Organometallic Cyclisation Reactions. Part II.† Formation of Molybdenum Arsine Complexes containing Five-membered Rings

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A reductive cyclisation reaction occurs when complexes of the type [Mo(η-C_5H_5)(CO)$_2$I(L)] (L is a halogen-substituted tertiary arsine) react with sodium amalgam in tetrahydrofuran giving *cyclic molybdenum–arsine* complexes. The stereochemical non-rigidity of the ring systems in solution has been interpreted in terms of a square-pyramidal–trigonal-bipyramidal isomerisation process. The cyclic complex dicarbonyl(η-cyclopentadienyl)(3-dimethylarsinopropyl-*C*^{1}*As*)molybdenum(II) readily undergoes hydride abstraction to form a cationic derivative of chelated allyldimethylarsine.

THE formation of alkyl intermediates in the catalytic hydrogenation of olefins by soluble transition-metal complexes is considered to be an important step in the overall reduction process. An insertion reaction occurs when tertiary phosphines bearing an unsaturated moiety react with metal hydrides [1] giving stable cyclic metal–carbon compounds derived from either Markownikoff or anti-Markownikoff addition depending on the metal employed.[2] We have found a convenient method for the preparation of chelated metal–carbon σ-bonded complexes which involves the reduction of a suitably substituted metal carbonyl halide with sodium amalgam.[3]

The substitution of a carbonyl group in [Mo(η-C_5H_5)(CO)$_3$I] by tertiary arsines and related ligands (L) to form the derivatives [Mo(η-C_5H_5)(CO)$_2$(I)L] followed by sodium-amalgam reduction provides the main preparative route [4,5] to the sodium salts of the substituted metal carbonyl anions [Mo(η-C_5H_5)(CO)$_2$L]$^-$. When a suitable halogen-substituted tertiary arsine is used in this

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† Part I is ref. 3.

[1] P. R. Brookes and R. S. Nyholm, *Chem. Comm.*, 1970, 169.

[2] M. A. Bennett and R. Watt, *Chem. Comm.*, 1971, 94.

[3] K. P. Wainwright and S. B. Wild, *J.C.S. Chem. Comm.*, 1972, 571.

[4] W. Hieber, M. Höfler, and J. Muschi, *Chem. Ber.*, 1965, **98**, 311.

[5] A. R. Manning, *J. Chem. Soc.* (*A*), 1967, 651.

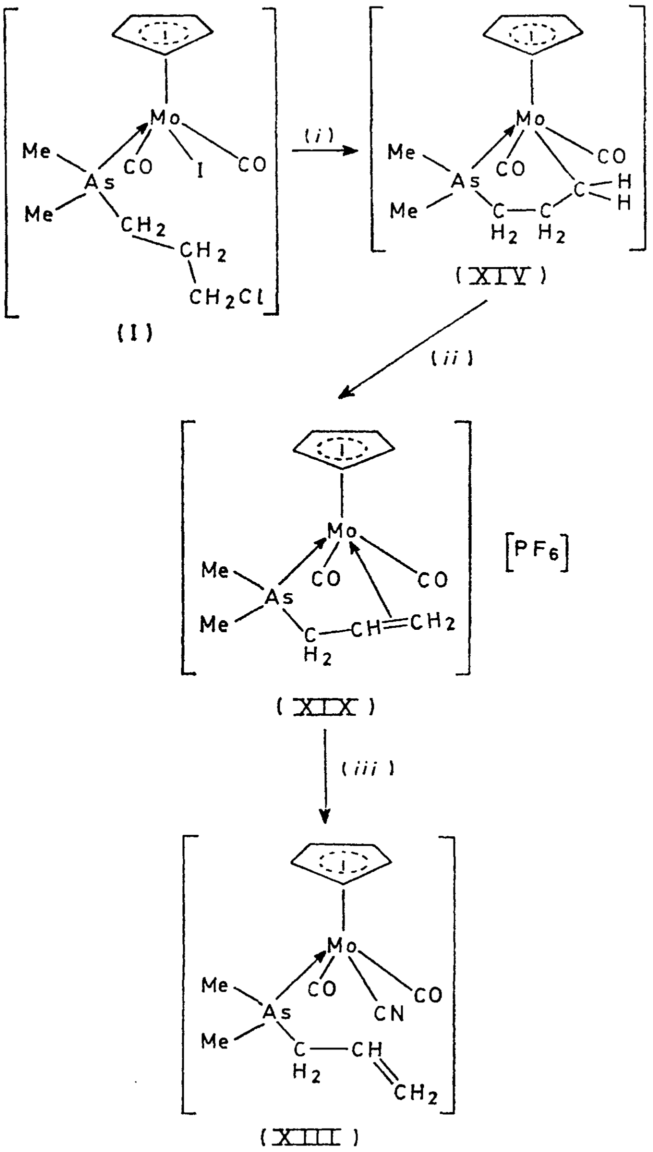
reaction an intramolecular elimination occurs between the anion generated in the reduction process and the organic halide. We describe here details of this reductive-cyclisation reaction and the preparation and properties of some five-membered molybdenum–arsenic rings derived from halogeno-alkyl- and -aryl-substituted tertiary arsines.

