Arene Molybdenum Chemistry: Some π-Allyl, Dihydride, Dinitrogen, and Carbonyl Derivatives

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Bis(arene)molybdenum (arene = benzene, toluene, or mesitylene) react with allyl chloride giving [(arene)Mo(π-C_3H_5)Cl]$_2$ dimers. With some tertiary phosphines these give (arene)Mo(π-C_3H_5)(R_3P)Cl which, depending on the nature of the phosphine, react with sodium borohydride and an excess of phosphine forming (arene)Mo(R_3P)$_3$ or (arene)Mo(R_3P)$_2H_2$. The hydrogen ligands may be reversibly displaced by molecular nitrogen giving dinitrogee derivatives (arene)Mo(R_3P)$_2N_2$ or [(benzene)Mo(Ph_3P)$_2$]$_2N_2$. Dinitrogen may be displaced by carbon monoxid- forming (arene)Mo(R_3P)$_2$CO derivatives. The compound [(toluene)Mo(Ph_3P)$_2$–N_2–(dmpe)Fe(π-C_5H_5)]$^+BF_4$n is also described.

WE set out to explore arene–molybdenum chemistry as part of a systematic search for highly reactive, electron-rich molybdenum systems. Recently we described the synthesis of some arene–molybdenum derivatives with tertiary phosphine and phosphite ligands, $C_6H_6Mo(R_3P)_3$.[1] Here we describe the preparation and properties of arene–molybdenum hydrides which react with molecular dinitrogen, some π-allyl molybdenum complexes and related compounds. A preliminary account of some of this work has been given.[2]

Chemical Studies.—The bis(arene)molybdenum compounds (arene)$_2$Mo (I; arene = benzene, toluene, or mesitylene) were used as starting materials for the preparation of the other arene–molybdenum compounds. The bisbenzene compound was first described by Fischer and Stahl,[3,4] and the toluene and mesitylene analogues are readily prepared by the same route. Since toluene and mesitylene have higher boiling points than benzene the preparations may be carried out at atmospheric pressure which is more convenient than with benzene which requires a vessel pressurised to about three atmospheres to achieve the required temperature of *ca.* 130°. The bistoluene and bismesitylene derivatives (I) are very soluble in all the common organic solvents and both the solids and solutions are decomposed almost immediately on exposure to air.

Treatment of the bis(arene)molybdenum compounds with dry allyl chloride causes rapid reaction and purple crystalline compounds are isolated in high yields. The data given in the Table, and the determination of the crystal structure by *X*-ray diffraction study of the benzenemolybdenum derivative,[5] show the products to be the π-allyl dimers [(arene)Mo(π-C_3H_5)Cl]$_2$ (II). The benzene derivative (II; arene = benzene) is insoluble in all common solvents whereas the toluene analogue is slightly soluble in toluene and moderately soluble in tetrahydrofuran. The mesitylene allyl compound is slightly soluble in tetrahydrofuran. All the compounds (II) show signs of decomposition in air after about an hour.

Treatment of the π-allyl dimers (II) with tertiary phosphines, *e.g.* $R_3P = Ph_2MeP$, causes cleavage of the chloro-bridge and the monomeric derivatives (arene)-Mo(π-C_3H_5)(PR_3)Cl (III) are formed in good yield. Also, when R_3P is triphenylphosphine then the benzene and toluene analogues (III; R = Ph) are formed. However the mesitylene analogue of (III; R = Ph) may not be prepared in this manner. In fact, the mesitylene dimer (II) dissolves in refluxing benzene in the presence of triphenylphosphine but not in the absence of the phosphine. Attempts to isolate a product from the benzene solution yields unchanged mesitylene dimer (II). This observation suggests that there is the following equilibrium in the benzene solution:

$$[(\text{mesitylene})\text{Mo}(\pi\text{-C}_3\text{H}_5)\text{Cl}]_2 + 2\text{Ph}_3\text{P} \rightleftharpoons 2(\text{mesitylene})\text{Mo}(\text{Ph}_3\text{P})\text{Cl}$$

Similar behaviour was noted for the benzene dimer (II) which dissolves reversibly in the presence of benzene and tricyclohexylphosphine. The compounds (III) are only slowly decomposed in air and they are soluble in benzene. The evidence for the formulation of the complexes (III) is given in the Table and is not further discussed.

It has been shown that bis(benzene)molybdenum

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[1] M. L. H. Green, L. C. Mitchard, and W. E. Silverthorn, *J. Chem. Soc.* (*A*), 1971, 2929.

[2] M. L. H. Green and W. E. Silverthorn, *Chem. Comm.*, 1971, 557.

[3] E. O. Fischer and H. O. Stahl, *Chem. Ber.*, 1956, **89**, 1805.

[4] E. O. Fischer, F. Scherer, and H. O. Stahl, *Chem. Ber.*, 1960, **93**, 2065.

[5] T. S. Camerom, C. K. Prout, and G. V. Rees, personal communication.

reacts with some tertiary phosphines giving the derivatives (benzene)$Mo(R_3P)_3$.[1] The analogous derivatives (toluene)$Mo(PPh_2Me)_3$ and (mesitylene)$Mo(PPh_2Me)_3$ are also readily prepared by a different route. For example, treatment of the compound $(MeC_6H_5)Mo(\pi\text{-}C_3H_5)$-$Ph_2MePCl$ with sodium borohydride in the presence of excess of the tertiary phosphine gives the triphosphine derivative (toluene)$Mo(Ph_2MeP)_3$ in good yield. The compound (mesitylene)$Mo(PPh_2MeP)_3$, may also be prepared by this method. These triphosphine derivatives are orange crystalline compounds soluble in benzene but insoluble in ethanol or light petroleum. The solutions are only slowly decomposed in air and the solids may be handled in air for brief periods without observable change.

