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CARBON–CARBON BOND FORMATION IN REACTIONS BETWEEN TOLYLMETHYLIDYNE(DICARBONYL)(CYCLOPENTADIENYL)TUNGSTEN AND ORGANO-CHROMIUM OR -ZINC COMPOUNDS

JOHN C. JEFFERY, ANDREW L. RATERMANN, and F. GORDON A. STONE

Department of Inorganic Chemistry, The University of Bristol, Bristol BS8 1TS (Great Britain)

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Summary

Treatment of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ with $[CrPh_3(thf)_3]$ (thf = tetrahydrofuran) or $ZnPh_2$ affords the η^3-tolyl(phenyl)benzyl complex $[W(CO)_2\{\eta^3\text{-}CH(C_6H_4Me\text{-}4)Ph\}(\eta\text{-}C_5H_5)]$, identified by an X-ray diffraction study as a species in which the tungsten atom is π-complexed to carbon atoms 1,2,7 of the CHC_6H_4Me-4 group. Similar compounds are obtained from the tolylmethylidyne tungsten complex and the di-organozinc reagents $ZnPr^i_2$ or $Zn(CH_2C_6H_4Me\text{-}4)_2$. However, diethylzinc affords a trimetal complex $[Zn\{W(CO)_2(\eta\text{-}MeCH:CHC_6H_4Me\text{-}4)(\eta\text{-}C_5H_5)\}_2]$, which in the presence of traces of water yields $[W(CO)_2\{\eta^3\text{-}CH(C_6H_4Me\text{-}4)Et\}(\eta\text{-}C_5H_5)]$. Possible modes of formation of the products are discussed.

Introduction

The studies described herein were prompted by the observation that when the complex $[W(\equiv C_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ [1] is used to prepare heteronuclear metal cluster compounds [2,3], the ditungsten species $[W_2\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ is sometimes produced as a by-product [4,5]. Indeed, treatment of the tolylmethylidynetungsten compound with $[Cr_2(CO)_4(\eta\text{-}C_5H_5)_2]$ affords the alkyne–ditungsten complex quantitatively [4]. The observed dimerisation of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ raises the interesting possibility that in a reaction with a suitable transition metal complex the tungsten species might trimerise or form higher oligomers. With this possibility in mind, the reaction between $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ and $[CrPh_3(thf)_3]$ (thf = tetrahydrofuran) was investigated. The chromium compound is known to react with diphenyl acetylene to afford a mixture of products, including hexaphenylbenzene and tetraphenylnaphthalene [6]. It was hoped that a corresponding reaction with $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ would produce cyclic polynuclear tungsten compounds containing W=C units, with possible incorporation of phenyl groups from chromium into

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the final product. In practice, as described below, the reaction followed a different course, and this is turn prompted studies involving the tolylmethylidyne tungsten complex and various di-organozinc compounds.

Results and discussion

Addition of solid $[CrPh_3(thf)_3]$ to $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ dissolved in tetrahydrofuran at room temperature, followed by chromatography of the mixture, afforded a red crystalline compound I. Microanalysis and the mass spectrum (Table 1) indicated that this product was a mononuclear rather than a polynuclear tungsten species. The ^1H and ^{13}C $\{^1H\}$ NMR spectra were complex and could not be satisfactorily analysed. In Table 2 only the major signals observed are listed for what appeared to be a dominant isomer. Since the data for I did not resolve the nature of this compound a single-crystal X-ray diffraction study was carried out.

The results of the X-ray work showed that I was a 1,2,7-η^3-tolylbenzyltungsten complex with a phenyl substituent at C^1 (C(21) in Fig. 1). The solution of the structure was hampered by a disorder problem (see Experimental). However, the overall molecular geometry is unambiguously established and selected bond distances and angles are listed in Table 3. The structure is closely related to that previously found for the compound $[Mo(CO)_2(\eta^3\text{-}CH_2C_6H_4Me\text{-}4)(\eta\text{-}C_5H_5)]$ [7]. In I the tungsten atom is η^3-coordinated to the three carbon atoms C(21), C(28) and C(29), and thus in the solid state the phenyl group is not bonded to the metal.

