Synthesis of σ-Aryl Compounds of Molybdenum, Rhenium, Ruthenium, and Rhodium from the Metal–Metal Bonded Binuclear Acetates of Molybdenum(II), Rhenium(III), Ruthenium(II,III), and Rhodium(II) †

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The interaction between diarylmagnesiums, $MgAr_2$ (Ar = C_6H_5, 2-$MeOC_6H_4$ and 4-FC_6H_4) and the metal–metal bonded binuclear bridged tetra-acetates, $M^{II}_2(CO_2Me)_4$, (M = Mo and Rh) and $Ru^{II,III}(CO_2Me)_4Cl$ in the presence of trimethylphosphine produces monomeric (Ru, Rh) or dimeric (Mo) aryls; for Ru and the 2-methoxyphenyl, hydrogen loss from the MeO group leads to formation of a metallocycle. In the absence of PMe_3, $Re_2(O_2CMe)_4Cl_2$ gives a dimeric binary aryl, $Re_2(2\text{-}MeOC_6H_4)_6$.

The compounds have been studied by ^1H, ^{31}P, and ^{13}C n.m.r. and i.r. spectroscopy. Likely structures are discussed.

WE have described the interactions of dialkylmagnesiums in the presence of trimethylphosphine with the binuclear metal–metal bonded acetates of chromium(II), molybdenum(II), ruthenium(II,III), and rhodium(II) [1] and of the interaction in the absence of PMe_3 with $Re_2(CO_2Me)_4Cl_2$.[2]

We now report similar studies using diarylmagnesiums, $MgAr_2$ (Ar = phenyl, 2-methoxyphenyl, and 4-fluorophenyl). N.m.r. spectroscopic data for new compounds are given in Tables 1 and 2.

TABLE 1

^1H and ^{13}C Nuclear magnetic resonance data of aryl compounds

Compound	^1H δ values [a]	Assignment	$^{13}C\{^1H\}$ [b]
(A) $Mo_2(O_2CMe)(C_6H_5)_3(PMe_3)_3$	8.50—7.20 (b, 15 H)	C_6H_5	182.73 (bs, O_2CMe), 142.88—141.33 (m) and 127.29—124.68 (m, C_6H_5), 24.77, 24.47 [c] (s, O_2CMe), 18.72—13.28 (m, PMe_3)
	2.55, 2.40 [c] (s, 3 H)	O_2CMe	
	1.15—0.55 (m, 27 H)	PMe_3	
(B) $Mo_2(O_2CMe)(4\text{-}FC_6H_4)_3(PMe_3)_3$	7.45—6.72 (b, 15 H)	4-FC_6H_4	183.29 [e] (s, O_2CMe), 143.47—142.18 (m), 114.18—112.62 (m, 4-FC_6H_4), 24.71, 24.35 (s, O_2CMe), 18.49—13.04 (m, PMe_3)
	2.34, 2.43 [d] (s, 3 H)	O_2CMe	
	1.10—0.50 (m, 27 H)	PMe_3	
(C) $Mo_2(2\text{-}MeOC_6H_4)_4(PMe_3)_2$	8.15—7.35 (b, 16 H)	(2-$MeOC_6H_4$)	
	4.70 (s, 12 H)	(2-$MeOC_6H_4$)	
	2.30—1.65 (m, 18 H)	PMe_3	
(D) $Mo_2(2\text{-}MeOC_6H_4)_4$	7.40—6.60 (b, 4 H)	(2-$MeOC_6H_4$)	
	3.70 (s, 3 H)	(2-$MeOC_6H_4$)	
(E) $Re_2(2\text{-}MeOC_6H_4)_6$	8.25—6.60 (b, 24 H)	2-$MeOC_6H_4$	[f] 141.5, 130.56, 128.46, 127.21, 120.52, 119.83, 111.44, 108.41 (s, 2-$MeOC_6H_4$), 55.54, 54.09 [c] (s, 2-$MeOC_6H_4$)
	3.20 (s, 18 H)	2-$MeOC_6H_4$	
(F) $Ru(C_6H_5)_2(PMe_3)_4$	8.07—7.12 (b, 10 H)	C_6H_5	
	1.24 (s, 36 H)	PMe_3	
(G) $Ru(2\text{-}CH_2OC_6H_4)(PMe_3)_4$	8.00—6.95 (b, 4 H)	(2-$CH_2OC_6H_4$)	
	5.35 [g] (tdd, 2 H)	2-$CH_2OC_6H_4$)	
	1.45—1.05 (m, 36 H)	PMe_3	
(H) $Rh(C_6H_5)(PMe_3)_3$	8.10—7.15 (b, 5 H)	C_6H_5	
	1.29 (s, 27 H)	PMe_3	
(I) $Rh(2\text{-}MeOC_6H_4)(PMe_3)_3$	7.60—6.70 (b, 4 H)	2-$MeOC_6H_4$	
	3.83 (s, 3 H)	2-$MeOC_6H_4$	
	1.20 (bs, 27 H)	PMe_3	