Analytical and spectroscopic data

Compound	Colour	M.p. or decomp. T °C [a]	Analytical data, % Found (Reqd.) C	H	I.r. data (mulls) cm^{-1}	^1H N.m.r. spectra [b]
$(MeC_6H_5)_2Mo$	Bright green	80	58·8 (60·0)	5·7 (5·8)		5·44, **10**, *s*, Ph; 8·16, **6**, *s*, Me [c]
(*sym*)-$Me_3C_6H_3)_2Mo$	Bright green	110	64·2 (64·3)	7·2 (7·2)		5·55, **6**, *s*, *br*, C_6H_3; 8·24 **18**, *s*, Me_3 [c]
$[(C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$	Purple	200 d	42·8 (43·1)	4·2 (4·4)	1533m [d]	
$[(MeC_6H_5)Mo(\pi\text{-}C_3H_5)Cl]_2$	Purple	160 d	45·3 (45·3)	5·0 (4·9)	1540s [d]	
[(*sym*-$Me_3C_6H_3)Mo(\pi\text{-}C_3H_5)Cl]_2$	Purple	180 d	49·7 (49·2)	6·0 (5·8)	1560s [d]	
$[C_6H_6)Mo(\pi\text{-}C_3H_5)(Ph_3P)Cl$	Purple	177 d	62·8 (63·2)	5·0 (5·1)	1525w [d]	
$(MeC_6H_5)Mo(\pi\text{-}C_3H_5)(Ph_3P)Cl$	Purple	179 d	64·0 (63·8)	5·5 (5·4)	1540w [d]	
$(C_6H_6)Mo(\pi\text{-}C_3H_5)(Ph_2MeP)Cl$	Purple	—	58·5 (58·6)	5·3 (5·4)	1530w [d]	2·88, **10**, *c*, Ph_2; 5·88, **6**, *s*, C_6H_6; 6·39, **1**, *c*, H_c; 7·07, **2**, *c*, H_s; 8·10, **3**, *d* ($J_{Me,P}$ 7·5) Me; 8·3—8·9, **2**, *c*, H_a [e]
$(MeC_6H_5)Mo(\pi\text{-}C_3H_5)(Ph_2MeP)Cl$	Purple	165	59·6 (59·4)	5·8 (5·6)	1540m [d]	
(*sym*-$Me_3C_3H_3)Mo(\pi\text{-}C_3H_5)(Ph_2MeP)Cl$	Purple	171	60·6 (60·9)	6·3 (6·1)	1560m [d]	
$(C_6H_6)Mo(\pi\text{-}C_3H_5)(PhMe_2P)Cl$	Purple	—	52·5 (52·5)	5·5 (5·7)	1528w [d]	
$(MeC_6H_5)Mo(Ph_2MeP)_3$	Orange	213 d	69·7 (70·0)	6·1 (6·0)		
(*sym*-$Me_3C_6H_3)Mo(Ph_2MeP)_3$	Orange	191 d	69·8 (70·2)	6·2 (6·3)		
$(C_6H_6)Mo(Ph_2P)_3H_2$	Red	130 d	72·5 (72·0)	5·7 (5·5)	1730s, 1775w [f]	
$(MeC_6H_5)Mo(Ph_3P)_2H_2$	Red	138 d	72·0 (72·3)	5·8 (5·5)	1740s, 1785w [f]	3·13, **30**, *c*, Ph_6; 6·20, **5**, *c*, Ph; 8·49, **3**, *s*, Me; 14·35, **2**, *t* ($J_{H_2,P}$ 50·2) MoH_2 [c]
(*sym*-$Me_3C_6H_3)Mo(Ph_3P)_2H_2$	Red	157 d	72·5 (72·7)	6·1 (6·0)	1745s, 1775sh [f]	
$(MeC_6H_5)Mo(Ph_2MeP)_2H_2$	Red	107	67·4 (67·1)	6·2 (6·1)	1735s, 1770w [f]	2·35, 3·03, **20**, *c*, Ph_4 5·90, **5**, *c*, Ph; 8·20, **6**, *d*($J_{Me,P}$ 6·6) Me; 8·45, **3**, *c*, Me; 14·85, **2**, *t*($J_{H_2,P}$ 50·0)MoH_2 [c]
$(C_6H_6)Mo(Ph_3P)_2CO$	Orange	195	70·6 (71·0)	5·0 (5·0)	1800vs [g] (1813) [h]	2·62, 3·08, **30**, *c*, Ph_6; 5·97, **6**, *t* ($J_{H_6,P}$ 1·8), C_6H_6 [c]
$(MeC_6H_5)Mo(Ph_3P)_2CO$	Orange	191	70·8 (71·4)	5·2 (5·2) [i]	1780vs [g] (1808) [h]	2·72, 3·15, **30**, *c*, Ph_6; 6·08, 6·35, **5**, *c*, Ph; 7·95, **3**, *s*, Me [c]
$[(C_6H_6)Mo(Ph_3P)_2]_2N_2$	Maroon	136 d	70·9 (70·8)	5·5 (5·1) [j]	1910 ± 5 [k]	
$(MeC_6H_5)Mo(Ph_3P)_2N_2$	Orange	100 d	70·0 (69·8)	5·2 (5·2) [l]	1988vs [m] (2000) [n]	2·88, 3·27, **30**, *c*, Ph; 6·29, 6·78, **5**, *c*, Ph; 8·20, **3**, *s*, Me [c]
s(*ym*-$Me_3C_6H_3Mo)Ph_3P)_2N_2$	Orange	109 d	69·0 (70·3)	5·7 (5·5) [o]	1975vs [m] (1983) [n]	
$(MeC_6H_5)Mo(Ph_2MeP)_2N_2$	Red	110 d	63·5 (64·2)	5·6 (5·6) [p]	1970vs [m]	
$[(MeC_6H_5)Mo(Ph_3P)_2\text{–}N_2\text{–}(dmpe)$ $Fe(\pi\text{-}C_5H_5)]^+BF_4^-$ [q]	Brown	—	58·5 (59·0)	5·0 (5·4) [r]	1930vs [m] (1945)	

