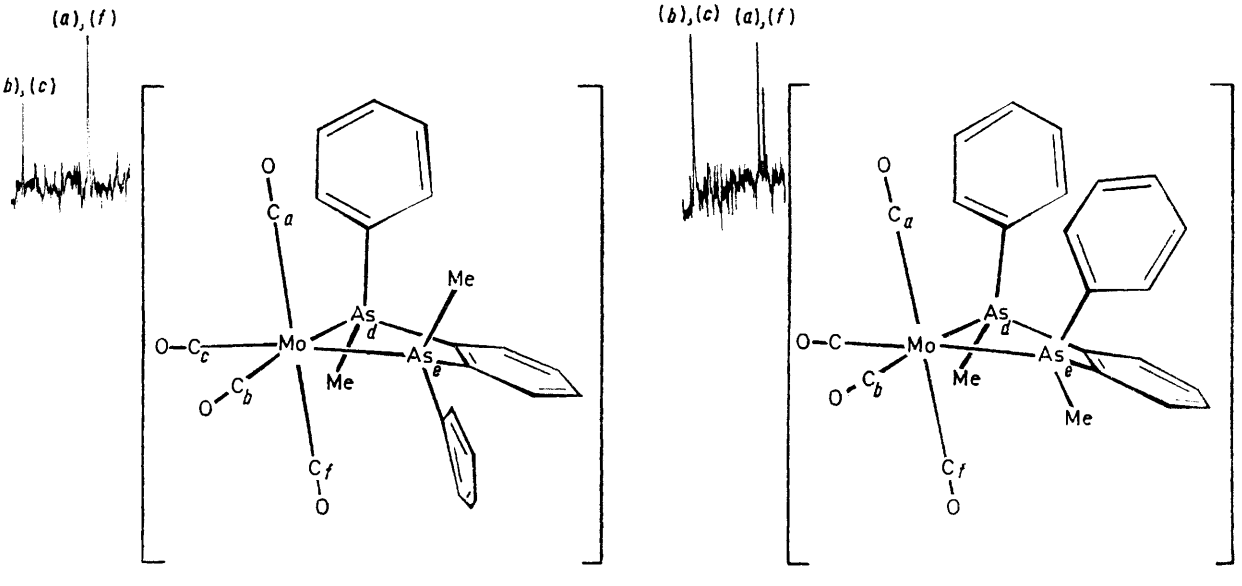
threo-(RS,SR)



(IIb)

erythro-(RR,SS)

When either of the diastereoisomers (Ia) of (Ib) was heated under reflux with molybdenum hexacarbonyl in ethanol in the presence of sodium tetrahydroborate, according to the method of Chatt *et al.*,[9] the diastereoisomeric tetracarbonylmolybdenum(0) complexes (IIIa) and (IIIb) were formed. The crystalline products are very soluble in common organic solvents and some details of their physical properties are given in Table 1.



(IIIa) (IIIb)

FIGURE 1 Configurations of *racemic*-(IIIa) and *meso*-(IIIb) together with the ^{13}C n.m.r. spectra of these complexes in the carbonyl region

^{13}C *N.m.r. Spectra.*—In Figure 1 the diastereoisomeric structures (IIIa) and (IIIb) appear together with an inset reproduction of their ^{13}C n.m.r. spectra in the carbonyl region. Full details of the ^{13}C n.m.r. spectra of the complexes (IIIa) and (IIIb) are presented in Table 2. The assignment of resonances corresponding to carbon nuclei *cis* and *trans* to the arsenic donor atoms is unambiguous. Two singlets of equal intensity at 208·6 and 217·7 p.p.m. were observed in the spectrum of the complex (IIIa) which correspond to the equivalent pairs of carbon nuclei of the *cis*-(*bc*) and *trans*-carbonyl groups (*af*), respectively. This assignment was verified in the spectrum of the diastereoisomeric complex (IIIb) where it was observed that the higher-field resonance was split into two components of equal intensity, $\Delta\delta(^{13}CO)$ 0·7 p.p.m., because of the obvious nonequivalence of the two carbon nuclei *cis* to the arsenic donor atoms in this molecule. The values observed for the carbonyl-group chemical shifts and the magnitude of the chemical-shift difference between the *cis*- and

TABLE 1

I.r. and ^1H n.m.r. spectral data for the molybdenum *o*-phenylenebis(methylphenylarsine) complexes