[a] In [$^2H_6$]benzene as solvent with $SiMe_4$ as internal reference, referenced to $SiMe_4$ (δ 0.0) at 60 MHz and 35 °C; relative intensity ( ); b = broad, m = multiplet. [b] In [$^2H_6$]benzene as solvent and internal reference (δ 128.7), referenced to $SiMe_4$ (δ 0.0) at 25.2 MHz at 28 °C. Peaks to high frequency of $SiMe_4$ are positive. [c] Relative intensity *ca.* 1 : 2. [d] Relative intensity *ca.* 1 : 1 [e] See ref. 1 for $^{13}C\{^1H\}$ data on bridging acetates. [f] In CD_2Cl_2 as solvent and internal reference (δ 76.9), referenced to $SiMe_4$ (δ 0.0) at 25.2 MHz at 28 °C. [g] $^3J_{^{31}P-^1H}$ = 15 Hz (*cis*), $J_{^{31}P-^1H}$ = 5, 2 Hz (*trans*).

Molybdenum Compounds.—(a) *Phenyl and 4-fluorophenyl.* The interaction of μ_4-tetra-acetato-dimolybdenum(II)(*Mo–Mo*), $Mo_2(CO_2Me)_4$, with the diarylmagnesium in diethyl ether containing an excess of PMe_3 produces blue solutions from which dark blue diamagnetic crystals of stoicheiometry $Mo_2(CO_2Me)Ar_3(PMe_3)_3$ [Ar = Ph (A), 4-FC_6H_4 (B)] can be isolated in high yield. In the absence of phosphine only decomposition occurs. Analytical and spectroscopic data are consistent with the structure (1a,b), in which the molybdenum is in the divalent state with a quadruple Mo–Mo bond. The presence of a μ-acetato-group is shown by ^1H and ^{13}C n.m.r. spectroscopy although in the i.r. region, identification of carboxylate stretches is uncertain due to obscuring absorptions of aryl and phosphine groups. Since there are only weak aryl absorptions above *ca.* 1 520 cm^{-1} it is evident that the CO_2Me group cannot be unidentate.[3]

Deuteriation experiments (see Experimental section) show that all three aryl groups are σ-bonded. While the ^1H and ^{13}C n.m.r. data are not rigorously diagnostic of structure, the $^{31}P\{^1H\}$ spectra consist of AB_2 and AMX type resonances, which clearly indicates the existence in solution of two isomers. On warming, the resonances

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† No reprints available.

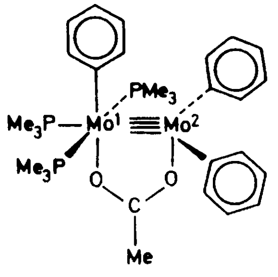
TABLE 2

$^{31}P\{^1H\}$ Nuclear magnetic resonance data

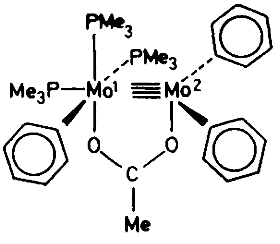
Compound		δ Values [a]
(A) $Mo_2(O_2CMe)(C_6H_5)_3(PMe_3)_3$	AB_2	[b] δ_A −9.80, δ_B −8.73, J_{AB} = 17.5 Hz
	AMX	δ_A = −12.51, δ_M −16.79, δ_X −19.19 J_{AX} = 16.9, J_{AM} = 13.8, J_{MX} = 7.5 Hz
(B) $Mo_2(O_2CMe)(4\text{-}FC_6H_4)_3(PMe_3)_3$	AB_2	δ_A −10.77, δ_B −9.36, J_{AB} = 18.8 Hz
	AMX	δ_A −13.21, δ_M −16.69, δ_X −19.44 J_{AX} = 17.6, J_{AM} = 12.8, J_{MX} = 7.5 Hz
(C) $Mo_2(2\text{-}MeOC_6H_4)_4(PMe_3)_2$		5.13 (s) 6.50 (s) [c]
(F) $Ru(C_6H_5)_2(PMe_3)_4$		−9.13 (s)
	A_2X_2 [d]	δ_A −7.02, δ_X −19.04, J_{AX} = 23.4 Hz
	AX_2	δ_A −13.79, δ_X −8.86, J_{AX} = 22.8 Hz
(G) $Ru(2\text{-}CH_2OC_6H_4)(PMe_3)_4$		[e] δ_A −5.95 (dd) δ_B −14.32 (td) δ_C −20.07 (td)
(H) $Rh(C_6H_5)(PMe_3)_3$		−16.33 d $J_{^{103}Rh-^{31}P}$ = 142.1 Hz −21.09 to −21.95 (m) [f]
(I) $Rh(2\text{-}MeOC_6H_4)(PMe_3)_3$		−15.65 d $J_{^{103}Rh-^{31}P}$ = 146.2 Hz −12.16 to −19.41 (m) [f]