[a] In vacuum, uncorrected. [b] Given as chemical shift (τ), relative intensity, multiplicity (*J* in Hz), assignment, *etc.* [c] In [$^2H_6$]benzene. [d] ν(C–C) of π-C_3H_5. [e] For numbering see the Scheme; in [$^2H_6$]benzene. [f] ν(Mo–H). [g] ν(C≡O). [h] In [$^2H_6$]-benzene. [i] M^+/e (parent ion) = 742. [j] N, 1·7 (2·0)%. [k] ν(N≡N) In Raman spectrum, no band in i.r. [l] N, 3·7 (3·8)%. [m] ν(N≡N) In i.r. [n] In toluene. [o] N, 3·9 (3·6)%. [p] N, 2·9 (4·5)%, see text. [q] dmpe = 1,2-bis(dimethylphosphino)ethane. [r] N, 2·5 (2·6)%. [s] For $[(MeC_6H_5)Mo(Ph_3P)_2\text{–}N^2\text{–}(dmpe)Fe(\pi\text{-}C_5H_5)]^+BF_4^-,MeC_6H_5$. N, 1·9 (2·4), P, 10·8 (10·4), F, 6·8 (6·4), C, 61·2 (61·5), H, 5·5 (5·7)%.

In contrast to the above reaction, reduction of the compound (toluene)$Mo(\pi\text{-}C_3H_5)(Ph_2MeP)Cl$ with sodium borohydride in the absence of free, excess phosphine yields the dihydride (toluene)$Mo(Ph_2MeP)_2H_2$. The analogous triphenylphosphine dihydrides (arene)Mo-$(R_3P)_2H_2$ (IV; R = Ph) are all prepared by reduction of the corresponding triphenylphosphine complexes (III) in the presence of excess of triphenylphosphine (see the Table).

The dihydrides (IV; R = Ph) are moderately soluble in benzene and tetrahydrofuran, the analogue where R_3 = Ph_2Me is rather more soluble. In solution all the compounds (IV) are rapidly decomposed by air whilst the solids are kinetically more stable and may be handled in air for brief periods.

Treatment of benzene solutions of the complexes (IV) with molecular nitrogen causes displacement of hydrogen and if the liberated hydrogen is displaced during the reaction then the dinitrogen derivatives [(benzene)Mo-$(Ph_3P)_2]_2N_2$ (V) or (arene)$Mo(PR_3)_2N_2$ (VI; arene = MeC_6H_5 or *sym*-$Me_3C_6H_3$) are formed. The rates of reaction of the compounds (IV) with molecular nitrogen change in the order: $C_6H_6Mo(Ph_3P)_2H_2 \gg MeC_6H_5Mo(Ph_3P)_2H_2 \sim MeC_6H_5Mo(Ph_2MeP)_2H_2 >$ *sym*-$Me_3C_6H_5Mo(Ph_3P)_2H_2$. The product of the preparation of (VI; arene = toluene) sometimes shows a band at 1960 cm^{-1} as well as the band at 1988 cm^{-1}, however solutions of this product only showed a single band, at 2000 cm^{-1}. It seems probable that the band at 1960 cm^{-1} arises from a different solid modification. The band disappears after recrystallisation from ether–ethanol solutions.

The yields of the binuclear compound (V) were limited by the fact that the compound slowly decomposes in benzene solution with deposition of a black solid, even at 6°. The compound (V) is only slightly soluble in benzene and insoluble in petrol. It dissolves in tetrahydrofuran with rapid evolution of nitrogen gas giving a deep red solution. Attempts to react the co-ordinated dinitrogen in compound (V) by hydrolysis, by reduction with lithium aluminium hydride or butyl-lithium did not yield any new nitrogen products.

The monomeric dinitrogen derivatives (VI) also decompose slowly in benzene at room temperature giving black insoluble precipitates. They appear to be somewhat more stable in diethyl ether solution and indefinitely stable in tetrahydrofuran.

The high solubility of the compound (toluene)$Mo(Ph_2MeP)_2N_2$ in all non-polar, inert solvents, together with the tendency towards slow decomposition makes it difficult to obtain highly pure samples. However, the data given in the Table together with the method of preparation is consistent with the proposed formulation.

Preliminary experiments show that unstable terminal dinitrogen compounds (benzene)$Mo(R_3P)_2N_2$, where $R_3 = Ph_2Me$ or $PhMe_2$ may also be prepared as above.

The dinitrogen compounds (V or VI) are moderately stable as the crystalline solids both thermally and to air. In air slight decomposition is observed after about a day whilst solutions are very rapidly decomposed. The compounds are also decomposed rapidly by chlorocarbon solvents such as CH_2Cl_2 and $CHCl_3$.