RESULTS AND DISCUSSION

Cyclisation of $AsR_2[(CH_2)_3Cl]$ ($R = Me$, Ph, *or* C_6H_4Me-*p*).—The reaction between $[Mo(\eta\text{-}C_5H_5)(CO)_3I]$ and $AsMe_2[(CH_2)_3Cl]$ [6] proceeds smoothly in refluxing benzene to give (I) as purple prisms, m.p. 85—86 °C (94%), after chromatography on alumina. Cyclisation was achieved in a few minutes by reduction of (I) with a three-fold excess of sodium amalgam in tetrahydrofuran (thf) as solvent giving (XIV) as air-stable yellow needles (96%), m.p. 107—108 °C, after sublimation (80 °C, 0.1 mmHg) and recrystallisation from benzene.* Evidence for the cyclisation was observed in its ^1H n.m.r. spectrum by the loss of the resonance due to the CH_2Cl protons and by the position of the C_5H_5 signal which occurred 0.31 p.p.m. upfield relative to (I). The phenyl and *p*-tolyl derivatives (XV) and (XVI) were prepared similarly as large yellow prisms after recrystallisation from toluene–light petroleum. Details of the reaction conditions required to form the intermediate iodo-complexes and some of their physical properties are in Table 1. In Table 2 information concerning the reductive-cyclisation reaction and some physical properties of the cyclic products is summarised.

Hydride-abstraction reactions. Trityl tetrafluoroborate readily abstracts a hydride ion from the β position of (XIV) to give the cationic species (XIX) (Scheme 1). The hexafluorophosphate salt showed a weak band at 1 525 cm^{-1} which is attributed to a co-ordinated olefinic bond. In addition, a cationic molybdenum species was indicated in the i.r. spectrum in the ν(CO) region where bands occurred at 2 015m and 1 930s cm^{-1} (Nujol), *ca.* 80 cm^{-1} to higher frequencies than those found in the neutral starting material. The allyl resonances in (XIX) are similar to those found in (IX) but are shifted downfield due to formation of the salt.

Some reactions of complex (XIX) have been investigated. With a methanol solution of potassium cyanide, the expected addition to the co-ordinated double bond did not occur, but resulted in displacement of the unsaturated residue giving (XIII) in small yield together with extensive decomposition. The presence of an unco-ordinated double bond in (XIII) was confirmed by comparison with the iodo-analogue, (IX), prepared by direct substitution of $[Mo(\eta\text{-}C_5H_5)(CO)_3I]$ with allyldimethylarsine.[7] Both (XIII) and its iodo-analogue clearly showed ν(C=C) at *ca.* 1 625 cm^{-1} which is characteristic of an unco-ordinated double bond. The downfield shift of the resonance of the C_5H_5 protons in the ^1H n.m.r. spectrum of (XIII) (Table 1) relative to the same resonance in (XIV) indicates decreased shielding of the cyclopentadienyl protons due to direct attachment of the cyanide group to the metal atom. The *cis* geometry of (XIII) is indicated by the i.r. spectrum in the ν(CO) region where the two bands observed showed the intensity variation accepted for *cis* complexes of this type.[5] The ^1H n.m.r. spectrum, which showed a sharp singlet methyl resonance at δ 1.51 p.p.m., is consistent with this formulation, the reduced chirality of the molecule resulting from the structural similarity of the adjacent cyano- and carbonyl groups. Accordingly, the chemical-shift difference between the diastereotopic methyl groups in (XIII) is expected to be small or negligible, as



SCHEME 1 (*i*), Na–Hg, thf; (*ii*), $[Ph_3C][BF_4]$, $[H_4N][PF_6]$; (*iii*), KCN, MeOH

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* 1 mmHg ≈ 13.6 × 9.8 Pa.

[6] G. A. Barclay, R. S. Nyholm, and R. V. Parish, *J. Chem. Soc.*, 1961, 4433.

[7] F. Challenger and L. Ellis, *J. Chem. Soc.*, 1935, 396.

TABLE 1

Details of reaction conditions, physical properties, and elemental analyses of the complexes $[Mo(\eta\text{-}C_5H_5)(CO_2)\text{-}(CO)_2(L)X]$

Complex	Reaction time (t/h) [a]	Recrystallisation solvent [b]	Yield (%)	M.p. (θ_c/°C)	Analysis [c] (%)		$\tilde{\nu}$(CO) [d]/ cm^{-1}	δ [e]/p.p.m.	
					C	H		As–Me	C_5H_5
cis-$[Mo\{AsMe_2(CH_2CH_2CH_2Cl)\}(\eta\text{-}C_5H_5)(CO)_2I]$ (I)	12	*f*	82	85—86	27.8 (27.4)	3.3 (3.3)	1 960s, 1 860ms	1.67, 1.58	5.38
cis-$[Mo\{AsPh_2(CH_2CH_2CH_2Cl\})(\eta\text{-}C_5H_5)(CO)_2I]$ (II)	12	*f*	91	144	41.0 (40.6)	3.4 (3.3)	1 960s, 1 870ms		5.32
trans-$[Mo\{As(C_6H_4Me\text{-}p)_2(CH_2CH_2CH_2Cl)(\eta\text{-}C_5H_5)(CO)_2I]$ (III)	14	*f*	85	118—120	42.7 (42.5)	3.7 (3.7)	1 968ms, 1 870s	2.40	5.33
cis-$[Mo\{AsMe_2(CH_2C_6H_4Cl\text{-}o)\}(\eta\text{-}C_5H_5)(CO)_2I]$ (IV)	14	*g*	85	103—104	33.7 (33.4)	3.05 (3.0)	1 980s, 1 880ms	1.56, 1.48	5.32
cis-$[Mo\{AsMe_2(CH_2C_6H_4Br\text{-}o)\}(\eta\text{-}C_5H_5)(CO)_2I]$ (V)	14	*g*	89	121—122	31.2 (31.1)	2.8 (2.6)	1 970s, 1 880ms	1.55, 1.51	5.33
cis-$[Mo\{AsMe_2(C_6H_4Me\text{-}o)\}(\eta\text{-}C_5H_5)(CO)_2I]$ (VI)	15	*f*	86	135—136	35.8 (35.4)	3.3 (3.4)	1 964s, 1 880ms	2.01, 1.93	5.33
cis-$[Mo\{AsMe_2(C_6H_4CH_2OMe\text{-}o)\}(\eta\text{-}C_5H_5)(CO)_2I]$ (VII)	14	*g*	95	118—119	36.0 (35.9)	3.6 (3.4)	1 962s, 1 870ms	2.02, 1.57	5.35
cis-$[Mo\{AsMe_2(C_6H_4CH_2OMe\text{-}o)\}Br(\eta\text{-}C_5H_5)(CO)_2]$ (VIII)	4	*g*	80	95—96	38.9 (39.0)	3.8 (3.8)	1 971s, 1 882ms	1.91, 1.87	5.36
trans-$[Mo\{AsMe_2(CH_2CH{=}CH_2)\}(\eta\text{-}C_5H_5)(CO)_2I]$ (IX)	20	*f*	80	66—68	29.6 (29.4)	3.3 (3.3)	1 955ms, 1 870s	1.56	5.38 [h]
cis-$[Mo(AsMe_2Ph)(\eta\text{-}C_5H_5)(CO)_2I]$ (X)	12	*g*	90	81—82	34.5 (34.3)	3.1 (3.1)	1 965s, 1 870ms	1.96, 1.90	5.37
cis-$[Mo\{AsMe_2(C_6H_4CH_2Br\text{-}o)\}(\eta\text{-}C_5H_5)(CO)_2I]$ (XI)		*g*	64	140—141	30.1 (29.8)	2.7 (2.6)	1 970s, 1 882ms	2.06, 1.97	5.24
cis-$[Mo\{AsMe_2(C_6H_4CH_2Br\text{-}o)\}Br(\eta\text{-}C_5H_5)(CO)_2]$ (XII)		*g*	75	145—146	33.5 (33.6)	2.8 (3.6)	1 960s, 1 910ms	1.99, 1.94	5.38

