Aryl and Aryne Complexes of Chromium, Molybdenum, and Tungsten. *X*-Ray Crystal Structures of $[Cr(2\text{-}MeC_6H_4)(\mu\text{-}2\text{-}MeC_6H_4)(PMe_3)]_2$, $Mo(\eta^2\text{-}2\text{-}MeC_6H_3)(2\text{-}MeC_6H_4)_2(PMe_2Ph)_2$, and $W(\eta^2\text{-}2,5\text{-}Me_2C_6H_2)(2,5\text{-}Me_2C_6H_3)_2(PMe_3)_2$†

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The interaction of $CrCl_3(thf)_3$ (thf = tetrahydrofuran) and 2-methylphenyl-lithium gives the chromium(IV) tetra-aryl $Cr(2\text{-}MeC_6H_4)_4$, which reacts with PMe_3 to give the dimeric chromium(II) complex $[Cr(2\text{-}MeC_6H_4)(\mu\text{-}2\text{-}MeC_6H_4)(PMe_3)]_2$ as a minor product along with $Cr(2\text{-}MeC_6H_4)_2(PMe_3)_2$. Both can be made also by arylation of $Cr_2(O_2CMe)_4$ in the presence of PMe_3. The interaction of $W(OPh)_6$ and the 2-methylphenyl and 2,5-dimethylphenyl Grignard reagents gives the corresponding tungsten(IV) tetra-aryls. The interaction of PMe_2Ph and $Mo(2\text{-}MeC_6H_4)_4$ and of PMe_3 with $W(2,5\text{-}Me_2C_6H_3)_4$ gives, respectively, the aryne complexes $Mo(\eta^2\text{-}2\text{-}MeC_6H_3)(2\text{-}MeC_6H_4)_2(PMe_2Ph)_2$ and $W(\eta^2\text{-}2,5\text{-}Me_2C_6H_2)(2,5\text{-}Me_2C_6H_3)_2(PMe_3)_2$ whose *X*-ray structures indicate that they are best formulated as having metallacyclopropene rings. Spectroscopic and electrochemical data are given and *X*-ray crystal structures of three compounds are reported.

The 2-methylphenyl group has proved useful for the isolation of homoleptic tetra-aryls of transition metals and the syntheses and *X*-ray structures for those of Os,[1] Ru,[2] Re,[2] and Mo[3] have been described; the osmium(V) cation[3] has also been characterised crystallographically.[4]

The interaction of $Re(2\text{-}MeC_6H_4)_4$ with small tertiary phosphines gives aryne compounds[5a] with loss of toluene, while $Os(2\text{-}MeC_6H_4)_4$ differs in undergoing reductive coupling reactions with PR_3, CO, and Bu^tNC, to give η^6-arene complexes.[5b]

This paper reports the completion of the Group 6 tetra-aryl compounds with the syntheses of the *o*-tolyls of chromium(IV) and tungsten(IV) and of the 2,5-dimethylphenyl of tungsten; reactions of the tetra-aryls with phosphines are described. Analytical and physical data for new compounds are collected in Table 1.

Results and Discussion

The Tetra-aryls of Chromium- and Tungsten-(IV).—*Chromium.* Although numerous tetra-alkyls,[6] including the unusual cyclohexyl,[1] have been described, the only tetra-aryl of Cr^{IV} is the mesityl,[7] which was obtained by oxidation of $Li[Cr(2,4,6\text{-}Me_3C_6H_2)_4]$ with either O_2 or Ph_3CCl.

The tetra *o*-tolyl is obtained in yields of *ca.* 20% by interaction of four equivalents of *o*-tolyl-lithium in diethyl ether with $CrCl_3(thf)_3$ (thf = tetrahydrofuran) at −78 °C; the reaction presumably involves some sort of disproportionation or oxidation but the nature of this is obscure. No tetra-aryl can be obtained when the Grignard reagent is used nor when $Cr(OBu^t)_4$ is used as starting material. The *o*-tolyl species $Cr(2\text{-}MeC_6H_4)_3(thf)_3$ has been mentioned[8] but no experimental details were given; it can be construed that $CrCl_3(thf)_3$ and $MgBr(2\text{-}MeC_6H_4)$ in tetrahydrofuran give deep blue solutions containing the complex.

The deep purple tetra *o*-tolyl is thermally stable to *ca.* 90 °C; it is stable indefinitely at room temperature under argon or N_2 and in air for periods of up to 2 h. However, exposure to direct sunlight causes rapid decomposition and the solid should be stored in the dark.

Like similar tetrahedral chromium(IV) species,[1,6,7] the compound is paramagnetic with two unpaired electrons [in toluene, by Evans' method, $\mu_{eff.} = 2.7(1)$; *cf.* $Cr(2,4,6\text{-}Me_3C_6H_2)_4$,[7] 2.89]. The *X*-band e.p.r. spectrum at 293 K in toluene has a single band at a field width of 3 360G (3.36×10^{-1} T); $g_{iso} = 2.015$. On cooling to 77 K the spectrum changes and is then almost identical to that of $Cr(CH_2SiMe_3)_4$,[9] which was the first chromium(IV) alkyl to be made; for discussion of the spectra see ref. 9. Cyclic voltammetry of $Cr(2\text{-}MeC_6H_4)_4$ was studied in acetonitrile (for conditions see Table 5); there were one-electron irreversible oxidation and reduction waves at +1.15 and −1.30V, respectively [*cf.* for $Mo(2\text{-}MeC_6H_4)_4$,[3] +0.63 and −1.82V].

Like most of the chromium(IV) alkyls, the aryl is unreactive towards H_2, N_2O, MeOH, and Bu^tOH although CO, Bu^tNC, MeC≡CH, and hex-3-yne react to give brown mixtures from which no clean products could be separated. However, the compound reacts rapidly with excess of trimethylphosphine in toluene giving orange solutions from which bi-*o*-tolyl (identified by its mass spectrum) and two chromium-containing complexes can be separated. The evaporated reaction mixture was extracted with hexane; slow cooling to −20 °C gave very low yields of green crystals that have been shown by *X*-ray diffraction to be $[Cr(PMe_3)(2\text{-}MeC_6H_4)(\mu\text{-}2\text{-}MeC_6H_4)]_2$ as discussed below. The yellow-brown mother-liquor gives an oil that contains a paramagnetic species that cannot be readily separated but is evidently $Cr(2\text{-}MeC_6H_4)_2(PMe_3)_2$.