It is interesting that only in the case of $[C_6H_6Mo(Ph_3P)_2]_2N_2$ is a binuclear product isolated. Solutions of this compound in benzene show noticeable lightening of the maroon colour under vacuum compared to the darker colour in a solution saturated with nitrogen gas. However, attempts to isolate a mononuclear species with a terminal dinitrogen by evaporation of benzene solutions with a stream of nitrogen gave only the binuclear derivative (V).

Benzene solutions of all the dinitrogen complexes react rapidly with hydrogen gas reforming the corresponding dihydrides in essentially quantitative yields.

Treatment of solutions of the dinitrogen compounds (V) and (VI; arene = toluene) with carbon monoxide at atmospheric pressure causes displacement of the dinitrogen and the terminal carbonyl derivatives (arene-$Mo(Ph_3P)_2CO$ (VII) are formed (see Table). They are very soluble in benzene and tetrahydrofuran and slightly soluble in light petroleum. Solutions are slowly decomposed on exposure to air.

Previously we have described [6] the dinitrogen derivatives $[(\pi\text{-}C_5H_5)Fe(dmpe)N_2(dmpe)Fe(\pi\text{-}C_5H_5)]^{2+}[BF_4^-]_2,2H_2O$, where dmpe is 1,2-bis(dimethylphosphino)ethane. Since there is some evidence which suggests that the enzyme nitrogenase may involve a Mo–N_2–Fe system in the reduction of dinitrogen we set out to see if we could prepare such a system.

Treatment of the compound $[(\pi\text{-}C_5H_5)Fe(dmpe)Me_2CO]^+BF_4^-$ [6] in acetone with (toluene)$Mo(Ph_3P)_2N_2$ under argon gives brown solids. The stoicheiometry of the product depends on the recrystallisation solvent and when toluene is used it appears that a molecule of toluene is incorporated in the lattice, giving a stoicheiometry corresponding to the formulation $[(MeC_6H_5)Mo(Ph_3P)_2N_2(dmpe)Fe(\pi\text{-}C_5H_5)]^+BF_4^-,MeC_6H_5$ (VIII) (see Table). The compound (VIII) forms golden-brown crystals moderately stable in air. Like the monomeric (toluene)-$Mo(Ph_3P)_2N_2$ the i.r. spectra of the brown solids depend on the recrystallisation method and, according to the preparation, two bands of variable intensity are found at 1945 and 1930 cm^{-1} which may be assigned to N≡N stretching frequencies. Samples recrystallised from acetone–light petroleum showed almost entirely the band at 1930 cm^{-1} whereas those containing toluene of recrystallisation show mostly the 1945 cm^{-1} band. Analyses obtained on the samples recrystallised from acetone–light petroleum were consistent with the formulation of the brown solid as the adduct $[(\pi\text{-}C_5H_5)Fe(dmpe)N_2(Ph_3P)_2Mo(MeC_6H_5)]^+BF_4^-$.

DISCUSSION

The structures proposed for the complexes (I—VII) on the basis of the above evidence, especially the data in the Table, are given in the Scheme.

It is shown that complexes of the type (arene)$Mo(R_3P)_3$ may be prepared where $R_3 = Ph_2Me$ or $PhMe_2$ whilst the analogues where $R_3 = Ph_3$ are not formed under the same conditions. It seems probable that this difference arises from steric overcrowding with the bulkier triphenylphosphine ligand. At an early stage in this work we noted that Hidae *et al.*[7] reported a compound of empirical stoicheiometry (toluene)$Mo(Ph_3P)_2N_2$ and we supposed that this compound might be the compound (VI; arene = toluene) which we subsequently prepared. However, it is clear from further studies by Hidae [8] that his compound is different from compound (VI; arene = toluene). For example, the solubility properties of our compound are very different from those of the Hidae complex (low solubility), also the reactions of our compound with hydrogen or carbon monoxide to give (toluene)molybdenum derivatives contrasts sharply with the reactions of Hidae's compound. Further N≡N stretching frequencies occur at slightly different positions.