Compound	ν(CO) Bands [a]/cm^{-1}	δ(As–CH$_3$) [b]/ p.p.m.
(Ia)		1·25
(IIIa)	2 020, 1 920, 1 905, 1 890	1·93
(IVa)	1 965, 1 860, 1 845	2·09, 1·35 [c]
(Va)	2 040, 1 958, 1 902	2·28 [d]
(Ib)		1·41
(IIIb)	2 028, 1 928, 1 900, 1 885	2·04 [c]
(IVb)	1 946, 1 864, 1 847	2·18
(Vb)	2 045, 1 980, 1 925	2·65 [d]

[a] In dichloromethane. [b] In deuteriochloroform with Me_4Si as internal standard; all resonances are singlets. [c] A solvent molecule of crystallisation (MeOH) was also clearly observed in the ^1H n.m.r. spectra of these complexes. [d] At room temperature.

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[9] J. Chatt, G. J. Leigh, and N. Thankarajan, *J. Organometallic Chem.*, 1971, **29**, 105.

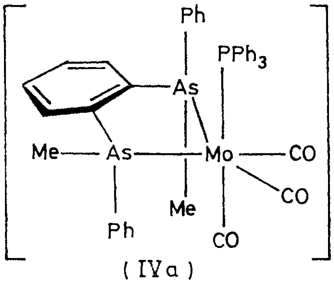
trans-carbonyl groups was in agreement with values previously reported for similar compounds. The complexes $[Mo(CO)_5L]$ (L = a tertiary phosphine or arsine, phosphite, or primary amine), show a range of chemical shifts, *viz.* 206·3—206·8 p.p.m., for carbon nuclei of carbonyl groups co-ordinated *cis* to the donor atom and in the range 208·7—211·0 p.p.m. for those of carbonyls in *trans*-positions. In the disubstituted complexes *cis*-$[Mo(CO)_4L_2]$ the same resonances for the *cis*- and *trans*-carbonyls occur at 210·6 and 218·5 p.p.m., respectively.[6d]

TABLE 2

^{13}C N.m.r. data (δ/p.p.m.) for the complexes *racemic*-(IIIa) and *meso*-(IIIb) [a]

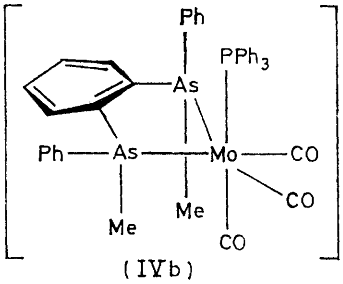
		(IIIa)	(IIIb)
o-Phenylene rin	$C_{1,2}$	142·0	141·9
	$C_{3,6}$	131·4	130·4
	$C_{4,5}$	129·4	129·3
Ph–As	C_1	139·4	139·7
	$C_{2,6}$	130·4	131·5
	$C_{3,5}$		130·3
	C_4	128·9	128·9
	CH_3–As	15·8	15·6
	cis-CO	208·6 (14) [b]	208·8, 208·1 (9·9)
	trans-CO	217·7 (14)	217·9 (15)

[a] The positions of the chemical shifts are referred to Me_4Si as internal standard. [b] Actual integration values obtained from the digital recorder of the spectrometer are given in parentheses.



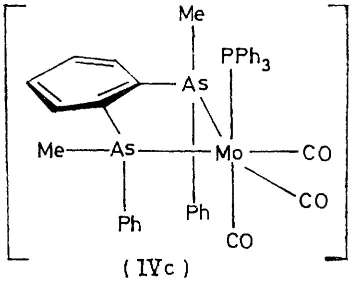
(IVa)

fac—racemic



(IVb)

fac—meso



(IVc)

fac—meso

I.r. Spectra.—Spectroscopic details for the various molybdenum carbonyl derivatives described here are given in Table 1. For the diastereoisomeric complexes (IIIa) and (IIIb), which possess C_2 and C_s idealised point-group symmetry respectively, four i.r.-active ν(CO) vibrations are expected.[10] Four bands were indeed observed in this region of the i.r. spectrum in both these complexes. The small variations in intensity and position of the bands in these spectra, however, does not allow assignment of a particular structure to be made on the basis of these results.