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† Bis(μ-2-methylphenyl)-bis(2-methylphenyl)bis(trimethylphosphine)-dichromium(II) (*Cr–Cr*), bis(dimethylphenylphosphine)[(5,6-η)-1-methylcyclohexa-1,3-dien-5-yne]bis(2-methylphenyl)molybdenum, [(5,6-η)-1,4-dimethylcyclohexa-1,3-dien-5-yne]bis(2,5-dimethylphenyl)-bis(trimethylphosphine)tungsten.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Analytical and physical data for new compounds

Compound	Colour	M.p. (°C)	Analysis * (%) C	Analysis * (%) H
$Cr(2\text{-}MeC_6H_4)_4$	Deep purple	90—91 (decomp.)	80.6 (80.7)	6.9 (6.8)
$Cr(2\text{-}MeC_6H_4)_2(PMe_3)_2$	Orange	110—112 (decomp.)	62.1 (60.6)	8.3 (8.2)
$Mo(\eta^2\text{-}2\text{-}MeC_6H_3)(2\text{-}MeC_6H_4)_2(PMe_3)_2$	Dark green	166—167	62.3 (62.5)	7.4 (7.4)
$Mo(\eta^2\text{-}2\text{-}MeC_6H_3)(2\text{-}MeC_6H_4)_2(PMe_2Ph)_2$	Dark green	146—148	69.0 (68.9)	6.6 (6.6)
$W(2\text{-}MeC_6H_4)_4$	Deep blue	123—125	61.1 (61.4)	5.1 (5.1)
$W(2,5\text{-}Me_2C_6H_3)_4$	Blue	132—133 (decomp.)	63.1 (63.6)	6.0 (6.0)
$W(\eta^2\text{-}2\text{-}MeC_6H_3)(2\text{-}MeC_6H_4)_2(PMe_3)_2$	Dark green	184—188	51.5 (53.3)	6.3 (6.3)
$W(\eta^2\text{-}2\text{-}MeC_6H_3)(2\text{-}MeC_6H_4)_2(PMe_2Ph)_2$	Dark green	154—157	60.4 (60.7)	5.7 (5.7)
$W(\eta^2\text{-}2,5\text{-}Me_2C_6H_2)(2,5\text{-}Me_2C_6H_3)(PMe_3)_2$	Dark green	180—182	55.3 (55.4)	6.8 (6.8)
$W(\eta^2\text{-}2,5\text{-}Me_2C_6H_2)(2,5\text{-}Me_2C_6H_3)(PMe_2Ph)_2$	Dark green	176—180	61.2 (62.0)	6.2 (6.2)

* Required values in parentheses.

Table 2. Selected bond lengths (Å) and angles (°) for $[Cr(2\text{-}MeC_6H_4)(\mu\text{-}2\text{-}MeC_6H_4)(PMe_3)]_2$

P(1)–Cr(1)	2.510(5)	C(11)–Cr(1)	2.444(9)
C(31)–Cr(1)	2.090(10)	Cr(1)–Cr(1B)	2.741(5)
Cr(1)–C(11B)	2.208(4)		
C(11)–Cr(1)–P(1)	89.7(3)	C(31)–Cr(1)–P(1)	84.7(3)
C(31)–Cr(1)–C(11)	168.8(3)	Cr(1B)–C(11)–Cr(1)	76.0(3)
Cr(1B)–Cr(1)–C(11B)	52.3(4)	P(1)–Cr(1)–C(11B)	154.7(5)
C(11)–Cr(1)–C(11B)	97.7(4)	Cr(1B)–Cr(1)–C(31)	133.0(4)
Cr(1B)–Cr(1)–P(1)	141.0(2)	Cr(1B)–Cr(1)–C(11)	51.4(3)
C(11B)–Cr(1)–C(31)	91.5(6)		

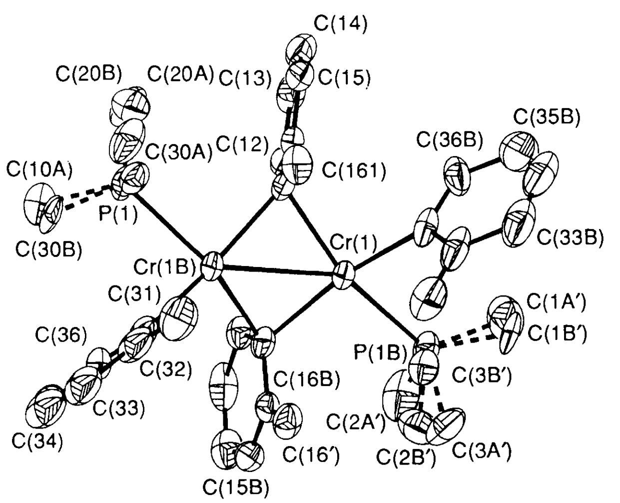

Figure 1. The structure of $[Cr(2\text{-}MeC_6H_4)(\mu\text{-}2\text{-}MeC_6H_4)(PMe_3)]_2$

Chromium(II) bis-alkyl and -mesityl compounds with a chelate diphosphine and $Cr(2,4,6\text{-}Me_3C_6H_2)_2(PMe_3)_2$ have been isolated[10] and shown to have essentially square geometries; $CrR_2(PR'_3)_2$, R = Ph, *o*-tolyl, or mesityl, R′ = Et or Et_2Ph, have been reported but were not fully characterised.[11] The reaction of $Cr(2\text{-}MeC_6H_4)_4$ with PMe_3 thus appears to be the reductive elimination (1) which gives the green dimer as a by-product. The addition of excess of PMe_3 to the yellow-brown solution followed by treatment with CO leads to the known compound $Cr(CO)_4(PMe_3)_2$.[12]

$$Cr(2\text{-}MeC_6H_4)_4 + 2\,PMe_3 \longrightarrow Cr(2\text{-}MeC_6H_4)_2(PMe_3)_2 + (2\text{-}MeC_6H_4)_2 \quad (1)$$

The dimeric compound, whose structure is described below, is similar to a trimethylsilylmethyl compound,[13] $[Cr(CH_2SiMe_3)(\mu\text{-}CH_2SiMe_3)(PMe_3)]_2$, made by alkylation of $Cr_2(O_2CMe)_4$ in the presence of PMe_3. Arylation of chromium(II) acetate by $MgBr(2\text{-}MeC_6H_4)$ in the presence of PMe_3 in thf produces a dark brown solution from which a mixture of green and orange crystals was obtained in low yields. Separation by crystallisation proved difficult so the crystals were separated manually. This green complex is identical to that obtained from $Cr(2\text{-}MeC_6H_4)_4$ while the orange product is $Cr(2\text{-}MeC_6H_4)_2(PMe_3)_2$. The magnetic moment in solution is 3.7 (*cf.* μ_B = 4.9 for the mesityl[10]), while the ^1H n.m.r. spectrum has paramagnetically shifted and broadened resonances for PMe_3 (δ − 20.9) and aryl protons (28.5, 25.6, 24.8) and presumably the *ortho*-methyl protons (−104.4). For the mesityl analogue[10] the *ortho*-methyls were not observed and a signal at δ −88.3 was assigned to the *para*-methyl groups.