[a] In refluxing benzene. [b] Crystalline crimson solids were obtained. [c] Calculated values are given in parentheses. [d] In $CHCl_3$. [e] In $CDCl_3$ with $SiMe_4$ as internal standard. [f] Diethyl ether. [g] Toluene–light petroleum. [h] Allyl resonances: δ 6.13—4.96 (brm, 3 H, $CH{=}CH_2$) and 2.91 p.p.m. (d, 2 H, CH_2, J_{HH} 7.3 Hz).

TABLE 2

Details of reaction conditions, physical properties, and elemental analyses of the cyclic complexes [a]

Complex	Starting material	Reaction time [b]	Recrystallisation solvent [c]	Yield (%)	M.p. (θ_c/°C)	Analysis [d] (%)		$\tilde{\nu}$(CO) [e]/ cm^{-1}	δ [f]/p.p.m.	
						C	H		As–Me	C_5H_5
$[Mo(CH_2CH_2CH_2AsMe_2)(\eta\text{-}C_5H_5)(CO)_2]$ (XIV)	(I)	30 min	*g*	94	107—108	39.7 (39.6)	4.8 (4.7)	1 940s, 1 860m	1.35, 1.25	4.95
$[Mo(CH_2CH_2CH_2AsPh_2)(\eta\text{-}C_5H_5)(CO)_2]$ (XV)	(II)	30 min	*h*	82	134—135	54.3 (54.1)	4.3 (4.3)	1 955s, 1 870m		5.04
$[Mo\{CH_2CH_2CH_2As(C_6H_4Me\text{-}p)_2\}(\eta\text{-}C_5H_5)(CO)_2]$ (XVI)	(III)	30 min	*i*	75	139—140			1 930s, 1 845m	2.43, 2.38, 2.29 [j]	4.94
$[Mo(C_6H_4CH_2AsMe_2\text{-}o)(\eta\text{-}C_5H_5)(CO)_2]$ (XVII)	(V)	16 h	*h*	70	126—128	46.9 (46.7)	4.3 (4.2)	1 922m, 1 850s	1.49	5.04
$[Mo(CH_2C_6H_4AsMe_2\text{-}o)(\eta\text{-}C_5H_5)(CO)_2]$ (XVIII)	(XI), (XII)	12 h	*h*	72	114—115	46.6 (46.7)	4.2 (4.2)	1 925s, 1 855m	1.61, 1.52	4.94
$[Mo\{AsMe_2(CH_2CH{=}CH_2)\}(\eta\text{-}C_5H_5)(CO)_2][PF_6]$ (XIX)	(XIV)		*k*	32	164 (decomp.)	28.1 (28.3)	3.3 (3.2)	2 015m, [l] 1 930s, 1 525w	1.71, 1.68 [m]	6.12
$[Mo\{AsPh_2(CH_2CH{=}CH_2)\}(\eta\text{-}C_5H_5)(CO)_2][PF_6]$ (XX)	(XV)		*k*	39	196 (decomp.)	41.2 (41.4)	3.7 (3.8)	2 020m, 1 961s, 1 530w		5.97
$[Mo\{As(C_6H_4Me\text{-}p)_2(CH_2CH{=}CH_2)\}(\eta\text{-}C_5H_5)\text{-}(CO)_2][PF_6]$ (XXI)	(XVI)		*k*	21	182 (decomp.)	43.1 (43.7)	3.4 (3.7)	2 031m, 1 965s, 1 541w	2.42 2.34 [j]	5.48

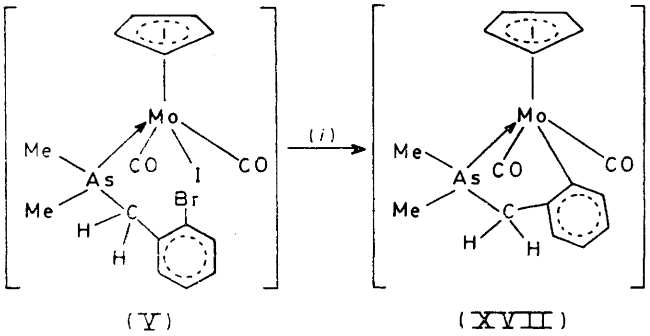
[a] Neutral complexes (XIV)—(XVIII) showed molecular ions in their mass spectra. [b] Stirring in tetrahydrofuran over excess of 1% Na–Hg. [c] Crystalline yellow solids were obtained. [d] Calculated values are given in parentheses. [e] In $CHCl_3$. [f] Referred to $SiMe_4$ as internal standard, $CDCl_3$ as solvent. [g] C_6H_6. [h] Toluene–light petroleum. [i] Toluene–heptane. [j] $p\text{-}CH_3C_6H_4As$. [k] Acetone–water. [l] In Nujol.