Compound I belongs to a class of tungsten and molybdenum complex first reported by King and Fronzaglia [8], and subsequently studied in more detail by Cotton and Marks [7] using both X-ray analysis and dynamic NMR spectroscopy. The latter technique showed that in these compounds the $M(CO)_2(\eta\text{-}C_5H_5)$ (M = Mo

TABLE 1

ANALYTICAL AND OTHER DATA

Compound	Colour	Yield [a]	$\nu_{max}(CO)$ [b] (cm^{-1})	Found (calcd.) (%) C	H	M [c]
$[W(CO)_2(\eta^3\text{-}PhCHC_6H_4Me\text{-}4)(\eta\text{-}C_5H_5)]$ (I)	Red	42	1950, 1878	51.4 (51.9)	3.6 (3.7)	486 (486)
$[W(CO)_2(\eta^3\text{-}Pr^iCHC_6H_4Me\text{-}4)(\eta\text{-}C_5H_5)]$ (II)	Red	55	1946, 1871	48.6 (47.8)	4.8 (4.5)	452 (452)
$[W(CO)_2(\eta^3\text{-}4\text{-}MeC_6H_4CH_2CHC_6H_4Me\text{-}4)(\eta\text{-}C_5H_5)]$ (III)	Orange	47	1948, 1867	54.9 (53.7)	4.5 (4.3)	514 (514)
$[Zn\{W(CO)_2(\eta\text{-}MeCH{=}CHC_6H_4Me\text{-}4)(\eta\text{-}C_5H_5)\}_2]$ (IV)	Yellow	72	1867, 1811 [d]	43.5 (43.5)	3.6 (3.7)	
$[W(CO)_2(\eta^3\text{-}EtCHC_6H_4Me\text{-}4)(\eta\text{-}C_5H_5)]$ (V)	Red	90 [e]	1946, 1871	46.6 (46.6)	4.1 (4.2)	438 (438)

[a] Based on $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ used. [b] Measured in light petroleum, unless otherwise stated. [c] Parent ion in mass spectrum. [d] Measured in Nujol. [e] Based on IV used.

TABLE 2

NMR DATA[a]

Compound	^{1}H (δ)[b]	^{13}C (δ)[c]
I[d]	2.30 (s, Me-4), 3.29 (br), 5.45 (s, C_5H_5), 6.53–7.40 (m, br).	231.7, 231.4 (CO), 146.3–121.8 (C_6H_4 and Ph), 99.8 [$C^1(C_6H_4Me$-4)], 90.2 (C_5H_5), 67.0 [$C^2(C_6H_4Me$-4)], 39.7 (CH), 20.0 (Me-4).
II	1.23 [d, 6 H, Me, *J*(HH) 7], 1.68 [d, 1 H, CH, *J*(HH) 6], 2.28 (s, 3 H, Me-4), 2.58 (m, 1 H, $\mathrm{C}\mathit{H}\mathrm{Me}_2$), 4.69 [d, 1 H, $HC^2(C_6H_4Me$-4), *J*(HH) 5], 5.41 (s, 5 H, C_5H_5), 6.94 (m, 3 H, C_6H_4).	
III	2.13 [d of d, 1 H, CH, *J*(HH) 7, 7] 2.28 (s, 3 H, Me-4), 2.33 (s, 3 H, Me-4), 3.7 [br m, 2 H, CH_2] 4.79 [d, 1 H, $HC^2(C_6H_4Me$-4), *J*(HH) 7], 5.22 (s, 5 H, C_5H_5), 6.64–7.29 (m, 7 H, C_6H_4).	232.5, 230.8 (CO), 139.9–125.0 (C_6H_4), 101.3 [$C^1(C_6H_4Me$-4)], 89.5(C_5H_5), 63.2 [$C^2(C_6H_4Me$-4)], 37.7, 37.1 (CH_2 and CH), 19.9 (Me-4).
IV[e]	1.96 [d, 3 H, $\mathrm{CH}\mathit{Me}$, *J*(HH) 6], 2.28 (s, 3 H, Me-4), 3.62 [d of q, 1 H, $\mathrm{C}\mathit{H}\mathrm{Me}$, *J*(HH) 6, 12], 3.96 [d, 1 H, $\mathrm{C}\mathit{H}\mathrm{C_6H_4Me}$-4, *J*(HH) 12], 5.14 (s, 5 H, C_5H_5), 7.06 (m, 4 H, C_6H_4)	226.3 [CO, *J*(WC) 165], 222.8 [CO, *J*(WC) 160], 132.0, 130.1, 129.4, 126.0 (C_6H_4), 91.7 (C_5H_5), 53.5 ($\mathrm{C}\mathit{H}\mathrm{C_6H_4Me}$-4), 37.8 ($\mathit{C}\mathrm{HMe}$), 23.1 ($\mathrm{CH}\mathit{Me}$), 21.4 (Me-4).
V[f]	1.13 [d of d, 3 H, $\mathrm{CH_2}\mathit{Me}$, *J*(HH) 7, 7], 1.89 [d of d, 1 H, $\mathrm{C}\mathit{H}\mathrm{Et}$, *J*(HH) 6, 8], 2.20 (m, 1 H, CH_2), 2.21 (s, 3 H, Me-4), 2.51 (m, 1 H, CH_2), 4.70 [d, 1 H, $HC^2(C_6H_4Me$-4), *J*(HH) 6], 5.42 (s, 5 H, C_5H_5), 6.63 [d, 1 H, C_6H_4, *J*(HH) 9], 6.68 [d, 1 H, C_6H_4, *J*(HH) 6], 6.94 [d, 1 H, C_6H_4, *J*(HH) 9].	232.5 [CO, *J*(WC) 182], 230.6 [CO, *J*(WC) 167], 131.9, 131.3, 129.5, 126.3 [$C^{3\text{-}6}(C_6H_4Me$-4)], 101.4[$C^1(C_6H_4Me$-4)], 89.5 (C_5H_5), 62.7 [$C^2(C_6H_4Me$-4)], 39.0 (CH), 24.5 (CH_2), 20.0 (Me-4), 15.7 ($\mathrm{CH_2}\mathit{Me}$).