[a] In benzene–10% [$^2H_6$]benzene and referenced to external 85% H_3PO_4 (δ 0.0) at 40.5 MHz. Peaks to high frequency of reference are positive. [b] 0 °C in toluene–10% C_6D_6. [c] At −40 °C in Et_2O–10% C_6D_6. [d] At −40 °C in thf–10% C_6D_6. [e] Labelling as in (4); $J_{P_A-P_B}$ = 25.2 Hz, $J_{P_A-P_C}$ = 27.9 Hz, $J_{P_B-P_C}$ = 14.8 Hz, P_B and P_C may be reversed. [f] At −40 °C in toluene–10% C_6D_6, complex patterns of at least 12 lines (H) and 18 lines (I) are observed.

coalesce giving two broad bands at 50 °C and a singlet at *ca.* 75 °C. Corresponding behaviour is found in the ^1H n.m.r. spectra. On cooling the original spectra are restored which suggests that rapid PMe_3 exchange occurs at elevated temperatures but is sufficiently slow at 35 °C for both isomers to be observed in $^{31}P\{^1H\}$ spectra. Attempts to separate isomers were unsuccessful. The ^1H spectra of both phenyl and fluorophenyl show two singlets due to acetate at 35 °C which coalesce to a singlet at 70 °C where the phosphines are equivalent and again the spectrum indicates isomers. Taken together the n.m.r. data are consistent with (1a), AB_2, and (1b), AMX. An AB_2 pattern should be obtained from an isomer with the aryl on Mo^1 in the axial position with respect to the Mo–Mo bond. However, as the CO_2Me group gives two CH_3 resonances in both phenyl and fluorophenyl compounds it seems reasonable to assume that the group *trans* to oxygen on Mo^1 is an aryl for isomer (1a) and a PMe_3 for the other (1b).



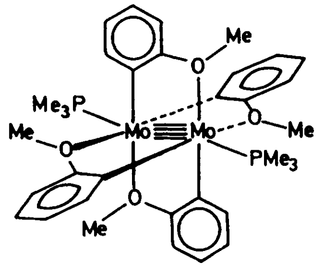
(1a)



(1b)

The spectra do not rigorously exclude a structure with three PMe_3 groups on one Mo atom and three aryls on the other but the unusual $^{31}P\{^1H\}$ spectra are inconsistent with this.

(b) 2-*Methoxyphenyl.* The reaction in this case yields $Mo_2(2\text{-}MeOC_6H_4)_4(PMe_3)_2$ (C). The dark blue-green crystalline and air-stable compound contains no acetate and the $^{31}P\{^1H\}$ spectrum is a singlet (+35 to −40 °C) consistent with structure (2) having PMe_3 groups on the Mo≡Mo bond axis. The aryl groups act like bridging bidentate carboxylate groups being formally 3-electron donors *via* carbon and the methoxy-oxygen. Increased stability with this type of chelate aryl is well known [4] and the bonding is doubtless similar to that of the 2,6-dimethoxyphenyl ligand in $Cr_2[2,6\text{-}(MeO)_2C_6H_3]_4$.[5] The spectroscopic data tell nothing of the relative orientations of the aryls and (2) shows only one possibility with mutually *cis* units.



(2)

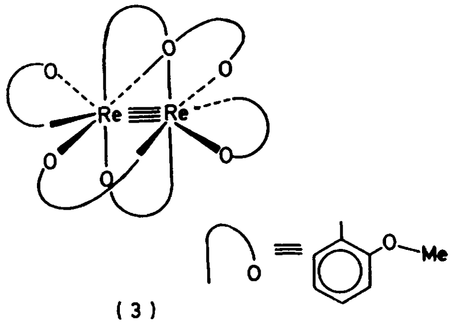
The compound is unstable in organic solvents at room temperature—the solutions turning grey-green and depositing a pink precipitate. Cryoscopic molecular-weight determinations (benzene) of fresh solutions give values *ca.* half that expected due to PMe_3 dissociation; this is also indicated by the ^1H and $^{31}P\{^1H\}$ spectra of other than fresh solutions.

The pink precipitate, which is exceedingly pyrophoric when dry, is $Mo_2(2\text{-}MeOC_6H_4)_4$ (D). It is soluble in CH_2Cl_2 and Me_2SO, being sufficiently stable in the latter to allow ^1H n.m.r. and molecular-weight studies and presumably it has a structure similar to (2) without the terminal phosphines.

