Chemistry of Di- and Tri-metal Complexes with Bridging Carbene or Carbyne Ligands. Part 18.[1] Synthesis of the Complexes $[MW(\mu\text{-}CC_6H_4Me\text{-}4)\{\mu\text{-}(\sigma:\eta^2\text{-}CO)\}(CO)(\eta\text{-}C_5H_5)_3]$ (M = Ti or Zr) and the Crystal Structure of the Titanium–Tungsten Compound *

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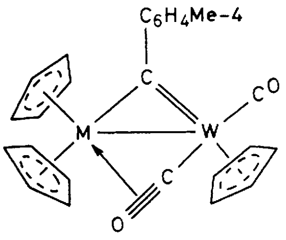
The compounds $[M(CO)_2(\eta\text{-}C_5H_5)_2]$ (M = Ti or Zr) react with $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ when heated in toluene to give the dimetal compounds $[MW(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}CO)(CO)(\eta\text{-}C_5H_5)_3]$, characterised by n.m.r. and i.r. spectroscopy. The structure of the titanium–tungsten compound has been established by a single-crystal *X*-ray diffraction study. As expected, the titanium–tungsten bond [2.977(4) Å] is bridged by the CC_6H_4Me-4 ligand [Ti–C 2.19(3) and W–C 1.91(2) Å, with double-bond character in the linkage to tungsten], and one of the two linear terminal carbonyl ligands on the W atom forms a η^2-donor bond to the Ti atom. The bridge system itself is nearly planar; but although the two cyclopentadienyl ligands on the Ti atom are at normal bonding distances and are approximately equivalently related to the bridge plane, they are in a staggered orientation to one another. The third cyclopentadienyl ligand completes the bonding around the W atom. The high thermal stability and relative inertness of the molecule can be ascribed, at least in part, to the compact arrangement of inert bulky ligands around the metal centres.

Since the compound $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4) readily combines with low-valent metal species, it is proving to be a versatile reagent for synthesising complexes with bonds between tungsten and other transition elements. In the products the heteronuclear metal–metal bonds are bridged by CR groups, and dinuclear metal compounds are now known with tungsten bonded to Pt,[2] Co,[3] Rh,[3,4] Ir,[5] Fe,[6] Mn, Re, and Cr.[3] These metals are all from sub-groups 6—8 of the Periodic Table. In order to determine whether a similar pathway can be used to prepare dimetal compounds with bonds between tungsten and metals of sub-groups 4 or 5, studies with appropriate mononuclear complexes of these elements are being conducted. Herein we describe reactions between $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and $[M(CO)_2(\eta\text{-}C_5H_5)_2]$ (M = Ti or Zr). The mononuclear titanium dicarbonyl species is known to react with PhC≡CPh affording initially the complex $[Ti(CO)(\eta\text{-}PhC_2Ph)(\eta\text{-}C_5H_5)_2]$, and subsequently the titanocycle $[Ti\{C(Ph)=C(Ph)C(Ph)=C(Ph)\}(\eta\text{-}C_5H_5)_2]$.[7] Since $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and PhC≡CPh have similar reactivity patterns in organometallic chemistry, it was anticipated that the former would react with $[Ti(CO)_2(\eta\text{-}C_5H_5)_2]$ also. The chemistry of $[Zr(CO)_2(\eta\text{-}C_5H_5)_2]$ has been less well studied,[8] but the compound is likely to function as a source of $Zr(\eta\text{-}C_5H_5)_2$ groups, as does $[ZrMe_2(\eta\text{-}C_5H_5)_2]$ which with PhC≡CPh affords the cyclic compound $[Zr\{C(Ph)=C(Ph)C(Ph)=C(Ph)\}(\eta\text{-}C_5H_5)_2]$.[9]

Results and Discussion

The compounds $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Ti(CO)_2(\eta\text{-}C_5H_5)_2]$ react in toluene at *ca.* 60 °C to give a red crystalline complex (1) in yields of 80%. Microanalytical data, the observation of a parent ion in the mass spectrum, and the spectroscopic properties were in accord with a formulation $[TiW(\mu\text{-}CR)(\mu\text{-}CO)(CO)(\eta\text{-}C_5H_5)_3]$ for (1). The compound is thermally very stable since it is also produced in the reaction between $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ and $[Ti(C_6H_4Me\text{-}4)_2(\eta\text{-}C_5H_5)_2]$ carried out in toluene at 100 °C for several hours.



	M
(1)	Ti
(2)	Zr

The tungsten-zirconium analogue (2) was prepared by heating $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ with $[Zr(CO)_2(\eta\text{-}C_5H_5)_2]$ in toluene. The mass spectrum of (2) also showed a parent ion, and in addition peaks corresponding to the successive loss of two CO groups were observed. Both (1) and (2) are thermally stable and relatively chemically inert. Compound (1) showed little sign of reactivity towards tertiary phosphines or alkynes below 80—100 °C, and above these temperatures some decomposition occurred.