The structure of the green dimer is shown in Figure 1 and bond lengths and angles are given in Table 2. The molecule lies on a two-fold axis perpendicular to and bisecting the Cr–Cr vector. The Cr_2C_2 four-membered ring is folded at the Cr–Cr vector with a dihedral angle of 145.5° between the Cr–C–Cr planes. The molecule is similar to the trimethylsilylmethyl;[13] this had a short Cr–Cr distance of 2.1 Å and metal–metal quadruple bonding was suggested. The longer Cr–Cr distance in the *o*-tolyl, 2.741(5) Å, and the magnetic moment (*ca.* 1.2 per Cr atom), which is higher than that of the trimethylsilylmethyl (0.9) but still well below the spin-only value for Cr^{II}, indicates a lower bond order for Cr–Cr interaction.

The *o*-tolyl bridge, CrC_2Cr, is unsymmetrical with Cr–C distances of 2.208(9) and 2.444(9) Å while the terminal Cr–C bond length is 2.09(1) Å and the Cr–P distance 2.510(5) Å.

The e.p.r. spectra of both orange and green compounds are not informative having overlapping signals centred at $g = 2.082$.

Tungsten. Both the compounds WR_4 (R = 2-MeC_6H_4 or 2,5-$Me_2C_6H_3$) have been made by interaction of the appropriate Grignard reagent with the hexaphenoxide $W(OPh)_6$ in tetrahydrofuran at 0 °C. Blue solutions are obtained from which, on work up, the crystalline aryls can be obtained in 10—15% yield. Similar arylation of WCl_6 in diethyl ether–tetrahydrofuran at −78 °C also gives blue solutions, but we have not been able readily to isolate the compounds in a pure state. Similar problems were encountered using lithium reagents.

The very air-sensitive compounds are paramagnetic with the magnetic moment, $\mu_{eff.} = 2.9$ (Evans' method in toluene), close to that for the spin-only value for two unpaired electrons, and similar to the values for Mo(2-$MeC_6H_4)_4$ and tetra(norbornyl)molybdenum (see ref. 3). The *X*-band e.p.r. spectrum of the *o*-tolyl at 293 K has a broad band at *ca.* $g = 2$ but in frozen toluene at 77 K has two signals with $g = 1.96$ and 2.30.

There are relatively few monomeric molecules of the type WX_4; examples with bulky aryl oxide ligands[14a] have an essentially planar WO_4 core attributed to the bulk of the ligands and also to π bonding, and are diamagnetic. The tetrabenzyl[14b] is also diamagnetic probably because of the postulated secondary interactions between the metal and the phenyl ring [*cf.* $Ti(CH_2Ph)_4$[14c]]. The present tungsten compounds are hence probably tetrahedral or slightly distorted tetrahedral like Mo(2-$MeC_6H_4)_4$.[3] We have been unable to obtain *X*-ray quality crystals of either compound.

Like those of the chromium tetra-aryl, reactions appear to be complicated and Bu^tNC, 2,6-$Me_2C_6H_3NC$, MeC≡CH, and hex-3-yne give brown solutions containing several products. The *o*-tolyl reacts with CO (30 lbf in^{-2}, *ca.* 2.07×10^5 Pa) at room temperature in toluene to give $W(CO)_6$ and the diaryl ketone essentially quantitatively (*cf.* interaction of WMe_6 and CO[15]).

Attempts to oxidise the compounds by use of silver salts and CuCl were unsuccessful, as were attempts to obtain oxo- or thio-aryls, WR_4X, X = O or S, by interaction with O_2, C_2H_4O, and S_8. Attempts to reduce the species using Li or sodium dihydronaphthylide in thf also failed. We were similarly unable to isolate cationic or anionic species from Mo(2-$MeC_6H_4)_4$[3] and so far the only $[MR_4]^+$ cations are those of osmium[3,4] and $[Mo(2,4,6\text{-}Me_3C_6H_2)_4]^+$, the latter being obtained as the triodide by iodine oxidation of Mo(2,4,6-$Me_3C_6H_2)_4$.[16]

Aryne Compounds of Molybdenum and Tungsten.—As noted above, Re(2-$MeC_6H_4)_4$ and PMe_3 or PMe_2Ph react under mild conditions to give toluene and the aryne species Re(η^2-2-MeC_6H_3)(2-$MeC_6H_4)_2(PR_3)_2$.[5a] The molybdenum tetra-*o*-tolyl[3] and both tungsten(IV) aryls described above react similarly with small tertiary phosphines, essentially quantitatively. The i.r. and n.m.r. spectra of all these aryne compounds are very similar.[5a,17]

The yields of the tungsten aryne complexes can be substantially increased by treating the initial blue solutions obtained from $W(OPh)_6$ directly with excess of phosphine, then passing the mixture through an alumina column (see Experimental section). Although Mo(2-$MeC_6H_4)_4$ reacts with PPr^i_3 on refluxing in toluene to give a brown solution, no pure product could be isolated; bulkier phosphines, PPh_3 and $P(C_6H_{11})_3$, do not react. Pyridine, NMe_3, Bu^tNC, and 2,6-$Me_2C_6H_3NC$ all gave mixtures of products for both Mo and W.

A tungsten aryne W(2-$MeC_6H_4)_4$(2-$MeC_6H_3)[Li(Et_2O)]_4$ has been previously characterised spectroscopically.[18]

The structures of Mo(η^2-2-MeC_6H_3)(2-$MeC_6H_4)_2(PMe_2Ph)_2$ and W(η^2-2,5-$Me_2C_6H_2$)(2,5-$Me_2C_6H_3)_2(PMe_3)_2$ are shown, respectively in Figures 2 and 3; bond lengths and angles are given in Tables 3 and 4. The structures are essentially equivalent, each molecule containing one π-bonded aryne [Mo–C 2.01, 2.06(1) Å, 'C≡C' 1.28(2); W–C 2.06(3), 2.10(2), 'C≡C' 1.43(3) Å] two σ-bonded aryls [Mo–C 2.12, 2.14(1); W–C 2.06, 2.16(2) Å], and two phosphines. The M–P bonds lie approximately in the same plane as the aryne ligand and if the latter is assumed to occupy only one co-ordination site the geometry at the metal centres can be described as distorted trigonal bipyramidal with the phosphines occupying the axial sites and the aryls in the other two equatorial sites. Notwithstanding this representation, and the rather different aryne 'C≡C' distances, the Mo–C and W–C distances coupled with the $^{13}C-\{^1H\}$ n.m.r. resonances favour a metallacyclopropenyl formulation for the aryne ligand, as for the isoelectronic cat-

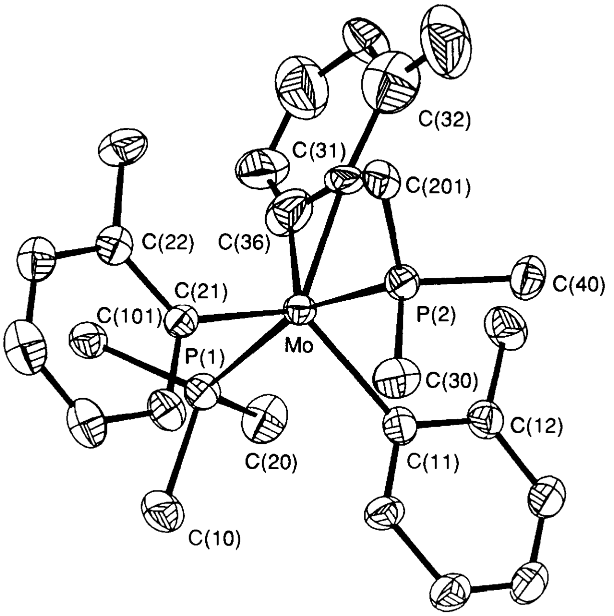

Figure 2. The structure of Mo(η^2-2-MeC_6H_3)(2-$MeC_6H_4)_2(PMe_2Ph)_2$. The remaining phenyl ring atoms at C(101) and C(201) on the phosphines have been omitted for clarity