found in this case. Treatment of (XIX) with Na(OMe) also caused extensive decomposition and a small amount of the known [8] $[\{Mo(AsMe_2)(\eta\text{-}C_5H_5)(CO)_2\}_2]$ (22%). The fate of the allyl group is uncertain, but the reaction is formally analogous to the elimination of an allyl group from an allylarsonium salt by cyanolysis.[9]

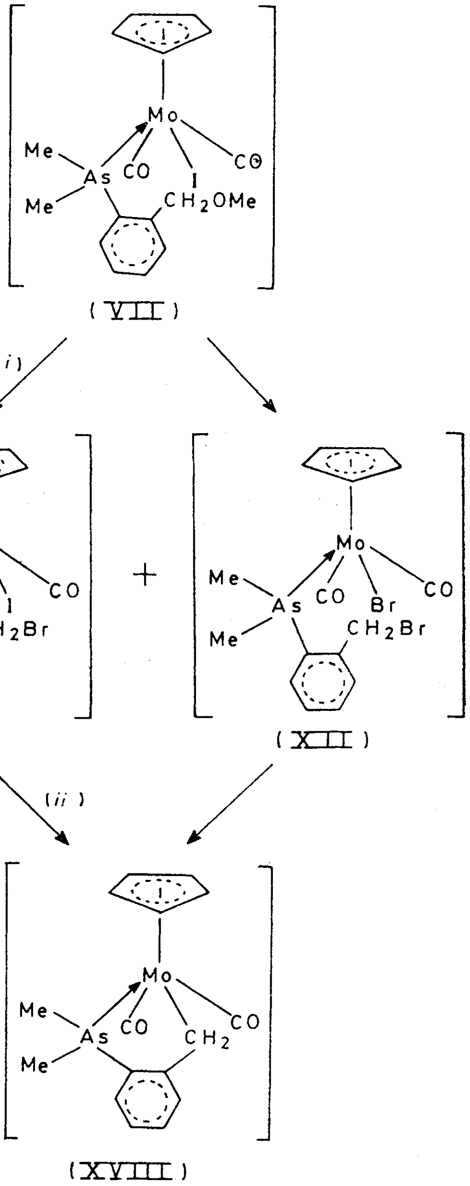
The phenyl, (XV), and *p*-tolyl complexes, (XVI), similarly underwent hydride elimination to give the cationic derivatives of allyldiphenylarsine, (XX), and allyldi(*p*-tolyl)arsine, (XXI), respectively (Table 2). The addition of cyanide to these complexes, however, led to extensive decomposition in both cases and neither neutral addition products nor cyanomolybdenum(II) complexes comparable with (XIII) could be isolated.

Cyclisation of $AsMe_2(CH_2C_6H_4Br\text{-}o)$.—Complexes (4) and (5) were readily prepared from the respective ligands, namely (*o*-chloro- and *o*-bromo-benzyl)dimethylarsine,[10] by refluxing with $[Mo(\eta\text{-}C_5H_5)(CO)_3I]$ according to Table 1. Reduction of (V) to the anion occurred within minutes, as evidenced by the disappearance of the deep crimson colour of the iodide, but the solution required stirring for a further 16 h to obtain a good yield of the cyclic complex (XVII) (Scheme 2). Complex (XVII) crystallises as stable yellow plates from benzene and its ^1H n.m.r. spectrum showed upfield shift of the cyclopentadienyl protons in agreement with ring formation. Reduction of (IV) readily gave the anion, but the cyclic complex formed in small yield (10%).

Cyclisation of $AsMe_2(C_6H_4CH_2Br\text{-}o)$.—(*o*-Bromomethylphenyl)dimethylarsine could not be obtained directly and was generated as a co-ordinated species by HBr cleavage of the corresponding *methoxymethyl* complex, (VII). Complex (VII) was dissolved in the minimum quantity of acetic anhydride, and the solution was cooled to *ca.* 4 °C and treated dropwise with aqueous HBr (48%) to give the *o*-bromomethylphenyl complexes (XI) and (XII) in good yield. Complex (VII) did not cleave with 48% HBr when acetic acid was used as the solvent or when HBr gas was bubbled through a solution of it in acetic anhydride or acetic acid. The mixture of products crystallises from the reaction mixture on standing, but must be collected and fractionally crystallised in an inert atmosphere. Whereas the iodide (XI) is air stable, the bromide (XII) decomposes rapidly on exposure to the atmosphere. Complex (XII) was also prepared directly by cleaving the *methoxymethylphenyl* complex (VIII) with 48% HBr in acetic anhydride. The mixture of (XI) and (XII) was reduced with sodium amalgam in the usual way and then stirred for 12 h to achieve the cyclisation (Scheme 3). Complex (XVIII) was obtained as pale yellow plates after recrystallisation from diethyl ether and its ^1H n.m.r. spectrum showed upfield shift of the C_5H_5 protons characteristic of cyclisation (Table 2).



SCHEME 2 (*i*), Na–Hg, thf



SCHEME 3 (*i*), HBr; (*ii*), Na–Hg, thf

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[8] R. G. Hayter, *Inorg. Chem.*, 1963, **2**, 1031.