Direct interaction of $Mo_2(CO_2Me)_4$ and $(2\text{-}MeOC_6H_4)_2Mg$ in the absence of PMe_3 in ether also give a pink product but we have been unable to separate it cleanly from magnesium acetate. Chromium(II) acetate gives a bright yellow compound with properties similar to those of $Cr_2(2\text{-}MeOC_6H_4)_4$ [6] but we were unable to obtain reproducible analytical data.

Rhenium Compounds.—In the absence of PMe_3, the acetate $Re_2(CO_2Me)_4Cl_2$ reacts with three equivalents of bis-2-methoxyphenylmagnesium to give dark green solutions from which the dark green, diamagnetic crystalline rhenium(III) aryl of formula $Re_2(2\text{-}MeOC_6H_4)_6$ (E), can be isolated in high yield. Although sparingly soluble in hydrocarbons it is quite soluble in acetone and chlorinated solvents.

The ^1H n.m.r. spectrum at 25 °C has aryl resonances and a singlet due to CH_3O. This broadens at 0 °C and at -20 °C becomes two singlets (ratio 2 : 1, separation *ca.* 7 Hz). The $^{13}C\{^1H\}$ spectrum at 25 °C shows two broadened resonances for CH_3O (*ca.* 2 : 1).



(3)

The spectra suggest that there are aryl groups in two environments as in (3). The terminal aryls are not necessarily chelated as in (3) and the singlet CH_3O (25 °C) confirms exchange between end and bridge positions, presumably by simple lift-off of the methoxy-oxygen. However, the $^{13}C\{^1H\}$ spectrum still permits two different CH_3O groups to be detected at 25 °C. The separation between these peaks is *ca.* 36 Hz so the coalescence temperature for the ^{13}C spectrum will be higher than that for the ^1H.

Interaction of $Re_2(CO_2Me)_4Cl_2$ and $MgAr_2$ in the presence of PMe_3 yields red-brown materials from which we have been unable to isolate pure compounds. Using $MgPh_2$ and $Mg(C_6H_4F)_2$ alone, petroleum-soluble brown but intractable products were also obtained.

Ruthenium Compounds.—(a) *Phenyl.* The acetate $Ru_2(CO_2Me)_4Cl$ reacts with Ph_2Mg in tetrahydrofuran containing PMe_3 to give the complex $RuPh_2(PMe_3)_4$ (F). This off-white, crystalline diamagnetic compound is surprisingly air sensitive and traces of moisture or oxygen cause rapid decomposition.

The ^1H resonance of CH_3–P is (25 °C) a slightly broadened singlet which broadens further on cooling. The $^{31}P\{^1H\}$ spectrum is also a singlet at room temperature but at -40 °C in diethyl ether under dinitrogen has an A_2X_2 triplet–triplet pattern consistent with a structure with *cis*-phenyl groups in *cis*-$RuPh_2(PMe_3)_4$ together with an AX_2, triplet–doublet pattern and a free PMe_3 (δ -62.9 [7]) resonance line suggesting the presence of a species with three phosphines per Ru. Since the i.r. spectra of Nujol mulls or solutions under N_2 have a strong sharp band at 2 128 cm^{-1} which disappears on sweeping with argon it is evident that in solution there are equilibria

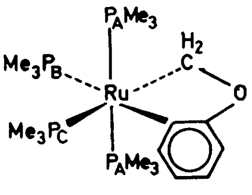
$$cis\text{-}RuPh_2(PMe_3)_4 \rightleftharpoons RuPh_2(PMe_3)_3 + PMe_3$$

$$RuPh_2(PMe_3)_3 + N_2 \rightleftharpoons RuPh_2(N_2)(PMe_3)_3$$

No nitrogen was detected by analysis in the solid and since the molecular weight under argon is only slightly low for $RuPh_2(PMe_3)_4$ the dissociation appears not to be extensive.

A reversible colour change is observed on heating the compound in solution. At room temperature solutions are pale yellow while at *ca.* 50 °C they become orange. The compound reacts with CO, NO, and alkenes although we have not yet fully investigated the products. No reaction took place after heating in a sealed tube for one week at 200 °C in neat PMe_3 or after u.v. irradiation (48 h) at room temperature in benzene or PMe_3.