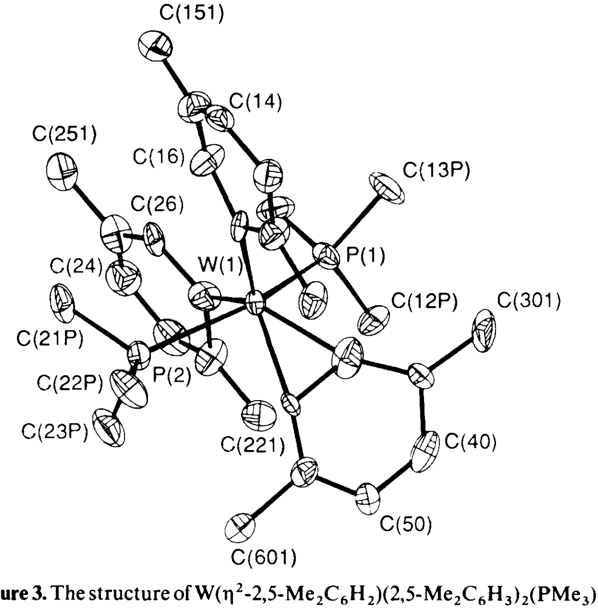

Figure 3. The structure of W(η^2-2,5-$Me_2C_6H_2$)(2,5-$Me_2C_6H_3)_2(PMe_3)_2$

Table 3. Selected bond lengths (Å) and angles (°) for Mo(η^2-2-MeC_6H_3)(2-MeC_6H_4)$_2$(PMe_2Ph)$_2$

P(1)–Mo	2.472(5)	P(2)–Mo	2.493(5)
C(11)–Mo	2.138(12)	C(21)–Mo	2.123(12)
C(31)–Mo	2.011(14)	C(36)–Mo	2.056(14)
C(32)–C(31)	1.522(19)	C(36)–C(31)	1.276(16)
C(33)–C(32)	1.417(18)	C(321)–C(32)	1.328(21)
C(34)–C(33)	1.443(18)	C(35)–C(34)	1.261(18)
C(36)–C(35)	1.595(19)		
P(2)–Mo–P(1)	161.1(1)	C(11)–Mo–P(1)	84.3(4)
C(11)–Mo–P(2)	82.9(4)	C(21)–Mo–P(1)	88.3(4)
C(21)–Mo–P(2)	86.9(4)	C(21)–Mo–C(11)	122.3(5)
C(31)–Mo–P(1)	111.7(5)	C(31)–Mo–P(2)	86.5(5)
C(31)–Mo–C(11)	115.7(5)	C(31)–Mo–C(21)	120.0(5)
C(36)–Mo–P(1)	75.2(5)	C(36)–Mo–P(2)	123.0(5)
C(36)–Mo–C(11)	115.5(5)	C(36)–Mo–C(21)	117.4(5)
C(36)–Mo–C(31)	36.6(4)	C(101)–P(1)–Mo	121.1(4)
C(10)–P(1)–Mo	114.4(5)	C(20)–P(1)–Mo	115.1(5)
C(201)–P(2)–Mo	121.5(4)	C(30)–P(2)–Mo	114.4(5)
C(40)–P(2)–Mo	115.0(5)	C(12)–C(11)–Mo	124.2(9)
C(16)–C(11)–Mo	118.7(8)	C(22)–C(21)–Mo	124.5(8)
C(26)–C(21)–Mo	117.9(8)	C(32)–C(31)–Mo	168.4(10)
C(36)–C(31)–Mo	73.6(9)	C(31)–C(36)–Mo	69.8(9)
C(35)–C(36)–Mo	159.6(9)	C(32)–C(31)–Mo	168.4(10)
C(36)–C(31)–Mo	73.6(9)	C(36)–C(31)–C(32)	118.0(13)
C(33)–C(32)–C(31)	112.7(13)	C(321)–C(32)–C(31)	121.7(15)
C(321)–C(32)–C(33)	125.6(15)	C(34)–C(33)–C(32)	122.5(13)
C(35)–C(34)–C(33)	129.9(15)	C(36)–C(35)–C(34)	106.4(13)
C(35)–C(36)–C(31)	130.2(11)		

Table 4. Selected bond lengths (Å) and angles (°) for W(η^2-2,5-$Me_2C_6H_2$)(2,5-$Me_2C_6H_3$)$_2$(PMe_3)$_2$

P(1)–W	2.464(8)	P(2)–W	2.467(8)
C(10)–W	2.105(21)	C(20)–W	2.056(27)
C(11)–W	2.065(23)	C(21)–W	2.167(25)
C(20)–C(10)	1.431(33)	C(60)–C(10)	1.410(32)
C(30)–C(20)	1.441(35)	C(40)–C(30)	1.478(39)
C(301)–C(30)	1.473(38)	C(50)–C(40)	1.470(43)
C(60)–C(50)	1.357(35)	C(601)–C(60)	1.504(39)
P(2)–W–P(1)	144.3(2)	C(10)–W–P(1)	108.8(7)
C(10)–W–P(2)	81.6(7)	C(20)–W–P(1)	76.0(8)
C(20)–W–P(2)	121.8(8)	C(20)–W–C(10)	40.2(9)
C(11)–W–P(1)	112.5(7)	C(11)–W–P(2)	88.0(6)
C(11)–W–C(10)	121.1(9)	C(11)–W–C(20)	116.8(11)
C(21)–W–P(1)	61.3(7)	C(21)–W–P(2)	83.1(7)
C(21)–W–C(10)	112.9(9)	C(21)–W–C(20)	115.4(11)
C(21)–W–C(11)	123.1(9)	C(11P)–P(1)–W	116.4(10)
C(12P)–P(1)–W	118.3(12)	C(13P)–P(1)–W	113.3(11)
C(21P)–P(2)–W	116.3(10)	C(22P)–P(2)–W	117.6(11)
C(23P)–P(2)–W	113.4(12)	C(20)–C(10)–W	68.1(14)
C(60)–C(10)–W	169.3(17)	C(30)–C(20)–W	161.7(22)
C(10)–C(20)–W	71.7(14)	C(12)–C(11)–W	120.7(16)
C(16)–C(11)–W	120.3(17)	C(22)–C(21)–W	124.4(19)
C(26)–C(21)–W	115.1(15)	C(20)–C(10)–W	68.1(14)
C(60)–C(10)–W	169.3(17)	C(60)–C(10)–C(20)	122.7(21)
C(30)–C(20)–C(10)	125.7(23)	C(40)–C(30)–C(20)	107.0(23)
C(301)–C(30)–C(20)	132.0(23)	C(301)–C(30)–C(40)	119.6(26)
C(50)–C(40)–C(30)	127.9(24)	C(60)–C(50)–C(40)	118.9(26)
C(50)–C(60)–C(50)	117.5(26)	C(601)–C(60)–C(10)	124.9(22)
C(601)–C(60)–C(50)	117.5(25)		