Triphenylphosphine-substituted fac-*Complexes.*—It is established that substitution of a carbonyl group by a unidentate ligand in complexes of the type $[M(CO)_4L]$ [where M = Cr, Mo, or W; L = a bidentate, *e.g.* 2,2′-bipyridyl or 1,2-bis(diphenylphosphino)ethane] invariably occurs *cis* to the donor atoms of the bidentate ligand.[11] A means therefore emerges of identifying the diastereoisomeric complexes (IIIa) and (IIIb) by examining ^1H n.m.r. spectra of their *cis*-substituted derivatives. When complex (IIIa) was irradiated in the presence of triphenylphosphine (1 mol) in tetrahydrofuran (thf) as solvent the bright yellow crystalline complex (IVa) was isolated. If the substitution occurs normally, that is in a *cis*-position, then this isomer has the *fac*-structure shown, and only one isomer is possible. The *fac*-structure for this complex is also indicated by the observation of three strong ν(CO) absorptions in the i.r. spectrum.[10,11] It is readily seen from the structure of (IVa) that there are two different environments of the methyl groups in this molecule and these were observed at 1·35 and 2·09 p.p.m. in the ^1H n.m.r. spectrum. In the parent molecule (IIIa) the methyl groups are in identical environments and were observed as a singlet at 1·93 p.p.m. The higher-field resonance which appeared at 1·35 p.p.m. in the spectrum of the *fac*-complex (IVa) is assigned to the protons of the methyl group which are shielded by the presence of the adjacent triphenylphosphine molecule.

In the *meso*-complex (IIIb) two different products are possible from this substitution reaction with triphenylphosphine depending on which of the *cis*-carbonyl groups is replaced. We were only able to observe one isomer under the conditions described here and have assigned configuration (IVb) to it on the basis of the chemical shift of the observed methyl resonance. The singlet methyl resonance appeared at 2·18 p.p.m. in the ^1H n.m.r. spectrum of (IVb) and indicates the *fac*-structure shown where the two equivalent methyl groups are *cis* to the carbonyl groups and *trans* to the triphenylphosphine ligand. On the other hand, if a meridional carbonyl group had been substituted in the *meso*-complex (IIIb), only one isomer would have resulted but in this situation both arsenic methyl groups would have been non-equivalent and hence two ^1H n.m.r. signals observed. It is noteworthy that the *fac*-isomer with configuration (IVb) is not expected from a stereochemical point of view because the triphenylphosphine molecule is occupying the most hindered of the two possible *cis*-positions. Formation of the complex (IVb) appears to indicate that the most-hindered carbonyl group is lost preferentially in this case and that the thf-substituted intermediate retains a fixed octahedral structure.

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[10] F. A. Cotton, *Inorg. Chem.*, 1964, **3**, 702.

[11] M. H. B. Stiddard, *J. Chem. Soc.*, 1963, 756.

Oxidation of the Diastereoisomeric Complexes (IIIa) *and* (IIIb) *with Iodine.*—It is well known [12] that addition of halogens to many disubstituted tetracarbonylmolybdenum(0) complexes leads to elimination of a carbon monoxide molecule and formation of a dihalogenomolybdenum(II) species. The overall reaction is termed an oxidative elimination and in the case of the complex [Mo(CO)$_4$(pdma)] [pdma = *o*-phenylenebis(dimethylarsine)] the products [Mo(CO)$_3$(pdma)X$_2$] (X = Br or I) have been isolated. We thus oxidised the diastereoisomeric complexes (IIIa) and (IIIb) with iodine in an attempt to obtain an alternative identification procedure. Simple mixing of the two reagents in stoicheiometric quantities in chloroform as solvent proceeded smoothly and carbon monoxide was evolved. The products, however, formed as large orange-red crystals of the corresponding solvent adducts, *viz.* equations (1) and (2).

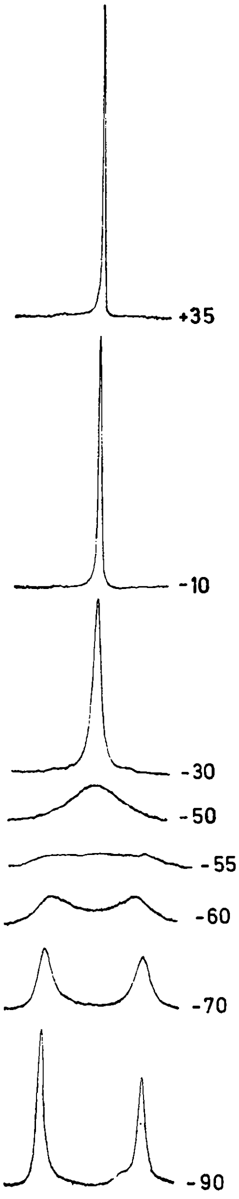

FIGURE 2 ^{1}H N.m.r. spectra (35% w/v) of *racemic*-(Va) in CH$_2$Cl$_2$ at various temperatures (°C) showing the arsenic–methyl resonances. Integration of the spectrum at −90 °C showed the signals to be of equal intensity