(b) *2-Methoxyphenyl.* The reaction of 2.5 equivalents of the diarylmagnesium with $Ru_2(CO_2Me)_4Cl$ and PMe_3 in tetrahydrofuran at 25 °C is slow (12 h). The yellow solution produced contains a mixture of species, including, according to ^{31}P n.m.r. spectroscopy, a bridged phosphido-complex. We have been unable to separate the components by crystallisation. On chromatography a yellow band eluted with toluene was found to contain $Ru_2Cl_2(PMe_3)_4$, to be discussed separately, while elution with tetrahydrofuran gives a white complex $Ru(2\text{-}CH_2OC_6H_4)(PMe_3)_4$ (G). Spectroscopic data indicates a structure (4), confirmation of which is provided by an *X*-ray crystallographic study.[8] The compound can be considered to arise by oxidative addition of a C–H bond of the methyl group across ruthenium followed by loss of H to give a Ru–CH_2– bond in a five-membered Ru^{II} heterocycle. The δ-elimination has a precedent in the formation of the heterocycle $Ru\{(CH_2)_2SiMe_2\}(PMe_3)_4$.[1]



(4)

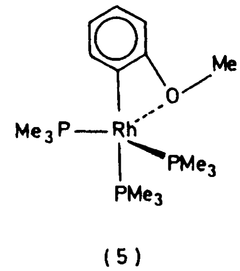
The ^1H n.m.r. spectrum shows methylene CH_2 protons giving a well defined first-order pattern of a 1 : 2 : 1 triplet ($^3J_{PH}$ = 15 Hz) of doublets of doublets ($^3J_{PH}$ = 5 and 2 Hz respectively). The triplet structure can be ascribed to splitting by the two mutually *trans* PMe_3 groups and the doublet of doublets from the two *cis*, non-equivalent PMe_3 groups. The *cis*-P coupling with CH_2 is thus apparently greater than *trans*-P coupling.

The $^{31}P\{^1H\}$ n.m.r. in benzene (10% C_6D_6) is consistent with (4) and has two triplets of doublets due to the *cis*-non-equivalent phosphines (see Table 2). The two *trans* equivalent phosphines give a doublet of doublets ($^2J_{P_AP_B} = 25.2$ Hz, $^2J_{P_AP_C} = 27.9$ Hz) as coupling to each of the mutually *cis* phosphines is slightly different.

Rhodium Compounds.—(a) *Phenyl.* Interaction of $Rh_2(CO_2Me)_4$, Ph_2Mg, and PMe_3 in diethyl ether produces the orange, crystalline compound $RhPh(PMe_3)_3$ (H), in high yield. Unlike the triphenylphosphine analogue,[9] the compound is readily obtained pure and decomposes only slowly in air.

N.m.r. spectra are temperature dependent. The CH_3-P singlet at room temperature becomes a broad doublet and a singlet at −20 °C and below. The $^{31}P\{^1H\}$ spectrum has a distorted doublet ($^1J_{RhP} = 142.1$ Hz) at room temperature and a pattern of at least 12 lines at −40 °C. The data does not permit a structural assignment though, as is usual with Rh^I compounds, a distorted square structure seems likely, possibly with solvent co-ordination in solution to give a fluxional 5-co-ordinate species.

(b) 2-*Methoxyphenyl.* The isolated yellow crystals of $Rh(2\text{-}MeOC_6H_4)(PMe_3)_3$ (I), are thermally more stable and less air sensitive than the phenyl, probably due to co-ordination of oxygen as in (5). The n.m.r. spectra are again temperature dependent, and complicated and we have not attempted an analysis. At 25 °C there is a ^1H singlet, and a $^{31}P\{^1H\}$ doublet with $^1J_{RhP} = 146.2$ Hz.



(5)

TABLE 3

Analytical data for aryl compounds

Compound	Colour	Found C(%)	Found H(%)	Found P(%)	Found M [a]	Required (C%)	Required (H%)	Required (P%)	Required M
(A) $Mo_2(O_2CMe)(C_6H_5)_3(PMe_3)_3$	Dark blue	49.4	6.5	13.0 [b]	707	49.0	6.3	13.1	710
(B) $Mo_2(O_2CMe)(4\text{-}FC_6H_4)_3(PMe_3)_3$	Dark blue	45.3	5.5	11.9 [c]	680	45.5	5.5	12.2	764
(C) $Mo_2(2\text{-}MeOC_6H_4)_4(PMe_3)_2$	Blue-green	53.5	6.5	7.0	384 [d]	52.8	6.0	8.0	772
(D) $Mo_2(2\text{-}MeOC_6H_4)_4$	Pink	53.8	4.5	<0.2	594 [e]	54.2	4.5	0.0	620
(E) $Re_2(2\text{-}MeOC_6H_4)_6$	Dark green	49.9	4.4		960 [f]	49.7	4.1		1014
(F) $Ru(C_6H_5)_2(PMe_3)_4$	Off-white	51.4	8.1	22.2	510	51.5	8.2	22.2	559
(G) $Ru(2\text{-}CH_2OC_6H_4)(PMe_3)_4$	White	44.6	8.3	24.3	508	44.6	8.2	24.3	511
(H) $Rh(C_6H_5)(PMe_3)_3$	Orange	44.4	8.0	23.4	408	44.1	7.8	22.8	408
(I) $Rh(2\text{-}MeOC_6H_4)(PMe_3)_3$	Yellow	44.7	7.7	19.4	455	43.8	7.8	21.2	438

[a] Cryoscopically in benzene. [b] Mo, found 25.6 (27.0). [c] F, found 7.3 (7.5). [d] See text. [e] Cryoscopically in Me_2SO. Osmometrically in CH_2Cl_2.