[9] L. Horner, W. Hofer, I. Ertel, and H. Kunz, *Chem. Ber.*, 1970, **103**, 2718.

[10] A. Tzschach and H. Nindel, *J. Organometallic Chem.*, 1970, **24**, 159.

The bromination of the dimethyl(*o*-tolyl)arsine complex (VI) with *N*-bromosuccinimide in CCl_4 did not produce the expected bromomethylphenyl derivative (XI), but led to exchange of the co-ordinated iodide along with extensive decomposition.

Structural Studies.—$[Mo(AsMe_2R)(\eta\text{-}C_5H_5)(CO)_2X]$, (I)—(XII). The co-ordination geometry of the molybdenum atom in complexes of the type $[Mo(\eta\text{-}C_5H_5)(CO)_2(L)X]$ approximates to that of a distorted square pyramid where the cyclopentadienyl group is occupying the apical position.[11] Thus, provided free rotation is possible about the Mo–As bond, the two As–Me groups in *trans* complexes (I)—(XII), or $AsC_6H_4Me\text{-}p$ groups in (III), are magnetically equivalent on a time-average basis but become diastereotopic and magnetically non-equivalent when the complexes are *cis*.[12,13] In Table 1, the ^1H n.m.r. data of a series of complexes $[Mo(AsMe_2R)(\eta\text{-}C_5H_5)(CO)_2I]$ are presented; two As–Me resonances were clearly observed in cases where the *cis* structure is assigned, and a singlet resonance was observed for the *trans* isomer (IX). The *trans* structure is also assigned to (III) on the basis of the observed $AsC_6H_4Me\text{-}p$ methyl resonance. Additional support for the *cis* and *trans* formulations is found in the i.r. spectra where the ν(CO) vibrations showed the intensity variations accepted for complexes of this type.[5]

Cyclic complexes. (i) $[\overline{Mo\{(CH_2)_3As}R_2\}(\eta\text{-}C_5H_5)(CO)_2]$ (R = Me, Ph, *or* $C_6H_4Me\text{-}p$), (XIV)—(XVI). In noncyclic complexes of the type $[Mo(\eta\text{-}C_5H_5)(CO)_2(L)X]$ (L = tertiary phosphine [12–14] and X = H or halide) the temperature dependence of the ^1H n.m.r. spectra has been interpreted in terms of a *cis–trans* isomerisation of the square-pyramidal geometry by means of a nondissociative intramolecular process involving a trigonal-bipyramidal transition state. In the solid state, complex (XIV) has been shown by *X*-ray crystallography [15] to have a distorted square-pyramidal structure; this is represented in Figure 1 where the molecule is viewed down the Mo–As bond axis. The two As–Me groups are clearly non-equivalent in both the eclipsed and staggered conformations of the chelate ring and are observed in the 90 MHz ^1H n.m.r. spectrum at δ 1.34 and 1.29 p.p.m. (solution in $C_6H_4Cl_2\text{-}o$ at 20 °C). The ^{13}C n.m.r. spectrum of (XIV) in $CDCl_3$ at 25 °C also showed two As–Me resonances at 41.9 and 42.9 p.p.m. On heating a *o*-dichlorobenzene solution of (XIV) to 90 °C, however, the two singlets collapsed and a new singlet appeared in the 90 MHz ^1H n.m.r. spectrum at δ 1.28 p.p.m. Since a *trans*-square-pyramidal geometry is not possible for (XIV), this behaviour may be interpreted in terms of an equilibrium between the approximately square-pyramidal isomer, (A), found in the solid state (and considered to be present in solution at lower temperatures) and the trigonal-bipyramidal isomer, (B) (or a symmetrical distortion of this), at the elevated temperature (Figure 1). If the equilibrium process is rapid compared with the ^1H n.m.r. time scale, effective site exchange of the As–Me groups occurs even though the equilibrium concentration of (B) may be small.[14] However, since we did not observe a broad resonance characteristic of a rapid process at any temperature, a relatively slow isomerisation process seems more likely. The spectra observed were independent of concentration and a detailed examination [16] of a series of iodo-complexes [of the type (I)—(XI)] and of related six-membered cyclic ring systems, where similar effects are observed at lower temperatures and allow a more accurate determination of chemical-shift values, similarly favours a nondissociative process. Accordingly, rapid processes, perhaps involving cleavage of the Mo–As bond, have not been considered.

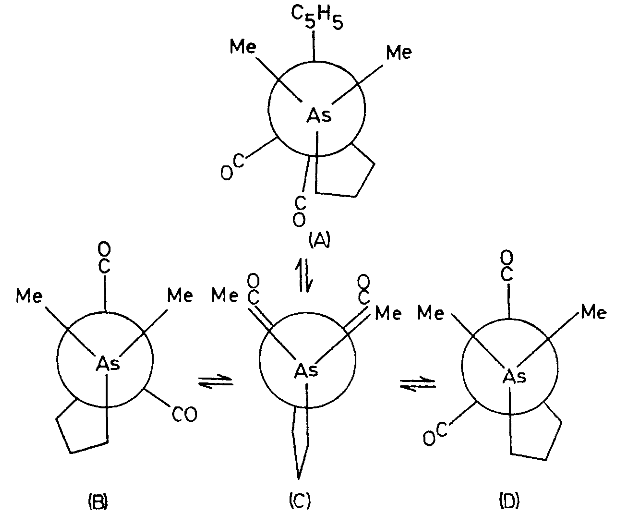

FIGURE 1 Representation of isomerisation of complex (XIV): (A), square-pyramidal isomer found in the solid state viewed down the Mo–As bond axis, showing non-equivalence of As–Me groups as observed in the ^1H n.m.r. spectrum at 20 °C; (B), eclipsed trigonal-bipyramidal isomer viewed down the As–Mo–C_5H_5 axis and believed to be present at 90 °C, as evidenced by the presence of equivalent As–Me groups in the ^1H n.m.r. spectrum; and (C) and (D), the relation between the staggered enantiomeric rotamers

It is noteworthy that this isomerisation does not take place readily ($\Delta G^\ddagger$ *ca.* 82.2 kJ mol^{-1}).* A related seven-co-ordinate complex which contains an optically active Schiff base as a bidentate ligand has been separated into optical antipodes, confirming the presence of an asymmetric molybdenum atom in the complex as well as the considerable stability of the system.[17]

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* Calculated from the Eyring equation using the observed value of Δδ(As–Me) to obtain the rate constant.