$$\text{(IIIa)} \xrightarrow[-\mathrm{CO}]{\mathrm{I_2/CHCl_3}} \underset{\text{(Va)}}{\textit{racemic}[\{o\text{-}\mathrm{C_6H_4(AsMePh)_2}\}\mathrm{Mo(CO)_3I_2}],\mathrm{CHCl_3}} \qquad (1)$$

$$\text{(IIIb)} \xrightarrow[-\mathrm{CO}]{\mathrm{I_2/CHCl_3}} \textit{meso}[\{o\text{-}\mathrm{C_6H_4(AsMePh)_2}\}\mathrm{Mo(CO)_3I_2}],\mathrm{CHCl_3} \qquad (2)$$

Both the di-iodo-complexes (Va) and (Vb) exhibited three strong ν(CO) absorptions in their i.r. spectra in solution but only small variations were observed in the actual positions of the bands in the different complexes. The ^{1}H n.m.r. spectra of these complexes in CDCl$_3$ at room temperature showed only one arsenic–methyl resonance in each case. This behaviour is typical of fluxional molecules. When a solution of the complex (Va) in dichloromethane was cooled the singlet broadened and eventually collapsed at a temperature of *ca.* −55 °C. As the temperature decreased further two new broad singlets appeared at 2·68 and 1·98 p.p.m. ^{1}H N.m.r. spectra for (Va) at various temperatures are shown in Figure 2. In view of the fluxional behaviour of these seven-co-ordinate complexes in solution we determined the crystal structures of the diastereoisomeric complexes (Va) and (Vb) in the solid state.[13] The different environments for the two methyl groups in both crystalline complexes is clearly noticeable in Figure 3. Seven-co-ordinate complexes of the type [ML$_5$L′] (L′ = bidentate ligand) can display four possible basic idealised stereochemistries which are very similar in respect to their total energy and also closely related to each other by small relative displacements of the ligating atoms.[13] The low-temperature results found here for the *racemic*-complex may be interpreted in terms of a ‘ freezing out ’ of the solid-state structure. The means by which the two singlets in the ^{1}H n.m.r. spectra of the complex are averaged at room temperature is rationalised by considering that the iodine ligand occupying the capped position of the trigonal prism moves freely from one of the square faces of the prism to the adjacent one. For the system studied here, where site exchange occurs between two uncoupled groups with equal populations, the rate constant found from the coalescence temperature was 9·3 s^{-1}. Applying Eyring's equation and using this value for the rate constant a free energy of activation ($\Delta G^\ddagger$) of 10·6 kcal mol^{-1} was obtained.* This energy is

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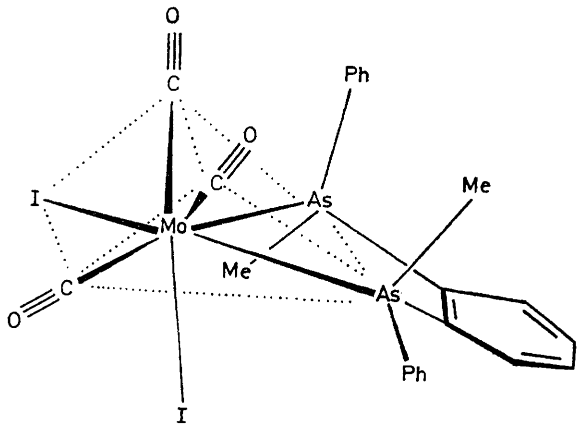
* 1 cal = 4·184 J.

[12] K. Edgar, B. F. G. Johnson, J. Lewis, and S. B. Wild, *J. Chem. Soc.* (*A*), 1968, 2851; J. Lewis and R. Whyman, *J. Chem. Soc.*, 1965, 5486.