ionic rhenium complex,[5a] [Re(η^2-2-MeC_6H_3)(2-MeC_6H_4)$_2$-(PMe_3)$_2$]$^+$. In the context of the aryne formulation it is important to note that its definition is not very precise for the molybdenum complex where a final difference map showed significant residual electron density which could not, however, be incorporated into any recognisable disorder model. In particular, there did not seem to be any indication of the alternative orientation of the tolyl ligand.

The differing symmetry of the complexes arising out of the presence, respectively, of *o*-tolyl and *p*-xylyl ligands is reflected in the n.m.r. spectra. While the molybdenum complex has a ^{31}P-{^1H} spectrum with a doublet of doublets, the tungsten xylyl complex shows only a singlet; this equivalence is also evident in the solid state.

The cyclic voltammetric data for the arynes are given in Table 5. Attempts to reduce the solutions chemically failed, although interaction with silver salts ($CF_3SO_3^-$, PF_6^-, BF_4^-) in thf initially gave blue solutions that gradually became deep green due to reduction by solvent to starting material. Evaporation of the blue solutions in thf or MeCN gave blue oils that did not crystallise.

Experimental

The general methods and techniques are those described previously (see refs. 3 and 19). All operations were carried out under argon or dinitrogen or in vacuum. N.m.r. spectra are in p.p.m. *vs.* $SiMe_4$ or H_3PO_4 (external) and i.r. spectra (cm^{-1}) in Nujol mulls.

Tetrakis(2-*methylphenyl*)*chromium*(IV).—To $CrCl_3(thf)_3$[20] (1.91 g, 5.1 mmol) in Et_2O (*ca.* 50 cm^3) was added 4 equivalents of Li(2-MeC_6H_4) (2.0 g, 20.4 mmol) in Et_2O (40 cm^3) at −78 °C. The resulting deep purple solution was stirred for 2 h and allowed to warm to room temperature. After removal of solvent, the residue was extracted with hexane (3 × 40 cm^3) which was reduced in volume (to *ca.* 25 cm^3), filtered, and cooled to −20 °C to give deep purple crystals. Yield: *ca.* 20%. If the reaction mixture is kept at room temperature too long, the yield is substantially reduced and an intractable green product formed. The i.r. spectrum shows only bands for the aryl ligand.[1–4]

Tetrakis(2-*methylphenyl*)*tungsten*(IV).—To a stirred solution of $W(OPh)_6$[21] (5.0 g, 6.75 mmol) in thf (150 cm^3) at 0 °C was added 6 equivalents of MgBr(2-MeC_6H_4) (46.5 cm^3 of 0.87 mol dm^{-3} solution in thf) and the mixture stirred (6 h) at 0 °C. The blue solution was decanted from a colourless crystalline precipitate and evaporated under vacuum. The residue was extracted with hexane (2 × 300 cm^3) which was concentrated (to *ca.* 200 cm^3) and allowed to stand for 2 h while an amorphous beige material precipitated. The solution was filtered, concentrated to *ca.* 60 cm^3, and cooled to −20 °C for 24 h, to yield *ca.* 0.3 g of blue crystals; further concentration and cooling of the mother-liquor gave an additional 0.2 g product. Yield: 0.5 g, 13%.

Tetrakis(2,5-*dimethylphenyl*)*tungsten*(IV).—To $W(OPh)_6$ (3.0 g, 4.0 mmol) was added MgBr(2,5-$Me_2C_6H_3$) (54 cm^3 of 0.45 mol dm^{-3} solution in thf) at 0 °C; after stirring for 6 h the solution was brown with a large amount of colourless precipitate. After decantation and evaporation of the solution, the residue was extracted with hexane (2 × 200 cm^3) which was concentrated to *ca.* 300 cm^3, cooled for 3 h at −78 °C, and filtered cold. Further concentration to *ca.* 100 cm^3 and cooling at −20 °C gave a blue-brown powder that was recrystallised from hexane at −50 °C to give a blue powder. Yield: 0.1 g, 4%.

Chromium(II) o-*Tolyl Trimethylphosphine Complexes*.—(*a*) To a hexane (40 cm^3) solution of Cr(2-MeC_6H_4)$_4$ (0.2 g, 0.48 mmol) at −78 °C was added 1 equivalent of PMe_3 (1.0 cm^3 of a 0.5 mol dm^{-3} solution in hexane) and the mixture allowed to warm slowly to room temperature. Solvent was then removed under vacuum and bi-*o*-tolyl sublimed onto a cold probe at −70 °C. The residue was extracted into hexane (30 cm^3) which was concentrated to *ca.* 5 cm^3 and cooled (−20 °C) to give a low

Table 5. Cyclic voltammetry of $M(2\text{-}MeC_6H_4)_2(\eta^2\text{-}2\text{-}MeC_6H_3)L_2$ complexes

M	L	Solvent*	$E_{\frac{1}{2}}$/V	
			Oxidation	Reduction
Mo	PMe_3	MeCN	(+0.59)	−0.78, −2.34
W	PMe_3	MeCN	(+0.37) (+0.87)	−0.85, −2.5
W	PMe_3	CH_2Cl_2	(+0.51)	−0.90
W	PMe_2Ph	thf		−0.75

* Data on OE-PP2 instrument with 0.2 mol dm^{-3} $NBu^n{}_4PF_6$ as supporting electrolyte at 20 °C with platinum working, tungsten auxiliary, and silver pseudo-reference electrodes. Sweep rate 50 mV s^{-1}. Values in parentheses indicate one-electron irreversible processes (E_p), reference ferrocene–ferrocenium (0.00 V).