[11] M. R. Churchill and J. P. Fenessey, *Inorg. Chem.*, 1968, **5**, 953.

[12] R. J. Mawby and G. Wright, *J. Organometallic Chem.*, 1970, **21** 169.

[13] J. W. Faller and A. S. Anderson, *J. Amer. Chem. Soc.*, 1970, **92**, 5852.

[14] P. Kalck, R. Prince, R. Poilblanc, and J. Roussel, *J. Organometallic Chem.*, 1970, **24**, 445.

[15] P. E. Brotherton, M. Mickiewicz, K. P. Wainwright, A. H. White, and S. B. Wild, *J.C.S. Dalton*, in the press.

[16] M. Mickiewicz and S. B. Wild, in preparation.

[17] H. Brunner and W. A. Hermann, *Angew. Chem. Internat. Edn.*, 1972, **11**, 418.

The cyclic complex (XVI) contains the di(p-tolyl)arsino-group as a diagnostic aid and its ^{1}H n.m.r. spectrum in o-dichlorobenzene appears to indicate the presence of two stable structures at 20 °C, three p-tolyl methyl resonances being observed (Figure 2). The two signals at δ 2.29 and 2.16 p.p.m. may be attributed to the diastereotopic p-MeC_6H_4As resonances of the square-pyrimidal isomer, and the third singlet resonance at δ 2.24 p.p.m. to the equivalent p-tolyl methyl resonances of the trigonal-bipyramidal isomer. When the solution was heated the signal at δ 2.24 p.p.m. increased in intensity whereas the diastereotopic p-tolyl methyl signal decreased in intensity and eventually collapsed at 115 °C ($\Delta G^‡$ *ca.* 85.3 kJ mol^{-1}). Apparently, the two isomers possess a similar stability at 20 °C and isomerise slowly by comparison with the ^{1}H n.m.r. time scale. The increased stability of the trigonal-bipyramidal isomer in this case may reflect the preference of the bulky di(p-tolyl)arsino-group for a position *trans* to the cyclopentadienyl ring, although the alternative equatorial siting of the Group 5 donor atom, as suggested [14] in the interpretation of the *cis–trans* isomerisation of [Mo(η-C_5H_5)$(CO)_2$H(PR_3)], cannot be excluded on the basis of these measurements. The i.r. spectrum of (XVI) in the ν(CO) region does not show the presence of two isomers. However, this may not be significant as it is not possible to distinguish between *cis*- and *trans*-[Mo(η-C_5H_5)$(CO)_2$(L)X] on this basis.[5]

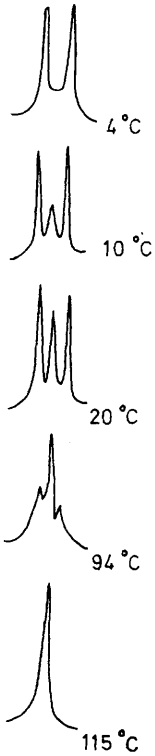

FIGURE 2 Temperature-dependent 90 MHz ^{1}H n.m.r. spectra of the AsC_6H_4Me-p methyl signals in [Mo{$CH_2CH_2CH_2As$-$(C_6H_4Me$-$p)_2$}(η-C_5H_5)$(CO)_2$] (XVI). The spectra at 4 and 10 °C were recorded in CH_2Cl_2, those at 20, 94, and 115 °C in $C_6H_4Cl_2$-o

(ii) [Mo($C_6H_4CH_2AsMe_2$-o)(η-C_5H_5)$(CO)_2$], (XVII). The 90 MHz ^{1}H n.m.r. spectrum of complex (XVII) in o-$C_6H_4Cl_2$ showed only one sharp As–Me resonance over the range −98 to 140 °C. This indicates a symmetrical environment for the As–Me groups and consequently the trigonal-bipyramidal structure, or a symmetrical modification of it, is favoured for (XVII) in solution. A singlet resonance at δ 3.41 p.p.m. was also observed for the $C_6H_4CH_2$ protons. The possibility of extreme stereochemical non-rigidity over the entire temperature range cannot be excluded, however, nor can the possibility of a non-detectable chemical-shift difference between the positions of the two As–Me resonances. We are presently undertaking an X-ray structure determination of this complex.[16]

(iii) [Mo($CH_2C_6H_4AsMe_2$-o)(η-C_5H_5)$(CO)_2$], (XVIII). A change in the equilibrium position between the two isomers also appears to occur in the spectrum of complex (XVIII) on heating to 149 °C. The two sharp As–Me resonances at δ 1.41 and 1.39 p.p.m. in the 90 MHz ^{1}H n.m.r. spectrum of (XVIII) at 20 °C in $C_6H_4Cl_2$-o coalesced to a single resonance at δ 1.39 p.p.m. at 149 °C ($\Delta G^‡$ *ca.* 99.6 kJ mol^{-1}). The $CH_2C_6H_4$ protons appeared as a broad singlet at δ 2.88 p.p.m. and not as a first-order AB quartet which would have been diagnostic of the square-pyramidal structure at the lower temperature.

The temperature dependence observed in the ^{1}H n.m.r. spectra of (XIV), (XVI), and (XVIII) is reversible and the position of the cyclopentadienyl resonance in each case is unaltered over the entire temperature range.