In the absence of PMe_3 petroleum-soluble red-brown but intractable products were obtained for both phenyl and 2-methoxyphenyl.

EXPERIMENTAL

Microanalyses were by Butterworth Microanalytical Consultancy Limited, Pascher (Bonn) and Imperial College Laboratories. Spectrometers: Perkin-Elmer R12B (^1H); Varian XL-100 (^1H, ^{13}C, ^{31}P, F.t.); Perkin-Elmer PE 457, 257 (i.r.). All operations were performed under oxygen-free nitrogen or argon or *in vacuo* and all solvents (except CH_2Cl_2) were dried over sodium and distilled under nitrogen before use. Dichloromethane was dried over calcium hydride and distilled under nitrogen. Light petroleum had b.p. 40—60 °C. Melting points were determined in sealed capillaries under nitrogen and are uncorrected. Analytical data are collected in Table 3.

μ-Acetato-triphenyltris(trimethylphosphine)dimolybdenum-(II)(Mo–Mo) (A).—Diphenylmagnesium (3.8 cm³ of a 0.7M-diethyl ether solution, 2.7 mmol) was added to $Mo_2(O_2CMe)_4$ (0.57 g, 1.3 mmol) suspended in diethyl ether (50 cm³) and trimethylphosphine (1 cm³) at 0 °C.

The solution rapidly became dark blue-green; after being stirred at 0 °C for 1 h, volatile material was removed from the mixture under reduced pressure and the blue residue extracted into light petroleum (40 cm³). The solution was filtered, concentrated to *ca.* 20 cm³, and cooled (−20 °C) to give dark blue *prisms* which were washed with cold, light petroleum (1 cm³) and dried *in vacuo*; yield 0.4 g (46%), m.p. 151—153 °C. I.r. (Nujol): ν 3 030m, 1 557w, 1 545w, 1 512m, 1 465s, 1 420s, 1 365w, 1 345w, 1 300m, 1 280s, 1 275m, 1 235w, 1 040w, 1 010w, 942s, br, 845m, 735m, 720s, 704s, and 672m cm⁻¹. A similar reaction in the absence of phosphine or using other phosphines (*e.g.* PMe_2Ph, $PPhMe_2$) led only to decomposition.

The compound is stable in air for *ca.* 15 min but decomposes immediately in solution when exposed to the atmosphere. It does not react with H_2 or C_2H_4 (1 atm, room temperature) but does so with NO, CO, MeC_2H, C_2H_2, and PhC_2H in benzene to give red-brown materials; we have not yet isolated any pure compounds. The compound did not sublime at 150 °C/10^{-2} mmHg and the remaining black solid did not redissolve in C_6H_6.

μ-Acetato-tris(4-fluorophenyl)tris(trimethylphosphine)dimolybdenum(II)(Mo–Mo) (B).—Bis(4-fluorophenyl)magnesium (4.5 cm³ of a 0.8M-Et_2O solution, 3.6 mmol) was added to $Mo_2(O_2CMe)_4$ (0.77 g, 1.8 mmol) suspended in diethyl ether (50 cm³) and trimethylphosphine (1 cm³) at 0 °C. The solution was stirred for 1 h at 0 °C, evaporated to dryness under reduced pressure, and the residue extracted into light petroleum (40 cm³); this was filtered and reduced to *ca.* 30 cm³. Cooling of this (−20 °C) yielded blue-green *crystals* which were washed with light petroleum (2 × 2.5 cm³) at −78 °C and dried *in vacuo*. A further batch of crystals was obtained from the original residue after extraction into light petroleum (20 cm^3), filtration, evaporation (to *ca.* 10 cm^3), and cooling (−20 °C); yield 0.4 g (32%), m.p. 145—149 °C (decomp.). I.r. (Nujol): ν 3 050w, 1 595w, 1 560m, 1 520w, 1 491s, 1 455s, 1 430s, 1 365w, 1 345w, 1 300w, 1 282m, 1 211s, 1 155s, 1 017w, 950s, 850w, 806m, 750m, 741w, 730w, 725w, 682w, and 678m cm^{-1}.

Decomposition occurs in the absence of phosphine. The compound is less air sensitive than (A) and lasts for *ca.* 1 h in the solid state but again decomposes immediately in solution when exposed to the atmosphere.