[a] Chemical shifts (δ) in ppm, coupling constants in Hz. Measurements at room temperature, unless otherwise stated. [b] Measured in CD_2Cl_2 unless otherwise stated. [c] Hydrogen-1 decoupled, chemical shifts positive to high frequency of $SiMe_4$, measured in CD_2Cl_2, unless otherwise stated, with [Cr(acac)$_3$] added. [d] Isomers present, data for major isomer listed (see text). [e] Carbon-13 spectrum measured at −40°C in thf/thf-d_8. [f] Hydrogen-1 spectrum measured at −30°C.

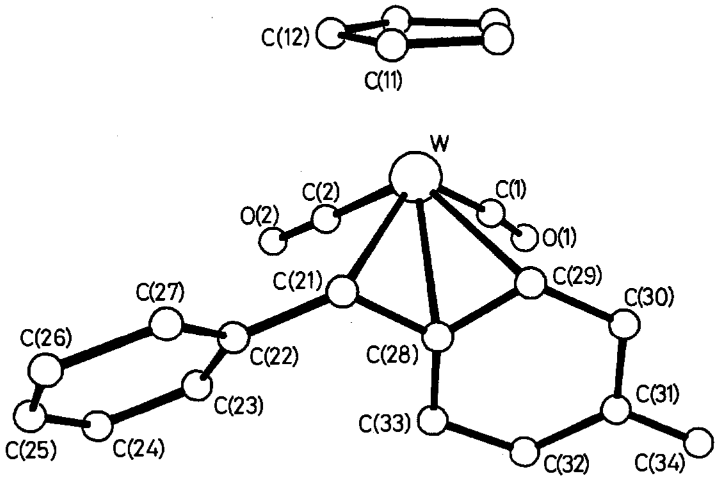


Fig. 1. Molecular structure of $[W(CO)_2\{\eta^3\text{-}CH(C_6H_4Me\text{-}4)Ph\}(\eta\text{-}C_5H_5)]$ (I), showing the atom numbering scheme.

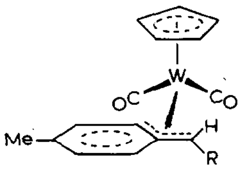
or W) fragment has access to four equivalent positions of attachment to the benzyl group. The situation with I is further complicated by the presence of the phenyl group. It is possible that in solution there might be an isomer of I with the tungsten atom η^3-bonded to the CHC_6H_5 group in contrast with the $\eta^3\text{-}CHC_6H_4Me\text{-}4$ attachment found in the solid state by the X-ray analysis. In view of this, and the earlier work [7] on the compounds $[M(CO)_2(\eta^3\text{-}CH_2C_6H_4Me\text{-}4)(\eta\text{-}C_5H_5)]$ (M = Mo or W), it is not surprising that, as mentioned above, the ^1H and $^{13}C\ \{^1H\}$ NMR spectra were complicated, suggesting the presence of more than one configuration for the molecule under the conditions of measurement.