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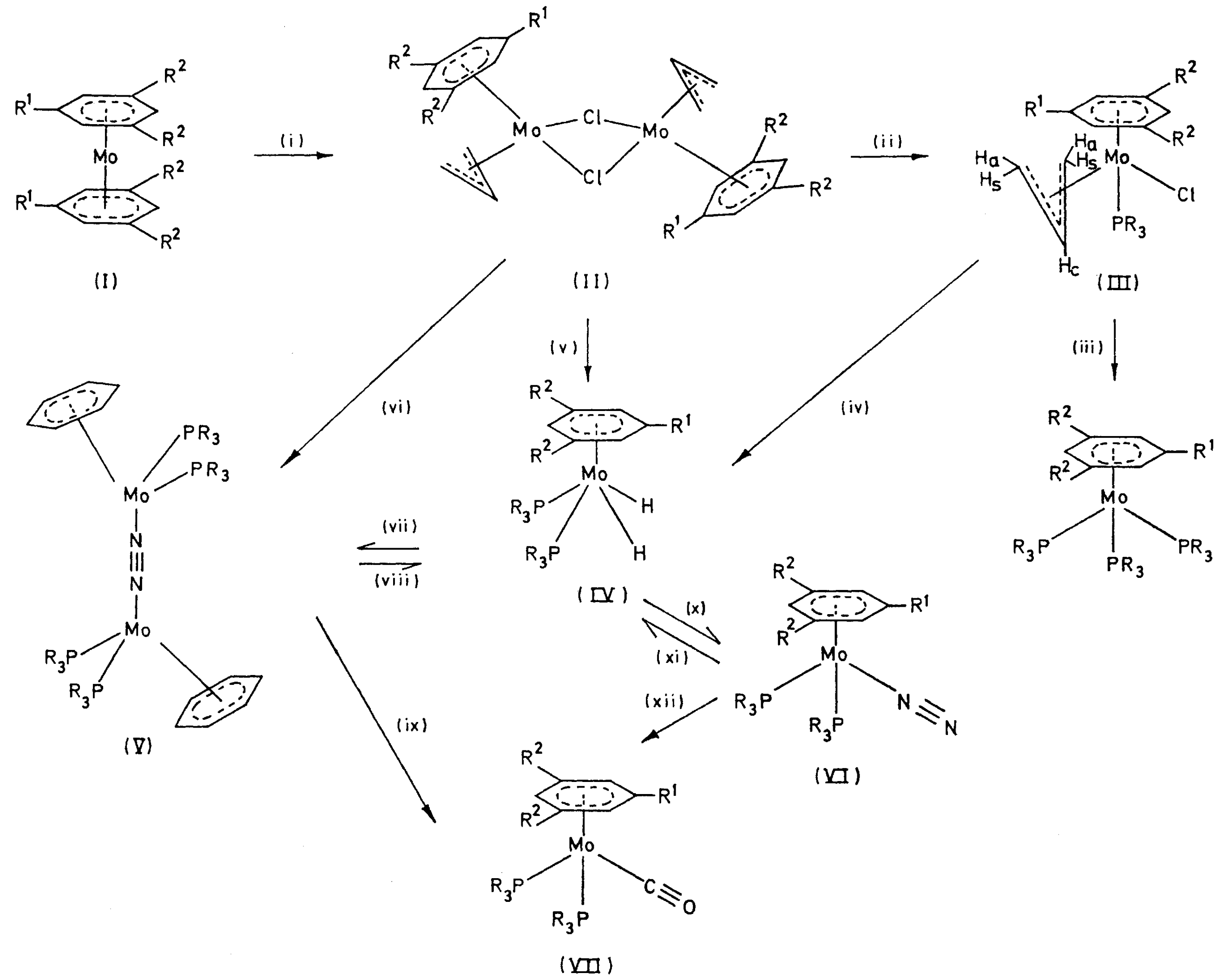
[6] W. E. Silverthorn, *Chem. Comm.*, 1971, 1310.

[7] M. Hidae, K. Tominari, Y. Uchida, and A. Misono, *Chem. Comm.*, 1969, 814 and 1392.

[8] M. Hidae, K. Tominari, and Y. Uchida, *J. Amer. Chem. Soc.*, 1972, **94**, 110.

The formation of the dinitrogen dimer (V) presumably proceeds *via* a mononuclear species similar to the compounds (VI). It may be that the absence of dimer formation in the toluene and mesitylene systems arises from increased steric effects or it may be that the isolation of the dimer (V) is favoured over the putative monomer by virtue of its greater insolubility.



SCHEME Compound A, $R^1 = R^2 = H$; B, $R^1 = Me$, $R^2 = H$; C, $R^1 = R^2 = Me$; i, for compounds A, B, and C, with $CH_2{=}CH{-}CH_2Cl$; (ii), with R_3P; A, $R_3 = PhMe_2$, Ph_2Me, Ph_3; B, $R_3 = Ph_2Me$, Ph_3; C, $R_3 = Ph_2Me$; (iii), compounds B and C, $R_3 = Ph_2Me$, with $NaBH_4$ and an excess of Ph_2MeP; (iv), compounds A and B, $R_3 = Ph_3$, with $NaBH_4$ and an excess of Ph_3P; or compound B, $R_3 = Ph_2Me$ with $NaBH_4$; (v), compound C with $NaBH_4$ with an excess of Ph_3P; (vi), compound A, with N_2, $LiBu^n$, and Ph_3P; (vii), N_2; (viii), H_2; (ix), CO; (x), $R_3 = Ph_3$ for compounds B and C, also $R_3 = Ph_2Me$ for B, with N_2; (xi), compounds B and C, $R_3 = Ph_3$ with H_2; (xii), compound B, $R_3 = Ph_3$ with CO

The dihydride compounds (IV) may be imagined to occur with either a *cis*- or *trans*-configuration. The ^1H n.m.r. data shows that either the compounds are fluctional or that they have *trans*-configuration since only one coupling constant between the ^{31}P and ^1H nuclei is observed. Low solubility has precluded very low temperature studies on this system. We have, however, recently observed[9] fluctional behaviour in some compounds $[(arene)Mo(PR_3)_3H_2]^{2+}$ so it is not unreasonable to suppose that the compounds (IV) are also fluctional.

The presence of an intense band assignable to ν(N≡N) in the Raman spectrum of the binuclear compound (V) and the absence of a corresponding band in the i.r. spectrum suggests that the compound has a centrosymmetric structure, such as is drawn in the Scheme.

The terminal carbonyl stretching frequencies of the compound (VII) are quite low for neutral molecules. This clearly supports the idea that transition metal sites which may bind molecular nitrogen must have rather strong π-donor properties.[10]

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[9] L. C. Mitchard, personal communication.