Deuteriation Experiments.—To the crystalline phenyl and 4-fluorophenyl compounds above (*ca.* 0.1 g) was added *ca.* 2 cm^3 of 6M-D_2SO_4 in D_2O. After being shaken with diethyl ether (2 × 5 cm) which was reduced to *ca.* 1 cm^3, mass spectroscopic analysis showed that only the monodeuteriated arene was formed: *m/e* 79 (C_6H_5D), *m/e* 97 (C_6H_4DF) plus *m/e* 74 ($C_4H_{10}O$), and *m/e* 59 ($C_2H_3O_2^+$, acetate).

Tetrakis(2-*methoxyphenyl*)*bis*(*trimethylphosphine*)*dimolybdenum*(II)(Mo–Mo) (C) *and Tetrakis*(2-*methoxyphenyl*)*dimolybdenum*(II)(Mo–Mo) (D).—Bis(2-methoxyphenyl)-magnesium (3.8 cm^3 of a 0.76M-diethyl ether solution, 2.9 mmol) was added to $Mo_2(O_2CMe)_4$ (0.62 g, 1.4 mmol) suspended in diethyl ether (55 cm^3) and trimethylphosphine (1 cm^3) at −78 °C. The solution was allowed to warm to 10 °C (1 h) and was then stirred at this temperature (1 h). After evaporation to dryness the residue was extracted into light petroleum (80 cm^3), filtered, and the solution evaporated to *ca.* 30 cm^3. Cooling (−20 °C) of the solution yielded deep blue-green *needles* which were washed with light petroleum (2 × 2 cm^3) and dried *in vacuo*; yield 0.3 g (28%), m.p. 75—80 °C (decomp.). I.r. (Nujol): ν 3 030w, 1 595m, 1 550w, 1 485s, 1 450m, 1 410m, 1 295s, 1 275m, 1 243s, 1 200m, 1 155m, 1 140m, 1 036m, 1 015m, 1 000m, 945s,br, 845w, 778m, 750s, 708m, and 689w cm^{-1}.

A solution of (C) (0.3 g, 0.39 mmol) was stirred in benzene at room temperature (24 h) and the pink precipitate of the *complex* (D) allowed to settle. The collected product was washed with thf (2 × 10 cm^3) and light petroleum (10 cm^3) and dried *in vacuo*; yield 0.22 g (90%), m.p. 220—240 °C (decomp.). I.r. (Nujol) ν 3 030w, 1 600w, 1 585w, 1 547w, 1 495w, 1 445s, 1 439m, 1 419m, 1 365w, 1 250s, 1 245m, 1 206m, 1 195w, 1 145m, 1 090m,br, 1 145m, 1 110m, 995m, 800s, 756m, 746m, and 718m cm^{-1}.

Hexakis(2-*methoxyphenyl*)*dirhenium*(III)(Re–Re) (E).—Bis(2-methoxyphenyl)magnesium (3.5 cm^3 of a 0.76M-diethyl ether solution, 2.7 mmol) was added to a suspension of $Re_2(O_2CMe)_4Cl_2$ (0.60 g, 0.88 mmol) in diethyl ether (60 cm^3) at −10 °C. The solution was then stirred (10 h) at room temperature, evaporated to dryness under reduced pressure, and the residue extracted with dichloromethane (30 cm^3). The solution was filtered, evaporated to *ca.* 7 cm^3, and cooled (−20 °C) to give dark green *prisms* which were recrystallised twice from CH_2Cl_2 (as above) washed with light petroleum (5 cm^3) and dried *in vacuo*; yield 0.3 g (34%), m.p. 180—200 °C (decomp.). I.r. (KBr disc): ν 3 065w, 3 045m, 2 940m, 2 920m, 2 880w, 2 820m, 1 568s, 1 510m, 1 450s, 1 440s, 1 419s, 1 285w, 1 562m, 1 240s, 1 217s, 1 211s, 1 165m, 1 158s, 1 111s, 1 055w, 1 045m, 1 021m, 1 007s, 923w, 840w, 790m, 784m, 775m, 752s, 747s, 740s, 718s, 592w, 570w, 530w, 470w, 450w, and 442w cm^{-1}.

cis-*Diphenyltetrakis*(*trimethylphosphine*)*ruthenium*(II) (F).—Diphenylmagnesium (6.2 cm^3 of a 0.53M-diethyl ether solution, 3.3 mmol) was added to a suspension of $Ru_2(O_2CMe)_4Cl$ (0.64 g, 1.35 mmol) in tetrahydrofuran (50 cm^3) and trimethylphosphine (1 cm^3). The solution was stirred for 2 h (room temperature) and evaporated to dryness. The yellow residue was extracted into warm (50 °C) light petroleum and filtered while still warm. After evaporation to *ca.* 20 cm^3 and cooling (−20 °C) the very pale yellow *microcrystals* produced were washed with cold, light petroleum (2 × 2 cm^3) and dried *in vacuo*. They recrystallised as off-white *prisms* from *ca.* 2 cm^3 of hot (*ca.* 50 °C) benzene at room temperature; yield 0.4 g (27%), m.p. 130—140 °C (decomp.). I.r. (petroleum solution; matched KBr cells under N_2); ν_{NN} = 2 128s cm^{-1}; (Nujol) 3 090w, 2 100s (see text), 1 550m,br, 1 435s,br, 1 295s, 1 275s, 1 179w, 1 050m, 1 005m, 930s,br, 850s, 730s, 700s, 655s, and 630m cm^{-1}.