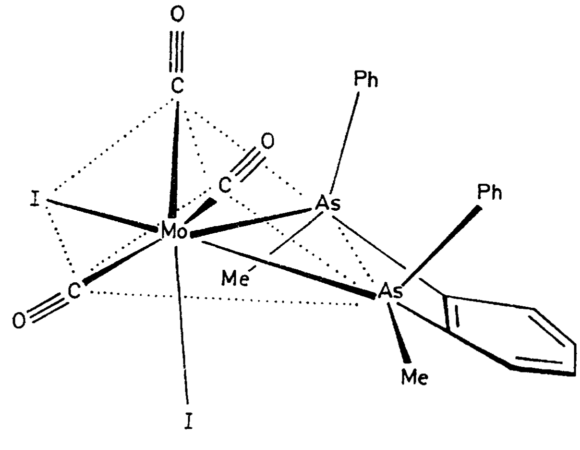
[13] P. D. Brotherton, J. C. Dewan, K. Henrick, D. L. Kepert, K. R. Trigwell, A. H. White, and S. B. Wild, unpublished work.

considerably larger than that found in seven-co-ordinate complexes containing seven unidentate ligands.[14]

In the case of the *meso*-complex (Vb), cooling of a dichloromethane solution of it to −90 °C caused the singlet observed at 2·65 p.p.m. at room temperature to broaden slightly. It is readily seen that the co-ordination geometry of the ligating atoms in both (Va) and (Vb) is identical and that the structures are best considered in terms of iodine-capped trigonal-prismatic models. The methyl groups are clearly in different environments in the solid state in both complexes and we have no evidence for the formation of the alternative more-hindered isomer of (Vb) where the capping iodine ligand is adjacent to the two phenyl rings. The *X*-ray studies also show the chloroform molecule of crystallisation in each structure. It thus appears that the more-rapid fluxional behaviour observed for (Vb) when compared with (Va) is due to influences outside the basic co-ordination sphere. The slight line broadening of the signal in the low-temperature ^{1}H n.m.r. spectrum of (Vb) may be attributed to a lower rate of molecular tumbling in solution at this temperature with the concomitant effect on the correlation time.



(Va)



(Vb)

FIGURE 3 Molecular configurations of crystalline (Va) and (Vb) obtained from *X*-ray studies (solvent molecules are not shown)

EXPERIMENTAL

All reactions were carried out under a dinitrogen atmosphere using purified solvents. Microanalyses were carried out by the Australian Microanalytical Service, Melbourne.

I.r. spectra were measured with a Perkin-Elmer 337 grating spectrometer using dichloromethane solutions in 0·1 mm sodium chloride cells. ^{1}H N.m.r. spectra at 35 °C were recorded at 60 MHz by means of a Varian A-60 spectrometer, and chemical shifts were measured relative to tetramethylsilane as internal standard. Variable-temperature ^{1}H n.m.r. spectra were recorded over the temperature range +35 to −90 °C with a Bruker HX-90 spectrometer. Temperatures were measured with a copper–constantan thermocouple located just below the sample tube and were calibrated using a similar thermocouple held coaxially in the spinning sample tube. ^{13}C N.m.r. spectra were recorded at 22·63 MHz using a Bruker HFX-13 spectrometer, operating in the Fourier-transform mode. Proton-noise decoupling was carried out using a 90 MHz broad-band decoupler. Spectra were recorded in CDCl$_3$ (80%, w/v), with a spectral width of 100 Hz cm^{-1}, using 8 k data points resulting in a 4 k frequency-domain spectrum.

The synthesis and separation of the diastereoisomers of *o*-phenylenebis(methylphenylarsine), (Ia) and (Ib), is to be reported elsewhere.

Tetracarbonyl[racemic-o-*phenylenebis*(*methylphenylarsine*)]*molybdenum*(0), (IIIa).—Molybdenum hexacarbonyl (6 g, 2·27 mmol), sodium tetrahydroborate (1·5 g), and *racemic*-*o*-phenylenebis(methylphenylarsine) (Ia) (10 g, 2·44 mmol) were heated in ethanol (300 cm^3) under gentle reflux for 5 h. The reaction mixture was cooled, concentrated under reduced pressure (to *ca.* 10 cm^3), diluted with water (300 cm^3), and then extracted with dichloromethane (3 × 100 cm^3). The combined dichloromethane extracts were dried (MgSO$_4$), concentrated (to *ca.* 15 cm^3), and carefully diluted with methanol to give the *racemic*-complex (IIIa) (12·24 g, 1·98 mmol, 87%) as pale lemon-yellow needles, m.p. 160—161 °C (Found: C, 46·3; H, 3·3. Calc. for C$_{24}$H$_{20}$As$_2$MoO$_4$: C, 46·6; H, 3·2%).