Table 6. Crystal data, details of intensity measurements and structure refinement*

Molecular Formula	$C_{68}H_{92}Cr_2P_2$	$C_{37}H_{30}MoP_2$	$C_{30}H_{44}P_2W$
M	667.044	632.533	650.477
a/Å	14.487(10)	10.248(6)	14.702(2)
b/Å	14.231(7)	29.941(2)	12.120(5)
c/Å	17.403(9)	10.740(5)	17.309(4)
β/°	104.59(5)	91.23(6)	99.61(2)
U/Å^3	3 427.33	3 294.65	3 040.98
Space group	*C*2/*c*	*P*2$_1$/*n*	*C*2
D_c/g cm^{-3}	1.276	1.275	1.421
μ/cm^{-1}	6.28	4.53	39.98
F(000)	1 496	1 296	1 312
h, k, l range	0—15	0—11	0—17
	0—15	0—11	0—14
	−19 to 19	−32 to 32	−20 to 20
Total no. of reflections	2 716	9 725	3 075
No. of unique reflections	2 408	4 573	2 815
No. of observed reflections	1 634	3 096	2 016
σ test	[$F > 3\sigma(F)$]	[$F > 6\sigma(F)$]	[$F > 3\sigma(F)$]
No. of parameters	226	355	297
Weighting scheme parameter *g* in $w = 1/[\sigma^2(F) + gF_o{}^2]$	0.003	0.002	0.008
Final *R*	0.0732	0.0673	0.0450
Final *R*′	0.0781	0.0662	0.0488

* Details in common: monoclinic; α = γ = 90°; *Z* = 4.

yield (<5%) of deep green crystals (m.p. 86 °C) of $[Cr(2\text{-}MeC_6H_4)(\mu\text{-}2\text{-}MeC_6H_4)(PMe_3)]_2$ which were collected; the remainder of the brown solution gave an oil which could not be purified or crystallised but contains $Cr(2\text{-}MeC_6H_4)_2(PMe_3)_2$.

(*b*) To a stirred solution of $Cr_2(O_2CMe)_4$ (0.2 g, 0.74 mmol) in thf (30 cm^3) at 0 °C was added PMe_3 (0.3 cm^3, 2.9 mmol) followed by 4 equivalents of $MgBr(2\text{-}MeC_6H_4)$ (3.4 cm^3 of a 0.87 mol dm^{-3} solution in thf) added dropwise. After warming to room temperature and stirring overnight the solution was evaporated and the brown residue extracted with hexane (1 × 30 cm^3) which was filtered, concentrated (to 10 cm^3), and cooled (−20 °C) to give green crystals of $[Cr(2\text{-}MeC_6H_4)(\mu\text{-}2\text{-}MeC_6H_4)(PMe_3)]_2$ (18 mg, 4%) and orange crystalline aggregates of $Cr(2\text{-}MeC_6H_4)_2(PMe_3)_2$ (18 mg, 7%) that were separated manually.

Molybdenum and Tungsten Aryne Compounds.—$Mo(\eta^2\text{-}2\text{-}MeC_6H_3)(2\text{-}MeC_6H_4)_2(PMe_3)_2$. To a solution of $Mo(2\text{-}MeC_6H_4)_4$[3] (0.83 g, 1.8 mmol) in toluene (30 cm^3) at −78 °C was added PMe_3 (0.4 cm^3, 3.8 mmol) and the solution allowed to warm; reaction to give a turquoise colour began at *ca.* −30 °C. After stirring (1 h) the solution was evaporated and the green solid extracted with warm hexane (3 × 20 cm^3). The filtered solution was concentrated (20 cm^3) and cooled (−20 °C) to give dark green crystals. Yield: 0.91 g, 97%. Mass spectrum (electron impact, e.i.): *m*/*z* 522 (522), M^+; 446 (446), $M^+ - PMe_3$; and 370 (370), $M^+ - 2PMe_3$. I.r.: 3 039m, 3 021m, 1 561vs, 1 544w, 1 438s (sh), 1 429m, 1 413m, 1 399m, 1 322w, 1 296m, 1 279m, 1 243m, 1 182w, 1 041m, 1 020s, 1 002w, 981m, 941vs, 848m, 817w, 786m, 761s, 710s, 665m, 639m, 547w, and 442m cm^{-1}. N.m.r. (C_6D_6, 26 °C): $^{31}P\text{-}\{^1H\}$, δ 7.09, 16.98 (AB quartet, *J* = 97.5); $^{13}C\text{-}\{^1H\}$, δ 15.91 (d, J_{PC} = 22.0, PMe_3), 16.49 (d, J_{PC} = 21.0, PMe_3), 24.82 (s, $2\text{-}MeC_6H_3$), 26.19 (s, $2\text{-}MeC_6H_4$), 120.27 (d, J_{PC} = 2.5, $2\text{-}MeC_6H_4$), 122.19 (d, J_{PC} = 2.0, $2\text{-}MeC_6H_4$), 125.95 (dd, J_{PC} = 7.4, 3.6, $2\text{-}MeC_6H_3$), 126.17 (t, J_{PC} = 3.6, $2\text{-}MeC_6H_4$), 128.52 (d, J_{PC} = 2.5, $2\text{-}MeC_6H_4$), 130.26 (s, $2\text{-}MeC_6H_3$), 130.49 (d, J_{PC} = 2.5, $2\text{-}MeC_6H_4$), 133.86 (d, J_{PC} = 2.4, $2\text{-}MeC_6H_3$), 138.46 (t, J_{PC} = 3.5, $2\text{-}MeC_6H_3$), 176.26 (dd, J_{PC} = 29.0, 6.0, $2\text{-}MeC_6H_3$, aryne C), 178.26 (dd, J_{PC} = 38.0, 6.0, $2\text{-}MeC_6H_3$, aryne C), and 207.37 ('t', 'J_{PC} = 12.0 Hz', $2\text{-}MeC_6H_4$, *ipso*-C).

$Mo(\eta^2\text{-}2\text{-}MeC_6H_3)(2\text{-}MeC_6H_4)_2(PMe_2Ph)_2$. From PMe_2Ph (0.57 cm^3, 4.0 mmol) and $Mo(2\text{-}MeC_6H_4)_4$ (0.87 g, 1.89 mmol). Work-up gave dark green crystals. Yield: 1.19 g (97%). Mass spectrum (e.i.): *m*/*z* 646 (646), M^+; 508 (508), $M^+ - PMe_2Ph$; 370 (370), $M^+ - 2PMe_2Ph$. I.r.: 3 087m, 3 056m, 1 577m, 1 562vs, 1 544m, 1 488m, 1 450vs, 1 434vs, 1 418s, 1 326m, 1 290s, 1 274m, 1 242m, 1 181m, 1 151m, 1 101m, 1 075m, 1 040m, 1 021s, 1 004s, 981m, 941vs, 907vs, 867m, 836m, 785m, 767s, 746s, 737vs, 699s, 669m, 637m, 551m, 445m, 422m, and

Table 7. Fractional atomic co-ordinates (× 10^4) for $[Cr(2\text{-}MeC_6H_4)(\mu\text{-}2\text{-}MeC_6H_4)(PMe_3)]_2$