o-*Phenyleneoxymethyltetrakis*(*trimethylphosphine*)*ruthenium*(II) (G).—Bis(2-methoxyphenyl)magnesium (8.5 cm^3 of a 0.33M-diethyl ether solution; 2.8 mmol) was added to $Ru_2(O_2CMe)_4Cl$ (0.4 g, 0.85 mmol) in tetrahydrofuran (40 cm^3). The solution was stirred for 12 h (room temperature) after which the volatile material was removed under reduced pressure and the residue extracted into warm (50 °C) light petroleum (50 cm^3) and filtered. The yellow solution was evaporated to dryness and the residue dissolved in toluene (10 cm^3) and filtered.

The solution was transferred to a 15 × 2 cm Fluorosil column which was eluted first with toluene (*ca.* 100 cm^3) and then with thf (*ca.* 100 cm^3). The thf fraction was evaporated to dryness and the residue recrystallised from *ca.* 3 cm^3 of toluene (−20 °C) to give white *needles* which were washed and dried as above; yield 0.25 g (29%). The compound turns yellow at *ca.* 175 °C and becomes progressively more orange until *ca.* 240 °C when it decomposes. I.r. (Nujol): ν 3 025m, 1 550w, 1 442s, 1 420s, 1 365m, 1 298s, 1 288s, 1 270s, 1 245w, 1 165s, 1 093w, 1 009m, 995m, 985s,br, 965s,sh, 850s, 840m, 830w, 800m, 746m, 718s, 704s, 663s, 634w, 542w, 508w, 363s, 338w, 317w, and 259w cm^{-1}.

Phenyltris(*trimethylphosphine*)*rhodium*(I) (H).—Trimethylphosphine (1 cm^3) was added to a suspension of $Rh_2(O_2CMe)_4$ (0.44 g, 0.99 mmol) in diethyl ether (40 cm^3) at 0 °C. Diphenylmagnesium (2.9 cm^3 of a 0.7M-diethyl ether solution; 2 mmol) was added to the yellow-brown suspension which was stirred (4 h) at room temperature. The volatile material was removed under reduced pressure, the residue extracted into light petroleum (40 cm^3), and the filtered solution evaporated to *ca.* 10 cm^3 and cooled (−20 °C) to yield orange-yellow *crystals*. These were washed with cold, light petroleum (1 cm^3) and dried *in vacuo*; yield 0.3 g (37%), m.p. 85—90 °C (decomp.). I.r. (Nujol): ν 3 040w, 1 570m, 1 470s, 1 420m, 1 365m, 1 300m, 1 280m, 1 175m, 1 060w, 1 018m, 940s, 850m, 818w, 732m, 708m, and 665w cm^{-1}.

The compound reacts with hydrogen to give an initial dark orange solution which becomes pale yellow after *ca.* 5 min (1 atm, room temperature). Benzene is liberated (^1H n.m.r.) and a broad resonance at *ca.* τ 19.3 in the ^1H n.m.r. indicates Rh–H bond formation although we have been unable to isolate a pure compound.

2-*Methoxyphenyltris*(*trimethylphosphine*)*rhodium*(I) (I).—Trimethylphosphine (0.7 cm^3) was added to a suspension of $Rh_2(O_2CMe)_4$ (0.43 g, 0.97 mmol) in diethyl ether (40 cm^3). Bis(2-methoxyphenyl)magnesium (9.7 cm^3 of a 0.2M-diethyl ether solution; 1.9 mmol) was added and the suspension stirred (5 h) at room temperature.

The volatile material was removed under reduced pressure, the residue extracted with light petroleum (50 cm^3), and the filtered solution was evaporated to *ca.* 3 cm^3 and cooled (−20 °C) to yield a yellow *solid*. This was recrystallised from toluene (5 cm^3) at −20 °C to give yellow crystals which were washed with light petroleum (2 × 2 cm^2) and dried *in vacuo*; yield 0.4 g (46%), m.p. 99—101 °C. I.r. (Nujol): ν 3 060w, 1 571m, 1 470s,br, 1 450s, 1 376s, 1 376m, 1 312m, 1 288s, 1 261w, 1 182m, 1 114w, 1 029m, 980m, 953s, 872w, 863m, 850m, 817m, 770m, 760m, 737m, 730m, and 677m cm^{-1}.

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