It is interesting to speculate on the mode of formation of I, since the overall process results in reduction of a C≡W bond to a single bond, as well as C–C bond formation involving a phenyl group derived from $[CrPh_3(thf)_3]$ [9]. Studies on the reaction of the latter with alkynes suggest that the initial step involves alkyne-insertion into a carbon–chromium bond to produce an intermediate ‘vinylchromium’ reagent [10]. If this pathway were followed in the reaction with $[W(\equiv CC_6H_4Me\text{-}$

TABLE 3

SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR $[W(CO)_2\{\eta^3\text{-}CH(C_6H_4Me\text{-}4)Ph\}(\eta\text{-}C_5H_5)]$ (I)

W–C(1)	1.89(3)	W–C(2)	1.83(4)	W–C(21)	2.32(3)
W–C(28)	2.35(3)	W–C(29)	2.41(3)	C(21)–C(28)	1.48(4)
C(28)–C(29)	1.40(5)	C(29)–C(30)	1.53(5)	C(30)–C(31)	1.37(5)
C(31)–C(32)	1.43(5)	C(32)–C(33)	1.44(4)	C(33)–C(28)	1.48(5)
C(1)–O(1)	1.21(4)	C(2)–O(2)	1.23(5)		
C(1)–W–C(2)	79(1)	C(1)–W–C(29)	83(1)	C(2)–W–C(21)	87(1)
C(22)–C(21)–C(28)	129(3)	C(21)–C(28)–C(29)	116(3)	C(21)–C(28)–C(33)	121(3)
C(29)–C(28)–C(33)	123(3)	C(28)–C(29)–C(30)	118(3)	W–C(1)–O(1)	173(3)
W–C(2)–O(2)	177(3)				



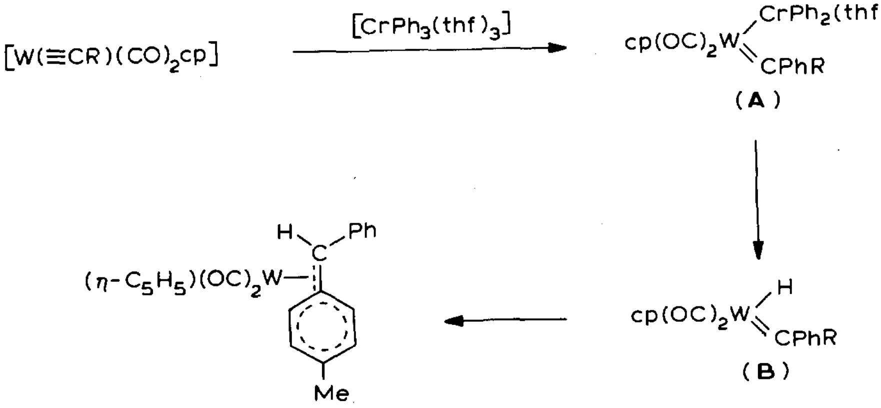
(I, R = Ph;
II, R = Pr^i;
III, R = $CH_2C_6H_4Me$-4;
V, R = Et)

$[Zn\{W(CO)_2(\eta\text{-}MeCH{=}CHC_6H_4Me\text{-}4)(\eta\text{-}C_5H_5)\}_2]$
(IV)

4)$(CO)_2(\eta\text{-}C_5H_5)$], the alkylidene–tungsten intermediate **A** shown in Scheme 1 might be produced. Conversion of **A** into **B** and into the final product I could proceed stepwise via a sequence of hydrogen migrations. That from **A** to **B** could involve a γ-hydride shift to tungsten from a coordinated thf or phenyl ligand on chromium. Alternatively, **B** might form from **A** by hydrolysis involving traces of moisture. However, this seems much less likely since the solvents were rigorously dried prior to use, and the reagent $[CrPh_3(thf)_3]$ is itself highly moisture sensitive and would preferentially react with any water which might be present.