Atom	*x*	*y*	*z*
Cr(1)	4 509(1)	1 735(1)	3 078(1)
P(1)	2 855(2)	1 504(2)	3 250(1)
C(11)	3 982(5)	1 374(6)	1 787(4)
C(12)	3 943(6)	406(6)	1 622(5)
C(13)	3 167(8)	29(7)	1 024(6)
C(14)	2 476(7)	572(8)	581(6)
C(15)	2 525(6)	1 484(9)	767(6)
C(16)	3 241(5)	1 945(6)	1 337(4)
C(161)	3 251(7)	2 979(6)	1 449(5)
C(31)	4 808(6)	2 284(7)	4 229(5)
C(32)	4 617(7)	3 241(9)	4 365(7)
C(33)	4 714(8)	3 660(12)	5 169(8)
C(34)	5 011(8)	2 941(13)	5 726(9)
C(35)	5 213(9)	2 084(14)	5 688(8)
C(36)	5 128(7)	1 684(10)	4 906(5)
C(321)	4 335(8)	3 864(9)	3 734(8)
C(10A)	2 689(13)	1 258(18)	4 221(10)
C(20A)	2 133(13)	604(14)	2 634(12)
C(30A)	1 996(11)	2 464(14)	2 894(12)
C(20B)	1 832(20)	1 512(25)	2 573(18)
C(30B)	2 651(14)	1 951(15)	4 159(12)
C(10B)	2 894(22)	204(22)	3 574(21)

All occupancies 1.0 except: C(10A), 0.650; C(10B), 0.350; C(20A), 0.653; C(20B), 0.347; C(30A), 0.602; C(30B), 0.398.

406m cm^{-1}. $^{31}P\text{-}\{^1H\}$ N.m.r.: δ 22.17, 24.58 (AB quartet, $J = 91$ Hz).

$W(\eta^2\text{-}2\text{-}MeC_6H_3)(2\text{-}MeC_6H_4)_2(PMe_3)_2$. From $W(2\text{-}MeC_6H_4)_4$ (0.27 g, 0.49 mmol) in hexane (30 cm^3) and PMe_3 (0.15 cm^3, 1.6 mmol), at ambient temperature. The solution was evaporated, extracted with hexane (30 cm^3) which was filtered, reduced to 15 cm^3, and allowed to stand to give green crystals. Yield: 94%. The aryne may also be recovered by addition of excess of PMe_3 to $W(2\text{-}MeC_6H_4)_4$ made *in situ*; the brown-green solution was transferred to an alumina column and eluted with toluene. Mass spectrum (e.i.): *m/z* 608 (608), M^+; other peaks due to loss of PMe_3. N.m.r.: ^1H, δ 0.49 (s, 6 H, 2-MeC_6H_4), 1.31 (d, 9 H, $J_{PH} = 7.7$, PMe_3), 1.33 (d, 9 H, $J_{PH} = 7.7$, PMe_3), 2.58 (s, 3 H, 2-MeC_6H_4), 6.57 (t, 2 H, $J = 7.8$, 2-MeC_6H_4), 6.96 (m, 4 H, 2-MeC_6H_4), 7.05 (d, 1 H, $J = 6.5$, MeC_6H_3), 7.19 (m, 3 H, 2-MeC_6H_4), and 8.05 (m, 1 H, MeC_6H_3); $^{13}C\text{-}\{^1H\}$, δ 17.35 (d, $J_{PC} = 25.7$), 18.25 (d, $J_{PC} = 24.4$, PMe_3), 25.1 (s, 2-MeC_6H_3), 26.2 (s, 2-MeC_6H_4), 120 (s, 2-MeC_6H_4), 122.9 (s, 2-MeC_6H_4), 127 (s, 2-MeC_6H_4), 130 (s, 2-MeC_6H_4), 131.1 (d, $J_{PC} = 34.4$, 2-MeC_6H_4), 134.3 (s, 2-MeC_6H_3), 139 (s, 2-MeC_6H_3), 185.1 (d, $J_{PC} = 25.4$, 2-MeC_6H_3), 186.5 (d, $J_{PC} = 29.4$, 2-MeC_6H_3), and 211 (t, $J_{PC} = 9$ Hz, 2-MeC_6H_3); $^{31}P\text{-}\{^1H\}$, δ 5.3 (d, $J_{PP} = 77.6$); and 12.9 (d, J_{PP} 77.5 Hz).

$W(\eta^2\text{-}2\text{-}MeC_6H_3)(2\text{-}MeC_6H_4)_2(PMe_2Ph)_2$. From $W(2\text{-}MeC_6H_4)_4$ (0.2 g, 0.37 mmol) and PMe_2Ph (0.1 cm^3, 0.74 mmol) in toluene at room temperature. Work-up as before gave dark green crystals. Yield: 0.24 g, 89%. N.m.r.: ^1H, δ 0.5 (s, 6 H, 2-MeC_6H_4), 1.55 (d, 6 H, $J_{PH} = 7.2$, PMe_2Ph), 1.66 (d, 6 H, $J_{PH} = 7.9$, PMe_2Ph), 2.21 (s, 3 H, 2-MeC_6H_3), and 6.55—8.01 (aromatic H); $^{31}P\text{-}\{^1H\}$, δ 10.8 (d, $J_{PP} = 75$, PMe_2Ph); and 18.1 (d, $J_{PP} = 75$ Hz, PMe_2Ph).

Table 8. Fractional atomic co-ordinates (× 10^4) for $Mo(\eta^2\text{-}2\text{-}MeC_6H_3)(2\text{-}MeC_6H_4)_2(PMe_2Ph)_2$

Atom	*x*	*y*	*z*
Mo	1 015(1)	1 495.3(4)	414(1)
P(1)	−25(4)	1 504(2)	−1 684(4)
P(2)	2 546(4)	1 665(1)	2 188(4)
C(11)	978(15)	2 206(5)	236(14)
C(12)	6(16)	2 492(6)	787(14)
C(13)	104(19)	2 959(6)	690(15)
C(14)	1 117(19)	3 156(6)	27(17)
C(15)	2 060(18)	2 892(6)	−518(15)
C(16)	1 981(16)	2 418(5)	−414(14)
C(21)	2 533(14)	1 099(5)	−324(13)
C(22)	2 621(15)	625(5)	−204(14)
C(23)	3 677(17)	389(6)	−732(16)
C(24)	4 643(17)	615(8)	−1 362(17)
C(25)	4 570(16)	1 072(7)	−1 519(15)
C(26)	3 520(15)	1 318(6)	−981(14)
C(121)	−1 143(17)	2 290(7)	1 479(17)
C(221)	1 583(18)	358(6)	472(18)
C(102)	428(9)	657(4)	−2 618(10)
C(103)	91(9)	253(4)	−3 184(10)
C(104)	−1 191(9)	177(4)	−3 593(10)
C(105)	−2 137(9)	506(4)	−3 435(10)
C(106)	−1 800(9)	911(4)	−2 869(10)
C(101)	−518(9)	986(4)	−2 461(10)
C(202)	2 993(10)	1 233(3)	4 487(9)
C(203)	3 506(10)	894(3)	5 242(9)
C(204)	4 212(10)	546(3)	4 717(9)
C(205)	4 406(10)	537(3)	3 436(9)
C(206)	3 894(10)	876(3)	2 680(9)
C(201)	3 187(10)	1 224(3)	3 205(9)
C(10)	972(18)	1 748(7)	−2 883(14)
C(20)	−1 456(16)	1 850(6)	−1 838(18)
C(30)	4 080(15)	1 915(6)	1 734(17)
C(40)	1 973(19)	2 073(6)	3 263(15)
C(31)	−176(17)	1 237(6)	1 692(18)
C(32)	−867(23)	1 074(8)	2 847(21)
C(33)	−2 134(19)	906(6)	2 575(17)
C(34)	−2 668(21)	881(8)	1 323(21)
C(35)	−2 201(20)	1 016(7)	313(19)
C(36)	−769(17)	1 196(6)	640(17)
C(321)	−293(24)	1 086(8)	3 967(23)