[10] P. K. Marples, F. Basolo, and R. G. Pearson, *Inorg. Chem.*, 1971, **10**, 765; K. G. Caulton, R. L. DeKock, and R. F. Fenske, *J. Amer. Chem. Soc.*, 1970, **93**, 515; C. H. Campbell, A. R. Dias, M. L. H. Green, T. Saito, and M. G. Swanwick, *J. Organometallic Chem.*, 1968, **14**, 349 and G. J. Leigh, 'Preparative Inorganic Reactions,' ed. W. L. Jolly, 1971, p. 165.

Finally, the data given in the Table suggests that the binuclear cation $[(MeC_6H_5)Mo(PH_3P)_2N_2(dmpe)Fe(\pi\text{-}C_5H_5)]^+$ has a structure essentially similar to that of the binuclear molybdenum compound (V). It may be noted that the band assigned to the $\nu(N\equiv N)$ in compound (VIII) occurs about midway between the $\nu(N\equiv N)$ of the compound (V) and the cation $\{[(\pi\text{-}C_5H_5)Fe(dmpe)]_2N_2\}^{2+}$.[6]

EXPERIMENTAL

All preparations and reaction were carried out in the absence of oxygen. Analytical data are given in the Table. ^{1}H N.m.r. spectra were determined on a JEOL JNMCO 60 HL instrument and calibrated with tetramethylsilane as external standard. Mass spectra were measured using an A.E.I. MS9 instrument. Raman spectra were determined on a Cary He–Ne instrument and we thank Dr. A. J. Downs for his assistance. I.r. spectra were determined on a Perkin-Elmer 457 instrument and were calibrated using polystyrene. Light petroleum was AnalaR, b.p. 30—40°. All solvents were dried by refluxing over and distillation from finely powdered calcium hydride. Bis(benzene)molybdenum was prepared by the published method.[4]

Bis(toluene)molybdenum.—Pure molybdenum pentachloride (25 g) and freshly sublimed and finely ground aluminium trichloride (60 g) were intimately mixed together in a dry box and then placed in a 500 ml, three-necked flask equipped with a reflux condenser and efficient stirrer. The flask was flushed with nitrogen and aluminium powder (3·5 g) was added followed by dry toluene (120 ml). The mixture was stirred under reflux at 125° (oil-bath) for 30 h. The flask was completely immersed in the oil-bath. The dark brown, tarry-solid product was transferred to a Schlenk tube and the supernatent red-brown toluene layer was decanted and discarded. The residue was dried as far as possible by removal of volatile material under reduced pressure at room temperature for 12 h.

A 2 l flask fitted with a sturdy and effective stirrer was filled with aqueous potassium hydroxide (30%, 1·5 l) and this was cooled in an ice-bath to 0 °C. The black tarry-solid was transferred in soft lumps using a spatula and strong counter-currents of nitrogen gas, to the potassium hydroxide solution.* The addition was carried out slowly (2 h) so that the mixture remained cold. The mixture was stirred for a further 6 h and towards the end of this period allowed to warm to room temperature. It was then filtered giving a green-brown residue and the filtrate was discarded. The residue was washed with water (2 × 400 ml) and then the excess moisture was removed under vacuum (6—12 h) at room temperature. The dried solid was transferred to a large Schlenk tube (1 l) and extracted with dry benzene (400 ml). The extract was filtered and the solvent removed under vacuum giving a dark red-brown tarry-solid. This was transferred to a round-bottomed flask (100 ml) with a single wide neck (B24) fitted with an air condenser of similar diameter (25 cm long). The residue was distilled (sublimed) onto the walls of the air condenser under vacuum (10^{-3} mmHg) from an oil-bath at 115°. The distillate was a clear green liquid which solidified on the walls of the condenser as a transparent green crystalline matrix. This was scraped into a Schlenk tube and stored (*ca.* 7·3 g, 34% based on $MoCl_5$). If required, further purification may be achieved by crystallisation from light petroleum or ethanol at −78°. It is, of course, necessary to exclude oxygen at all stages during the isolation and purification procedures.

Bis(mesitylene)molybdenum was prepared in the same manner as above except that the oil-bath was at 110° during the first stage of the reaction. Yield *ca.* 35% based on $MoCl_5$.

The μ-Chloro-(π-allyl)(benzene)molybdenum Dimer.—Bis(benzene)molybdenum (1·2 g) in dry benzene (250 ml) was treated with distilled allyl chloride (1·5 ml) at room temperature. The initial green solution rapidly turned dark red-violet and purple crystals separated. The mixture was allowed to stand for 12 h then the purple crystalline product was separated and washed with benzene and dried *in vacuo* (*ca.* 0·67 g, 56%). A higher yield (80—90%) of slightly less pure product can be obtained if the reaction is carried out at 40° for 1 h.

The toluene analogue $[(MeC_6H_5)Mo(\pi\text{-}C_3H_5)Cl]_2$ is similarly prepared using light petroleum solutions starting from bis(toluene)molybdenum. It may be recrystallised from tetrahydrofuran–ethanol, *ca.* 60%.

The mesitylene analogue $[(sym\text{-}Me_3C_6H_3)Mo(\pi\text{-}C_3H_5)Cl]_2$ is made in the same way, *ca.* 80%. It is slightly soluble in tetrahydrofuran.