It is interesting to note that the C≡W bond in $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ is also reduced on treatment of the latter with the hydroborating reagent 9-borabicyclo[3.3.1]nonane [11]. The product of this reaction is structurally similar to I, with the phenyl group replaced by a BC_8H_{14} substituent.

Formation of I, using the reagent $[CrPh_3(thf)_3]$, prompted a study of reactions between $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ and di-organozinc compounds [12], since it seemed possible that the zinc species would also promote C–C bond forming processes. When the alkylidynetungsten complex in light petroleum is treated with $ZnPh_2$ in diethyl ether, compound I was again formed. Moreover, analogous products II and III were obtained using $ZnPr^i_2$ and $Zn(CH_2C_6H_4Me\text{-}4)_2$, respectively. However, $ZnEt_2$ and the tolylmethylidynetungsten complex afforded an



SCHEME 1. cp = η-C_5H_5, R = C_6H_4Me-4, thf = tetrahydrofuran.

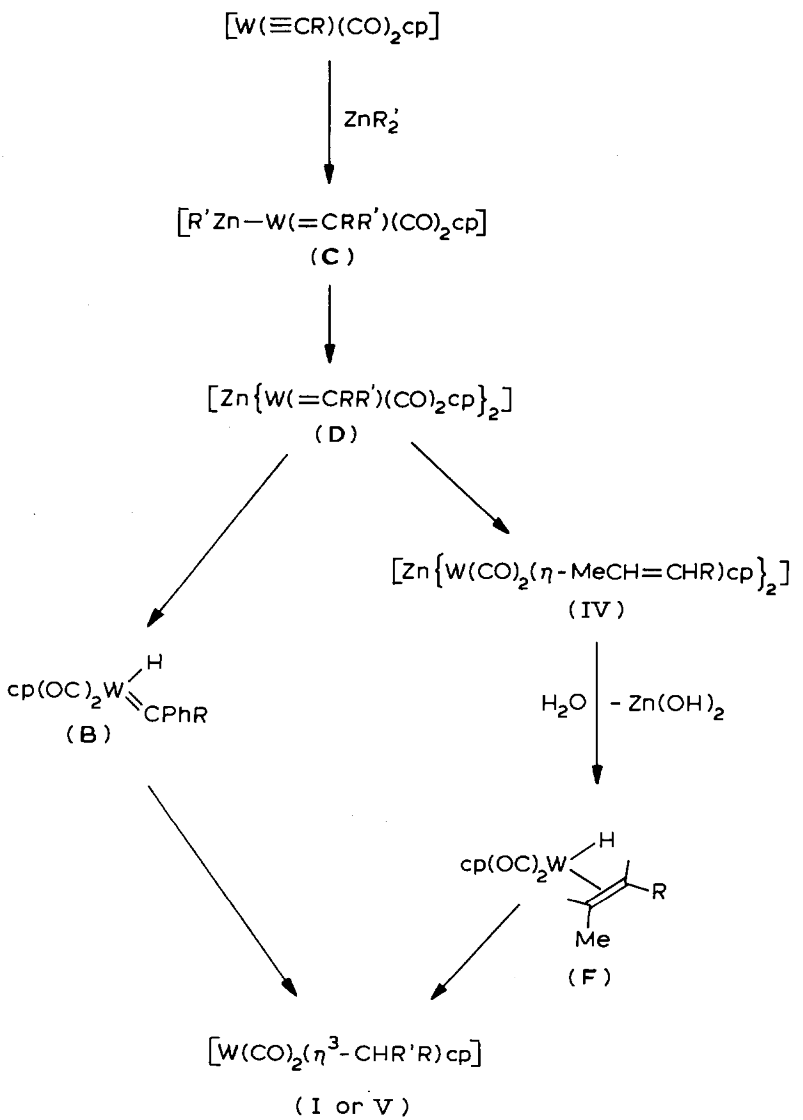
isolable tungsten–zinc compound IV. Although it was not possible to grow crystals of IV suitable for an X-ray diffraction study, the compound was adequately characterised by the data given in Table 1 and 2. Thus the ^1H NMR spectrum showed that no ethyl group was present. Instead, signals due to the protons of a *trans*-$MeCH{=}CH(C_6H_4Me\text{-}4)$ ligand were identified (Table 2), the *J*(HH) coupling of 12 Hz indicating the *trans*-olefin configuration [13]. The ^{13}C $\{^1H\}$ NMR spectrum had resonances at δ 53.5 and 37.8 ppm, these being characteristic for the ligated carbon nuclei of an aryl-substituted olefin bound to a metal [14]. In a coupled ^{13}C spectrum, measured at $-40°C$, these signals were doublets [*J*(CH) 77 and 70 Hz, respectively], slightly broadened due to olefin rotation, but confirming the presence of the CH=CH group. In the room temperature ^{13}C $\{^1H\}$ NMR spectrum the two CO resonances are also broad, but when measured at $-40°C$ the signals are sharp.