EXPERIMENTAL

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

Infrared spectra were recorded on a Perkin-Elmer 337 grating spectrometer and solution spectra were obtained using KBr cells of 0.2 mm path length. ^{1}H N.m.r. spectra at 25 °C were recorded at 60 MHz on a Varian A-60 spectrometer and chemical shifts are measured relative to tetramethylsilane as internal standard. Variable-temperature ^{1}H n.m.r. spectra were obtained over the range −90 to 140 °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 by the use of a 90 MHz broad-band decoupler. Spectra were recorded in $CDCl_3$ (80%, w/v), with a spectral width of 6 024 Hz cm^{-1}, using 8k data points resulting in a 4k frequency-domain spectrum.

The compounds iododimethylarsine, allyldimethylarsine,[7] (3-chloropropyl)dimethylarsine,[6] (o-chloro- and o-bromobenzyl)dimethylarsine,[10] and dimethyl(o-tolyl)arsine [18] were prepared according to the literature.

[18] G. Kamai and B. D. Chernikal'skii, *Doklady Akad. Nauk S.S.S.R.*, 1963, **149**, 850.

(3-*Chloropropyl*)*diphenylarsine*, (XXI).—The slow addition of the Grignard reagent prepared from Mg (7 g) and bromobenzene (45 g) in diethyl ether (150 cm^3) to a cold stirred solution of dichloro(3-chloropropyl)arsine (25 g) in diethyl ether (100 cm^3) gave, after hydrolysis with aqueous ammonium chloride and extraction into diethyl ether, a solution of the crude product which was dried (Mg[SO$_4$]) and distilled to give the pure *product*, b.p. 153—155 °C (0.1 mmHg) (25.2 g, 72%) (Found: C, 58.8; H, 5.3; Cl, 12.4. $C_{15}H_{16}AsCl$ requires C, 58.8; H, 5.3; Cl, 11.6%); δ (in CCl$_4$) 7.34 (10 H, m, C_6H_5), 3.37 (2 H, t, J_{HH} 6 Hz, CH_2Cl), and 1.97 p.p.m. (4 H, m, CH_2CH_2).

(3-*Chloropropyl*)*di*(p-*tolyl*)*arsine*, (XXIII).—A Grignard reagent from *p*-bromotoluene (34.2 g), magnesium (4.8 g), and diethyl ether (80 cm^3) was added slowly to a solution of dichloro(3-chloropropyl)arsine (22.3 g) in diethyl ether (60 cm^3) with rapid stirring. The solution was stirred at room temperature for 1 h, hydrolysed with ammonium chloride solution, extracted into diethyl ether, and dried (Mg[SO$_4$]). Distillation gave the pure *compound*, b.p. 160—165 °C (0.1 mmHg) (25 g, 75%) (Found: C, 62.5; H, 3.7. $C_{17}H_{22}AsCl$ requires C, 62.5; H, 3.7%); δ (in CDCl$_3$) 7.35 (10 H, m, C_6H_5), 3.47 (2 H, t, J_{HH} 6.5 Hz, CH_2Cl), 2.30 (6 H, s, As–CH_3), and 2.00 p.p.m. (4 H, m, CH_2CH_2).

Methyl o-*Dimethylarsinobenzyl Ether*, (XXIV).—*Method* 1. The reaction between *o*-bromobenzyl methyl ether [19] (14 g) and activated magnesium (1.75 g) was complete after stirring for 1 h at room temperature. The solution of the Grignard reagent was cooled to −5 °C and slowly treated with AsMe$_2$I (16.2 g) with vigorous stirring of the reaction mixture. The stirring was continued for a further 2 h after the addition of AsMe$_2$I was complete and then excess of aqueous [H$_4$N]Cl was added. The mixture was extracted into diethyl ether, dried (Mg[SO$_4$]), and distilled to give the pure product as a pale yellow *liquid*, b.p. 124—130 °C (14 mmHg) (9.7 g, 62%) (Found: C, 53.1; H, 6.7. $C_{10}H_{15}AsO$ requires C, 53.1; H, 6.7%); δ (in CDCl$_3$) 7.15 (4 H, m, C_6H_4), 4.50 (3 H, s, OCH_3), 3.25 (2 H, s, CH_2), and 1.10 p.p.m. (6 H, s, As–CH_3).

Method 2. The same compound was obtained in 42% yield from the reaction between sodium dimethylarsenide (from sodium and AsMe$_2$I in tetrahydrofuran) and *o*-chlorobenzyl methyl ether in thf at room temperature.

Preparation of the Metal Complexes [Mo(η-C$_5$H$_5$)(CO)$_2$(L)X].—The appropriate carbonyl halide [Mo(η-C$_5$H$_5$)(CO)$_3$X] (*ca.* 10 mmol) and the tertiary arsine ligand (*ca.* 10 mmol) were heated under reflux in benzene until the i.r. spectrum of an aliquot portion of the reaction mixture showed the absence of ν(CO) bands of the starting material. The crude product was obtained from the reaction mixture by removing the solvent and then purified by chromatography on an alumina column (neutral, activity 1) using benzene as eluant. Evaporation of the eluate followed by a recrystallisation of the residue gave the pure complexes in Table 1, where they appear together with details of the reaction conditions, solvent employed in the recrystallisation, and analytical data.