Chloro-(π-allyl)triphenylphosphine(benzene)molybdenum.—A suspension of the finely powdered dimer $[(C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$ (1·38 g) in benzene (100 ml) was treated with triphenylphosphine (2·8 g) and the mixture was refluxed for 1 h. The resulting red-purple solution was filtered and ethanol (*ca.* 100 ml) added. The solution was concentrated under reduced pressure and then cooled to −15° giving small purple crystals which were washed with light petroleum and dried under vacuum, *ca.* 79%. The analogous compounds $(C_6H_6)Mo(\pi\text{-}C_3H_5)(R_3P)Cl$, where $R_3 =$ $MePh_2$ or Me_2Ph; $(MeC_6H_5)Mo(\pi\text{-}C_3H_5)(R_3P)Cl$, where $R_3 =$ Ph_3 or $MePh_2$; and $(sym\text{-}Me_3C_6H_3)Mo(\pi\text{-}C_3H_5)(Ph_2MeP)Cl$ were similarly prepared and recrystallised from benzene–ethanol.

Tris(diphenylmethylphosphine)(toluene)molybdenum.—Powdered $(MeC_6H_5)Mo(\pi\text{-}C_3H_5)(Ph_2MeP)Cl$ (0·34 g) was added to diphenylmethylphosphine (0·5 ml) in ethanol–water (4 : 1, 50 ml) and the mixture was treated with an excess of sodium borohydride (0·5 g) and stirred for 12 h. The resulting solution was concentrated (10 ml) giving an orange solid which was separated, washed with water, dried, and recrystallised from benzene–ethanol giving orange crystals. These were separated, washed with a little ethanol and then dried *in vacuo*, *ca.* 43%. The mesitylene analogue $(sym\text{-}Me_3C_6H_3)Mo(Ph_2MeP)_3$ was similarly prepared in 25% yield starting from $(sym\text{-}Me_3C_6H_3)Mo(\pi\text{-}C_3H_5)(Ph_2MeP)Cl$. No dihydride compounds (IV) were obtained in the above reactions. The compounds are moderately soluble in benzene.

Dihydrido(bistriphenylphosphine)(benzene)molybdenum.—Triphenylphosphine (4·5 g) and a suspension of powdered $(C_6H_6)Mo(\pi\text{-}C_3H_5)(Ph_3P)Cl$ in aqueous ethanol (95%, 150 ml) were treated with an excess of sodium borohydride (3·0 g) and the mixture was rapidly stirred under a hydrogen or argon atmosphere for 5 h. A red-orange solid was formed which was separated by decantation and washed with ethanol (95%, 2 × 100 ml) and dried *in vacuo*. Recrystallisation from benzene–ethanol gave red crystals which were

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* We have been advised by a referee that these tars may be highly pyrophoric and that the water used to dissolve the potassium hydroxide must be most rigorously de-oxygenated. Our tars were quite docile but this may have been fortuitous.

dried *in vacuo, ca.* 97%. The toluene analogue $(MeC_6H_5)Mo(Ph_3P)_2H_2$ was similarly prepared starting from $(MeC_6H_5)Mo(\pi\text{-}C_3H_5)Ph_3PCl$ in 93% yield.

Dihydrido(bistriphenylphosphine)(mesitylene)molybdenum.—Triphenylphosphine (4 g) and powdered $[(sym\text{-}Me_3C_3H_3)Mo(\pi\text{-}C_3H_5)Cl]_2$ (1·0 g) in ethanol (95%, 100 ml) were treated with an excess of sodium borohydride (3 g) and the mixture was stirred under hydrogen for 5 days. The resulting orange solid was washed with ethanol (2 × 100 ml), dried *in vacuo* and then recrystallised from benzene–ethanol giving red crystals which were dried under vacuum, *ca.* 55%.

Dihydrido(bisdiphenylmethylphosphine)(toluene)molybdenum.—Powdered $(MeC_6H_5)Mo(\pi\text{-}C_3H_5)(Ph_2MeP)Cl$ (0·5 g) in aqueous ethanol (80%, 100 ml) was treated with an excess of sodium borohydride (0·5 g) and the mixture was stirred under argon for 2 days. The orange residue was separated, washed with ethanol, and dried. Recrystallisation from benzene–ethanol at −78° gave red crystals which were dried *in vacuo, ca.* 31%.

μ-Dinitrogen-[bis(triphenylphosphine)molybdenum].—

Method A. A stirred suspension of finely divided powdered dimer $[(C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$ (0·5 g) in benzene (100 ml) and under a slow stream of nitrogen gas was treated with triphenylphosphine (1·5 g) and then with n-butyl-lithium in hexane (5 ml 1·5M). Within 5 min all the solid dissolved giving an orange-red solution. After 30 min water was added carefully (25 ml) and the benzene layer was separated and treated with light petroleum (b.p. 100—120°, 100 ml). The solution was filtered and the filtrate was concentrated under reduced pressure to *ca.* 50 ml and then cooled to 0°. A deep maroon solid separated from the solution and was collected, washed with light petroleum–ether, and dried under vacuum, 0·65 g. Treatment of the mother liquor with a slow stream of nitrogen gas for a further 30 min followed by concentration and cooling yielded another 0·25 g of product. Total yield was 65%.

Method B. The dihydride $(C_6H_6)Mo(Ph_3P)_2H_2$ (0·5 g) and triphenylphosphine (0·25 g) in dry benzene (100 ml) were treated with a slow stream of nitrogen gas at 6° for 8 h. Light petroleum (b.p. 100—120°, 100 ml) was added and the solution was filtered, concentrated under reduced pressure, and the concentrate was cooled to −15° yielding the pure *compound* (*ca.* 0·25 g, 55%).