$W(\eta^2\text{-}2,5\text{-}Me_2C_6H_2)(2,5\text{-}Me_2C_6H_3)_2(PMe_3)_2$. To a stirred solution of $W(OPh)_6$ (2.0 g, 2.7 mmol) in thf at 0 °C was added $MgBr(2,5\text{-}Me_2C_6H_3)$ (36 cm^3 of 0.45 mol dm^{-3} thf solution). After stirring for 6 h at 0 °C the solution was filtered, evaporated, and the brown residue dissolved in toluene (50 cm^3) to which PMe_3 (1.0 cm^3) was added. After stirring for 2 h the green solution was transferred to a short alumina column and the product eluted with toluene (40 cm^3); evaporation and crystallisation of the residue from hexane gave green crystals. Yield: 0.5 g, 28% based on $W(OPh)_6$. N.m.r.: ^1H, δ 0.78 (s, 6 H, 2,5-$Me_2C_6H_3$), 1.47 (t, 18 H, $J_{PH} = 3.6$, PMe_3), 2.44 (s, 6 H, 2,5-$Me_2C_6H_3$), 2.79 (s, 6 H, 2,5-$Me_2C_6H_2$), 6.46 (d, 2 H, $J_{HH} = 7.3$, 2,5-$Me_2C_6H_3$), 6.91 (s, 2 H, 2,5-$Me_2C_6H_2$), 6.99 (d, 2 H, $J_{HH} = 7.4$ Hz, 2,5-$Me_2C_6H_3$), and 7.24 (s, 2 H, 2,5-$Me_2C_6H_2$), $^{31}P\text{-}\{^1H\}$, δ 4.8 (s, PMe_3).

$W(\eta^2\text{-}2,5\text{-}Me_2C_6H_2)(2,5\text{-}Me_2C_6H_3)_2(PMe_2Ph)_2$. As above but using PMe_2Ph to give green crystals. Yield: 0.42 g, 20%. N.m.r.: ^1H, δ 0.88 (s, 6 H, 2,5-$Me_2C_6H_3$), 1.68 (t, 12 H, $J_{PH} = 7.0$, PMe_2Ph), 2.05 (s, 6 H, 2,5-$Me_2C_6H_3$), 2.28 (s, 6 H, 2,5-$Me_2C_6H_2$), 6.34 (s, 2 H, 2,5-$Me_2C_6H_3$), 6.41 (d, 2 H, $J_{HH} = 7.0$ Hz, 2,5-$Me_2C_6H_3$), and 6.91—7.13 (24 H, aromatic H); $^{31}P\text{-}\{^1H\}$, δ 11.2 (s, PMe_2Ph).

X-*Ray Crystallography*.—Measurements for all compounds were made on crystals sealed under argon in thin-walled glass capillaries. Cell dimensions and intensity data were measured using standard procedures and software on an Enraf–Nonius CAD4 diffractometer operating with graphite-monochromated Mo-K_α radiation in the ω—2θ scan mode.[22] Intensity data were corrected for absorption empirically and the structures solved *via* Patterson methods. Refinements were accomplished by full-

Table 9. Fractional atomic co-ordinates (× 10^4) for $W(\eta^2\text{-}2,5\text{-}Me_2C_6H_2)(2,5\text{-}Me_2C_6H_3)_2(PMe_3)_2$

Atom	*x*	*y*	*z*
W	2 400.2(4)	0	2 266.9(4)
P(1)	4 013(4)	570(5)	2 285(4)
P(2)	1 000(4)	351(5)	2 841(3)
C(10)	1 573(14)	686(15)	1 273(11)
C(20)	2 459(16)	357(26)	1 115(15)
C(30)	2 744(18)	369(22)	358(15)
C(40)	1 975(23)	847(26)	−201(15)
C(50)	1 090(20)	1 268(23)	−36(16)
C(60)	895(18)	1 169(19)	700(14)
C(11P)	4 194(19)	1 767(18)	1 675(14)
C(12P)	4 700(20)	983(29)	3 224(19)
C(13P)	4 756(18)	−557(25)	2 055(22)
C(21P)	1 085(16)	75(43)	3 866(14)
C(22P)	−67(18)	−326(22)	2 385(21)
C(23P)	691(24)	1 875(28)	2 871(22)
C(301)	3 511(23)	−179(24)	60(16)
C(601)	−23(19)	1 592(24)	846(16)
C(11)	2 287(14)	−1 644(17)	2 550(11)
C(12)	1 910(15)	−2 421(18)	1 971(12)
C(13)	1 941(20)	−3 627(22)	2 141(15)
C(14)	2 250(15)	−3 977(15)	2 942(14)
C(15)	2 691(22)	−3 167(22)	3 507(16)
C(16)	2 677(23)	−2 035(20)	3 305(15)
C(121)	1 486(19)	−2 129(22)	1 131(14)
C(151)	3 103(25)	−3 542(27)	4 300(19)
C(21)	2 994(16)	1 235(15)	3 108(16)
C(22)	3 030(19)	2 456(20)	2 934(14)
C(23)	3 373(17)	3 153(24)	3 602(21)
C(24)	3 605(18)	2 706(28)	4 397(19)
C(25)	3 525(18)	1 620(21)	4 499(18)
C(26)	3 205(15)	852(20)	3 926(12)
C(221)	2 742(21)	2 849(21)	2 098(18)
C(251)	3 758(20)	1 155(29)	5 360(18)

matrix least squares with anisotropic displacement factors for all non-hydrogen atoms. All three structures showed varying levels of disorder in the aryl ligands and it was therefore considered inappropriate to add hydrogen atoms in the final refinements. Disorder also occurs in the orientations of the trimethylphosphine groups where methyl occupancies range from 0.347 to 0.653. Refinement of an inverted set of co-ordinates for the tungsten structure gave *R* and *R′* values of 0.0523 and 0.0634, respectively, confirming the original assignment. The phenyl rings of the phosphine in the molybdenum complex were treated as idealised hexagons and refined as rigid groups. Standard weighting schemes were applied to give acceptable agreement analyses. Details of the crystal data and experimental parameters are given in Table 6. Fractional atomic co-ordinates are listed in Tables 7—9.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank the S.E.R.C. for a studentship (to B. McG.) and *X*-ray facilities and the National Science Foundation, Washington D.C., for a N.A.T.O. Fellowship (G. McD.).

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Received 31*st May* 1990; *Paper* 0/02443K