The IR spectrum of IV has two carbonyl stretching bands at relatively low frequency (1867 and 1815 cm^{-1}). Two trinuclear metal compounds $[Zn\{M(CO)_3(\eta\text{-}C_5H_5)\}_2]$ (M = Mo or W) structurally related to IV have been prepared [15,16], and the molybdenum species studied by X-ray diffraction [16]. These two complexes also show CO stretching bands below 1900 cm^{-1}; a feature attributed to the presence of $Zn \cdots OC$ interactions. The mass spectrum of IV does not show a parent ion; the most abundant peak (*m/e* 132) corresponding to $MeCH{=}CH(C_6H_4Me\text{-}4)$.

Although IV is stable under nitrogen at room temperature, it is exceedingly moisture sensitive, quickly forming V, a species analogous to I–III. In order to characterise further the reaction of IV with traces of water, the compound was treated with D_2O. Examination of the ^1H NMR spectrum and mass spectrum of the species produced revealed that one deuterium atom had been incorporated and 90% of the product was $[W(CO)_2\{\eta^3\text{-}MeC(D)HCHC_6H_4Me\text{-}4\}(\eta\text{-}C_5H_5)]$.

It is interesting to speculate on the pathway leading to the formation of I–V when the di-organozinc compounds are used as reagents (Scheme 2). Intermediates **C** and **D** resemble **A** of Scheme 1, since they implicate alkylidenetungsten species. Isolation of IV makes the existence of **D** plausible, and formation of a ditungsten–zinc intermediate correlates with the high reactivity of di-organozinc compounds [12]. For **D**, two different decomposition pathways might be possible, depending on the nature of R′. If the latter is an ethyl group from $ZnEt_2$, a relatively fast 1,2-hydride shift could lead to the rearrangement of $W{=}CEt(C_6H_4Me\text{-}4)$ into $W(\eta^2\text{-}MeCH{=}CHC_6H_4Me\text{-}4)$, thus leading to IV (Scheme 2). Such rearrangements involving carbene ligands are known with both mono- and di-nuclear complexes [17–20]. Subsequent hydrolysis of IV would then afford V via **F**.

With $ZnPh_2$ the formation of a tungsten–olefin complex akin to IV would not be possible, since the intermediate **D** with R′ = Ph has no hydrogen on a carbon atom β to tungsten available for a 1,2-shift rearrangement. When $ZnPh_2$, $ZnPr^i_2$ or $Zn(CH_2C_6H_4Me\text{-}4)_2$ are employed it is possible that the diethyl ether which is present is the source of the hydride required to form **B** from either **C** or **D**. Organozinc compounds are known to associate strongly with ethers through $O \rightarrow Zn$ bonds [12], and if a $W\text{–}Zn\text{–}OEt_2$ system were present in a sterically crowded etherate of **C** or **D** a γ-hydride shift to tungsten might occur, allowing formation of **B**. The step from **B** to I has precedent in the earlier observation [21] that treatment of the stable alkylidene-tungsten complex $[WI({=}CHC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ with $K[BH(CHMeEt)_3]$ affords $[W(CO)_2(\eta^3\text{-}CH_2C_6H_4Me\text{-}4)(\eta\text{-}C_5H_5)]$, the parent com-



SCHEME 2. cp = η-C_5H_5, R = C_6H_4Me-4, R′ = Ph or Et.

plex of I–III, rather than the hydrido-alkylidene compound [WH(=CHC_6H_4Me-4)$(CO)_2$(η-C_5H_5)], which is evidently thermodynamically unstable.