cis-[(o-*Bromomethylphenyl*)*dimethylarsine*]*dicarbonyl*(η-*cyclopentadienyl*)*iodomolybdenum*, (XI).—The complex [Mo{AsMe$_2$(C$_6$H$_4$CH$_2$OMe-*o*)}(η-C$_5$H$_5$)(CO)$_2$I], (VII) (1 g), was dissolved in acetic anhydride (25 cm^3) and the solution cooled to 4 °C. Aqueous HBr (45%, 4 cm^3) was added dropwise to the cooled solution. An orange precipitate forming immediately; this was washed with water and recrystallised from toluene by the addition of light petroleum to give the required complex (XI), m.p. 140—141 °C (0.7 g, 64%) (Found: C, 30.1; H, 2.7. $C_{16}H_{17}AsBrIMoO_2$ requires C, 29.8; H, 2.6%); δ (in CDCl$_3$) 7.30 (4 H, m, C_6H_4), 5.33 (5 H, s, C_5H_5), 4.60 (2 H, s, CH_2), 2.06 (3 H, s, As–CH_3), and 1.97 p.p.m. (3 H, s, As–CH_3). I.r. spectrum (in CHCl$_3$): 1 970s and 1 882m cm^{-1}.

cis-*Bromo*[(o-*bromomethylphenyl*)*dimethylarsine*]*dicarbonyl*(η-*cyclopentadienyl*)*molybdenum*(II), (XII).—Under similar conditions, the complex [Mo{AsMe$_2$(C$_6$H$_4$CH$_2$OMe-*o*)}Br(η-C$_5$H$_5$)(CO)$_2$], (VIII) (0.2 g), dissolved in acetic anhydride (5 cm^3) reacted with aqueous HBr (48%, 5 cm^3) to give a pink precipitate of *complex* (XII), which was obtained pure after one recrystallisation from toluene–light petroleum as crimson needles, m.p. 145—146 °C (0.15 g, 75%) (Found: C, 33.6; H, 2.9. $C_{16}H_{17}AsBr_2MoO_2$ requires C, 33.6; H, 3.0%); δ (in CDCl$_3$) 7.41 (4 H, m, C_6H_4), 5.38 (5 H, s, C_5H_5), 4.72 (2 H, s, CH_2), 1.99 (3 H, s, As–CH_3), and 1.94 p.p.m. (3 H, s, As–CH_3). I.r. spectrum (in CHCl$_3$): 1 960s and 1 910m cm^{-1}.

Reductive-cyclisation Reactions.—The reduction of [Mo{AsMe$_2$(CH$_2$CH$_2$CH$_2$Cl)}(η-C$_5$H$_5$)(CO)$_2$I], (I), to the cyclic complex (XIV) is as an example of the preparative procedure.

cis-*Dicarbonyl*(η-*cyclopentadienyl*)(3-*dimethylarsinopropyl*-C^{1}As)*molybdenum*(II), (XIV). Complex (I) (5 g) was dissolved in thf (200 cm^3) and treated with an excess of 1% sodium amalgam (150 g). The crimson colour of complex (I) rapidly disappeared on shaking the reaction mixture, and when the solution was completely yellow (*ca.* 30 min) the amalgam was removed and the solvent distilled *in vacuo* to leave a residue containing the crude product. Yellow crystals of pure complex (XIV) were obtained after sublimation at 80 °C (0.1 mmHg) (dry-ice–acetone probe) and recrystallisation from benzene, m.p. 107—108 °C (3.2 g, 94%).

Minor variations of the same procedure, details of which are given in Table 2, produced the remaining cyclic complexes.

Hydride-abstraction Reactions.—(η-2,3-*Allyldimethylarsine*)*dicarbonyl*(η-*cyclopentadienyl*)*molybdenum*(II) *hexafluorophosphate*, (XIX). Complex (XIV) (1.04 g) was dissolved in dichloromethane and a solution of trityl hexafluorophosphate (1.1 g) in dichloromethane (10 cm^3) was added dropwise with stirring over a period of 5 min. The resulting precipitate was collected, washed with diethyl ether, and dried *in vacuo* to give fine yellow crystals of the salt, m.p. 164 °C (decomp.) (0.47 g, 32%). The other salts were prepared similarly and details of their physical properties are in Table 2.

Some Reactions of Complex (XIX).—*With sodium methoxide*. The salt (XIX) (0.37 g) was suspended in methanol (10 cm^3) and the solution maintained under a nitrogen atmosphere while a solution of sodium methoxide in methanol [from sodium (0.1 g) and methanol (10 cm^3)] was added. The mixture was stirred for 3 h, the solvent removed, and the residue chromatographed (benzene on neutral alumina). The red band was collected, dried, and the solution evaporated to dryness. Recrystallisation of the residue from benzene–n-heptane produced red crystals (0.05 g, 22%) of di-μ-dimethylarsenido-bis[dicarbonyl(η-cyclopentadienyl)molybdenum(II)], m.p. 300—305 °C (decomp.) (lit.,[8] 307—309 °C).

With potassium cyanide. A solution of potassium

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[19] F. G. Holliman and F. G. Mann, *J. Chem. Soc.*, 1947, 1638.

cyanide (0.04 g) in methanol (10 cm^3) was added to a stirred suspension of (XIX) (0.04 g) in methanol (10 cm^3). The mixture was stirred for 3 h, the solvent removed, and the residue chromatographed (benzene–methylene chloride on neutral alumina). The single yellow band was collected, the solvent evaporated, and the crude product sublimed (100 °C, 0.1 mmHg) to give yellow crystals (*ca.* 12 mg) of *cis*-(allyldimethylarsine)dicarbonylcyano(η-cyclopentadienyl)molybdenum(II), (XIII) (Found: C, 40.4; H, 4.2. $C_{13}H_{16}AsMoNO$ requires C, 40.1; H, 4.1%); δ (in $CDCl_3$) 6.09—4.99 (3 H, m, CH_2CH), 5.40 (5 H, s, C_5H_5), 2.81 (21 H, d, J_{HH} 7.8 Hz, CH_2), and 1.51 p.p.m. (6 H, s, As–CH_3). I.r. spectrum (in $CDCl_3$): 3 065w, 2 905m, 2 230m, 2 090m, 1 975s, 1 880m, 1 630m, and 1 420 cm^{-1}.

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