Tetracarbonyl[meso-o-*phenylenebis*(*methylphenylarsine*)]-*molybdenum*(0), (IIIb).—Treatment of molybdenum hexacarbonyl (2 g, 0·76 mmol) with sodium tetrahydroborate (0·8 g) and *meso*-*o*-phenylenebis(methylphenylarsine) (Ib) (3·3 g, 0·81 mmol) by the above method yielded the corresponding *meso*-complex (IIIb) (3·26 g, 0·53 mmol, 65%) as off-white microcrystals, m.p. 142—143 °C (Found: C, 46·2; H, 3·3. Calc. for C$_{24}$H$_{20}$As$_2$MoO$_4$: C, 46·6; H, 3·2%).

fac-*Tricarbonyl*[racemic-o-*phenylenebis*(*methylphenylarsine*)]*triphenylphosphinemolybdenum*(0)-*Methanol* (1/1), (IVa).—The *racemic*-complex (IIIa) (0·61 g, 1·0 mmol) and triphenylphosphine (0·26 g, 1·0 mmol) in tetrahydrofuran

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[14] L. Malatesta, M. Freni, and V. Valenti, *Gazzetta*, 1964, **94**, 1278; E. L. Muetterties and K. J. Packer, *J. Amer. Chem. Soc.*, 1964, **86**, 293; R. J. Gillespie and J. W. Quail, *Canad. J. Chem.*, 1964, **42**, 2671; F. N. Tebbe and E. L. Muetterties, *Inorg. Chem.*, 1968, **7**, 172.

(thf) (10 cm^3) were irradiated with u.v. light for 3 h. The solvent was removed *in vacuo* and the residue dissolved in benzene (10 cm^3) and diluted with methanol to give the *racemic*-complex (IVa) (0·71 g, 0·8 mmol, 82%) as yellow cubes, m.p. 183—183·5 °C (Found: C, 57·0; H, 4·3. Calc. for $C_{42}H_{39}As_2MoO_4P$: C, 57·0; H, 4·4%).

fac-*Tricarbonyl*[meso-o-*phenylenebis*(*methylphenylarsine*)]-*triphenylphosphinemolybdenum*(0)*–Methanol* (1/1), (IVb).—A solution of the *meso*-complex (IIIb) (0·31 g, 0·5 mmol) and triphenylphosphine (0·13 g, 0·5 mmol) in thf (10 cm^3) was similarly irradiated for 2 h. Evaporation of the solvent gave a solid residue * which when recrystallised from benzene–methanol gave the *meso*-complex (IVb) (0·27 g, 0·6 mmol, 61%) as pale yellow crystals, m.p. 170—171 °C (Found: C, 56·7; H, 4·2. Calc. for $C_{42}H_{39}As_2MoO_4P$: C, 57·0; H, 4·4%).

Tricarbonyldi-iodo[racemic-o-*phenylenebis*(*methylphenylarsine*)]*molybdenum*(II)*–Chloroform* (1/1), (Va).—The *racemic*-complex (IIIa) (1·54 g, 2·5 mmol) in chloroform (20 cm^3) was treated with a solution of iodine (0·63 g, 2·5 mmol) in chloroform (100 cm^3) and stirred rapidly for 0·5 h at room temperature. Carbon monoxide was evolved and orange-red cubes of the 1 : 1 chloroform adduct (Va) (1·83 g, 1·9 mmol, 75%), m.p. 226—229 °C, remained after concentration of the reaction mixture and the addition of methanol (Found: C, 29·7; H, 2·3. Calc. for $C_{24}H_{21}As_2Cl_3I_2MoO_3$: C, 29·8; H, 2·2%).

Tricarbonyldi-iodo[meso-o-*phenylenebis*(*methylphenylarsine*)]*molybdenum*(II)*–Chloroform* (1/1), (Vb).—The *meso*-complex (IIIb) (0·92 g, 1·5 mmol) in chloroform (25 cm^3) was oxidised with a solution of iodine (0·38 g, 1·5 mmol) in chloroform (100 cm^3) and the reaction mixture stirred efficiently for 0·5 h. After carbon monoxide (1 mol) had been liberated, the volume of the solution was reduced and methanol added, the *meso*-complex (Vb) (0·89 g, 0·93 mmol, 62%) forming as yellow-orange crystals of the 1 : 1 chloroform adduct, m.p. 200—203 °C (Found: C, 30·1; H, 2·3. Calc. for $C_{24}H_{21}As_2Cl_3I_2MoO_3$: C, 29·8; H, 2·2%).

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* The ^1H n.m.r. spectrum showed only one isomer present in this residue.