Although in principle the reagents ZnPr$^i_2$ or Zn($CH_2C_6H_4$Me-4$)_2$ could lead to an intermediate **D** with the possibility of a subsequent rearrangement to a ZnW_2 species containing a W(η-Me_2C=CHR) or a W(η-RCH=CHR) (R = C_6H_4Me-4) group, this pathway may well be kinetically less favourable on steric grounds than a γ-hydride shift to tungsten from an etherate W–Zn ← O$(CH_2Me)_2$. It is noteworthy that the species [(η-C_5H_5)$(OC)_3$MZnCl] and [Zn{M$(CO)_3$(η-C_5H_5)}$_2$] (M = Mo or W), structurally similar to intermediates **C** and **D** (Scheme 2), form ether complexes from which the ether can only be removed with difficulty [15,16].

Experimental

All experiments were carried out under oxygen-free nitrogen using Schlenk tube techniques. Light petroleum refers to that fraction b.p. 40–60°C. The compounds $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ [1] and $[CrPh_3(thf)_3]$ [9] were prepared as described in the literature. Diethylzinc was a commercial sample, and $ZnPh_2$, $ZnPr^i_2$ and $Zn(CH_2C_6H_4Me\text{-}4)_2$ were prepared from $ZnCl_2$ and the appropriate organolithium or Grignard reagent [12]. Data for the new compounds are given in Tables 1 and 2.

Reaction of $[CrPh_3(thf)_3]$ with $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$

Solid $[CrPh_3(thf)_3]$ (0.25 g, 0.27 mmol) was added to a thf (20 cm^3) solution of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.22 g, 0.54 mmol), and the mixture stirred for 24 h. At this stage an IR spectrum revealed that most of the tungsten compound had been consumed. The mixture was diluted with diethyl ether (10 cm^3), and filtered through an alumina pad (3 × 5 cm). Solvent was removed in vacuo, and the red residue dissolved in diethyl ether/light petroleum (1/5, 5 cm^3), and chromatographed on a alumina column (3 × 15 cm). Elution with light petroleum afforded unreacted $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.30 g). Elution with light petroleum/diethyl ether mixture (1/1) gave a red solution. Reduction in volume to ca. 3–5 cm^3 and cooling to −20°C gave red crystals of $[W(CO)_2(\eta^3\text{-}PhCHC_6H_4Me\text{-}4)(\eta\text{-}C_5H_5)]$ (I) (0.22 g).

Synthesis of the complexes $[W(CO)_2(\eta^3\text{-}RCHC_6H_4Me\text{-}4)(\eta\text{-}C_5H_5)]$ (I–III) using di-organozinc compounds

The general procedure was the same for all syntheses and a typical experiment is described. A diethyl ether (10 cm^3) solution of $ZnPr^i_2$ (3.78 mmol) was added to $[W(=CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.20 g, 0.49 mmol) dissolved in light petroleum (10 cm^3). After 30 min the mixture was filtered through alumina (3 × 5 cm), and solvent removed in vacuo. The residue was sublimed (0.1 mmHg/90°C) onto a water-cooled probe, affording red crystals of $[W(CO)_2(\eta^3\text{-}Pr^iCHC_6H_4Me\text{-}4)(\eta\text{-}C_5H_5)]$ (II) (0.12 g).

Reaction between $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ and $ZnEt_2$

A light petroleum (10 cm^3) solution of $ZnEt_2$ (16 mmol) was added to a stirred light petroleum solution (20 cm^3) of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.55 g, 1.34 mmol). The mixture was allowed to stand at 25°C for 12 h during which time the solution turned yellow, and yellow crystals formed. Solvent was removed with a syringe, and the crystals washed with light petroleum (10 cm^3) and dried in vacuo affording $[Zn\{W(CO)_2(\eta\text{-}MeCH{=}CHC_6H_4Me\text{-}4)(\eta\text{-}C_5H_5)\}_2]$ (IV) (0.40 g). A similar synthesis using a diethyl ether/light petroleum solvent mixture also afforded IV but in lower yield. There was no evidence for the direct formation of V without the intermediacy of IV even in the presence of diethyl ether, provided rigorously dried reagents were employed.