Dinitrogenbis(triphenylphosphine)toluenemolybdenum.—The dihydride $(MeC_6H_5)Mo(Ph_3P)_2H_2$ (1·3 g) in dry tetrahydrofuran (40 ml) was treated with nitrogen gas at 150 atm. and 22° in a rocking autoclave for 8 h. The autoclave was vented and refilled with nitrogen gas every 2 h in order to remove liberated hydrogen gas. The solvent was removed from the reaction mixture under reduced pressure and the residue was washed with light petroleum (25 ml) at −10°. The resulting orange solid was extracted with diethyl ether (200 ml), the solution was filtered and then concentrated under reduced pressure to 50 ml. Ethanol (95%, 50 ml) was added and the solution was concentrated to 25 ml and then cooled to −78° when an orange solid separated which was collected and dried *in vacuo* (*ca.* 0·8 g, 60%).

The mesitylene analogue $(sym\text{-}Me_3C_6H_3)Mo(Ph_3P)_2N_2$ was similarly prepared from $(sym\text{-}Me_3C_6H_3)Mo(Ph_3P)_2H_2$ (1·4 g) except that the reaction was carried out for 110 h. The product was recrystallised from ether–ethanol, *ca.* 55%.

Dinitrogenbis(diphenylmethylphosphine)toluenemolybdenum.—The dihydride $(MeC_6H_5)Mo(Ph_2MeP)_2H_2$ (0·15 g) in dry tetrahydrofuran (30 ml) was treated with nitrogen gas at 150 atm. and 22° in a rocking autoclave for 10 h. The autoclave was vented every 2 h. The solvent was removed from the reaction mixture under reduced pressure and the residue was extracted with ethanol (95%, 75 ml). The solution was filtered and then concentrated to 25 ml and cooled to 0° for 15 min. A small quantity of orange crystals separated which were shown to be mainly the triphosphine $(MeC_6H_5)Mo(Ph_2MeP)_3$. The supernatant liquor was separated and kept at 0° for 24 h. Red crystals separated (*ca.* 20 mg) which were collected and dried *in vacuo.* The i.r. spectra and analytical data showed that the product was the dinitrogen compound $(MeC_6H_5)Mo(Ph_2MeP)_2N_2$ contaminated with a little of the trisphosphine analogue. The compound was not further purified.

The Compound $[(MeC_6H_5)Mo(Ph_3P)_2\text{-}\mu\text{-}N_2\text{-}(Me_2PCH_2CH_2PMe_2)Fe(\pi\text{-}C_5H_5)]^+BF_4^-$.—The compound $[(\pi\text{-}C_5H_5)Fe(dmpe)(Me_2CO)]^+BF_4^-$ [6] (115 mg) in pure acetone (75 ml) at −78° was treated with the compound $(MeC_6H_5)Mo(PPh_3)_2N_2$ (225 mg) and the solution was stirred at −78° under argon for 15 min and then at −15° for 15 min. Light petroleum (b.p. 100—120°, 75 ml) was added and the cold solution was filtered. The filtrate was concentrated under reduced pressure at −15° yielding a finely divided, brown solid, *ca.* 50%. Recrystallisation was from acetone–light petroleum (b.p. 100—120°) at −15° giving the pure *compound.*

Recrystallisation from acetone–toluene at −15° yields a crystalline product as golden-brown needles. These were shown to contain toluene by analysis and i.r. data (see Table).

Carbonyl(bistriphenylphosphine)(benzene)molybdenum.— A powdered suspension of the dimer $[(C_6H_6)Mo(Ph_3P)_2]_2N_2$ (0·275 g) in benzene (100 ml) at 6° was treated with a slow stream of carbon monoxide for 1 h. The reaction solution was allowed to warm to room temperature and carbon monoxide was passed for a further 1·5 h. The solvent was removed under reduced pressure and the residue was recrystallised from ether–ethanol at 0° giving orange crystals which were washed with a small quantity of cold ethanol and dried *in vacuo, ca.* 63%.

Carbonylbis(triphenylphosphine)toluenemolybdenum.— A solution of $(toluene)Mo(Ph_3P)_2N_2$ (0·172 g) in tetrahydrofuran (25 ml) was treated with a slow stream of carbon monoxide for 2 h. The solvent was removed under reduced pressure and the residue dissolved in benzene and the solution was placed on an alumina column made up in benzene. Elution with diethyl ether gave an orange band which was collected and the solvent was removed under reduced pressure. The residue was recrystallised from ether–ethanol giving orange crystals of the pure *compound, ca.* 74%.

Reaction of the Compounds $(Arene)Mo(R_3P)_2N_2$ *with Hydrogen.*—The dinitrogen derivative $(MeC_6H_5)Mo(Ph_3P)_2N_2$ (0·1 g) in dry tetrahydrofuran (25 ml) was treated with a slow stream of hydrogen gas at 22° at atmospheric pressure for 15 min. The solvent was removed under reduced pressure and the residue washed with light petroleum and dried *in vacuo.* The product was identified as the dihydrido-complex $(MeC_6H_5)Mo(Ph_3P)_2H_2$ from the i.r. and analytical data, *ca.* 0·08 g. In a similar manner, the dihydrido-derivative $(sym\text{-}Me_3C_6H_3)Mo(Ph_3P)_2H_2$ was prepared from the dinitrogen analogue in essentially quantitative yield. The dihydride $(C_6H_6)Mo(Ph_3P)_2H_2$ was prepared from the binuclear $[(C_6H_6)Mo(Ph_3P)_2]_2N_2$ and hydrogen in benzene at 6° in high yield.

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