Crystal structure determination

Crystals of I were grown from tetrahydrofuran/light petroleum at −20°C. Diffracted intensities were collected at room temperature from a crystal of dimensions ca. 0.50 × 0.21 × 0.15 mm. Data were collected on a Nicolet P3m four-circle diffractometer, according to methods described earlier [3]. During data reduction, it became apparent that an intermittent fault with the X-ray power supply had developed and 140 intensities which showed evidence of unacceptable voltage 'spikes' were rejected. Of the remaining 2543 independent intensities collected (θ–2θ scans) to $2\theta \leqslant 45°$, 1283 had $F \geqslant 5.0\sigma(F)$, where $\sigma(F)$ is the standard deviation based on counting statistics and only these were used in the solution and refinement of the structure, after the data had been corrected for Lorentz, polarisation, and X-ray absorption effects. The latter by an analytical procedure [22].

Crystal data for I. $C_{21}H_{18}O_2W$, $M = 486.2$, orthorhombic, *a* 8.804(4), *b* 18.57(2), *c* 21.75(2) Å, *U* 3555(5) Å^3, $Z = 8$, D_x 1.82 g cm^{-3}, $F(000) = 1872$, space group *Pbca* (no. 61), Mo-K_α X-radiation (graphite monochromator), $\bar{\lambda}$ 0.71069 Å, μ(Mo-K_α) 66.5 cm^{-1}.

The structure was solved, and all non-hydrogen atoms were located, by conventional heavy-atom and difference-Fourier methods. The structure is apparently disordered with a 95% probability of the molecule being sited with the tungsten atom at (0.1027, 0.6323, 0.5977) and a 5% site occupancy of the alternative (Wa) position (0.399, 0.637, 0.598). The data in Table 3 refer to the molecule with 95% site occupancy, and although Wa was included in the refinement it was not possible to

TABLE 4

ATOMIC COORDINATES ($\times 10^4$) AND ISOTROPIC THERMAL PARAMETERS (Å^2 $\times 10^3$)

Atom	*x*	*y*	*z*	*U*
W	1026(2)	6323(1)	5976(1)	56(1) [a]
C(11)	−1072(29)	7109(8)	6106(12)	90(12)
C(12)	−823	6705	6651	87(11)
C(13)	−1078	5967	6513	63(9)
C(14)	−1485	5916	5883	63(10)
C(15)	−1481	6622	5631	65(10)
C(1)	1629(37)	5414(18)	5674(15)	67(10)
O(1)	2113(30)	4825(12)	5542(11)	90(7)
C(2)	2338(44)	6031(18)	6580(17)	83(11)
O(2)	3160(31)	5813(13)	6995(13)	110(9)
C(21)	2495(30)	7352(13)	5894(12)	43(8)
C(22)	3527(35)	7709(16)	6365(14)	59(10)
C(23)	4771(43)	7329(18)	6665(15)	83(12)
C(24)	5619(42)	7771(20)	7061(17)	98(13)
C(25)	5208(51)	8494(21)	7177(18)	109(14)
C(26)	4018(38)	8937(16)	6919(14)	64(9)
C(27)	3130(49)	8444(21)	6489(18)	102(13)
C(28)	2914(39)	6872(15)	5377(13)	58(9)
C(29)	1756(37)	6708(16)	4958(15)	64(9)
C(30)	2137(45)	6188(16)	4434(16)	75(10)
C(31)	3597(36)	5943(16)	4361(14)	55(9)
C(32)	4722(38)	6078(16)	4819(14)	63(10)
C(33)	4454(36)	6554(16)	5332(14)	62(10)
C(34)	3914(47)	5520(21)	3858(19)	109(14)
Wa [b]	3990(36)	6375(15)	5983(13)	50

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalised U_{ij} tensor. [b] Disordered molecule (Wa) has 5% site occupancy, other atoms associated with this site not located.

locate and refine the remaining atoms associated with this site. Because of the problem with disorder and the comparatively poor quality of the data, only the tungsten atom was refined with an anisotropic thermal parameter and hydrogen atoms were not included in the refinement. Refinement by blocked-cascade least-squares led to R 0.072 (R_w 0.075), and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.001|F|^2]$ gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks $\geqslant 1$ e Å^{-3}. Scattering factors were from ref. 23. All computations were carried out on an 'Eclipse' (Data General) computer with the 'SHELXTL' system of programs [22]. Atom coordinates are given in Table 4. Structure factors, anisotropic thermal parameters, and a complete listing of bond distances and angles are available from the authors.

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