The spectroscopic data for (1) and (2) (Experimental section) were very similar, and provided useful structural information. The ^1H n.m.r. spectra showed resonances corresponding to $\eta\text{-}C_5H_5$ groups in three environments in (1) and (2). Two of these chemical shifts were very similar, with the third somewhat different, in accord with the presence of $M(\eta\text{-}C_5H_5)_2$ and $W(\eta\text{-}C_5H_5)$ groups in the two compounds. In the $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of both complexes the very characteristic signal for a μ-*C*R group was observed at δ 391.4 and 391.2 p.p.m. for (1) and (2), respectively, the resonance for (2) showing ^{187}W satellites, *J*(WC) 129 Hz. The two spectra

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* μ-[σ : η-Carbonyl-*C*(W)*CO*(Ti)]-1-carbonyl-1,2,2-tri(η-cyclopentadienyl)-μ-*p*-tolylmethylidyne-tungstentitanium(*W–Ti*).

Supplementary data available (No. SUP 23445, 24 pp.): H-atom co-ordinates, thermal parameters, complete bond lengths and angles, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Selected bond lengths (Å) and angles (°) for [TiW(μ-CC_6H_4Me-4)(μ-CO)(CO)(η-C_5H_5)$_3$] (1)

(*a*) Distances

Ti-W	2.977(4)	W-C(1)	1.90(3)
Ti-C(1)	2.20(3)	Ti-O(1)	2.27(2)
C(1)-O(1)	1.21(4)	W-C(2)	1.91(2)
Ti-C(2)	2.19(3)	C(2)-C(3)	1.48(3)
W-C(01)	2.04(3)	C(01)-O(01)	1.10(3)
mean Ti-C(cp) *	2.40(3)	mean W-C(cp)	2.38(2)
mean C-C(cp)	1.40(4)	mean C-C(tolyl)	1.38(3)

(*b*) Angles

Ti-W-C(1)	47.5(7)	W-Ti-C(1)	39.5(7)
W-C(1)-Ti	93(1)	W-C(1)-O(1)	165(2)
Ti-C(1)-O(1)	77.7(14)	Ti-O(1)-C(1)	70.8(14)
O(1)-Ti-C(1)	31.4(8)	Ti-W-C(2)	47.4(6)
W-Ti-C(2)	39.9(4)	Ti-C(2)-W	92.7(8)
W-C(2)-C(3)	138.1(15)	Ti-C(2)-C(3)	128.8(13)
Ti-W-C(01)	92.0(7)	W-C(01)-O(01)	178(2)

* cp = η-C_5H_5.

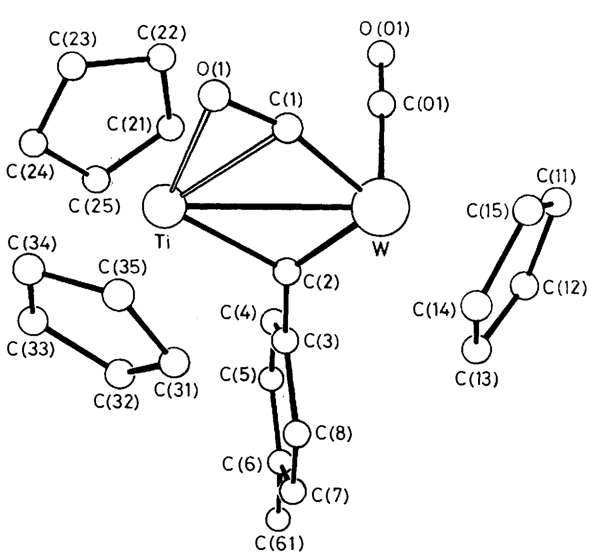

Figure 1. Molecular structure of [TiW(μ-CC_6H_4Me-4)(μ-CO)(CO)(η-C_5H_5)$_3$] (1), showing the crystallographic numbering scheme

differed, however, with respect to the ^{13}CO resonances. In the spectrum of (1) two signals are present of equal intensity at δ 227.2 and 222.5 p.p.m., whereas in the spectrum of (2), also measured at room temperature, only one signal (δ 222.7) was seen. However, on cooling a solution of (2) to -80 °C two peaks for CO groups appeared, but with very similar chemical shifts (δ 222.9 and 222.3 p.p.m.). This behaviour is discussed further below.

The i.r. spectra of the two compounds in the CO stretching region showed two bands: at 1 921 and 1 638 cm^{-1} for (1), and at 1 937 and 1 578 cm^{-1} for (2). The low-frequency band in the spectrum of each compound provides strong evidence for the presence in the complexes of a CO group terminally bound to a metal atom with a second CO ligand adopting a σ:η^2-bridge-bonding mode, a type of interaction first observed in [Mn_2{μ-(σ:η^2-CO)}$(CO)_4(dppm)_2$] (dppm = $Ph_2PCH_2PPh_2$).[10] Moreover, the molybdenum-zirconium compounds [MoZr(Me){μ-(σ:η^2-CO)}$(CO)_2$(η-C_5H_5)$_3$] and [MoZr(μ-OCMe){μ-(σ:η^2-CO)}(CO)(η-C_5H_5)$_3$], which also contain this kind of bridging CO ligand, have bands at 1 545 and 1 534 cm^{-1}, respectively.[11] These absorptions are close in frequency to the corresponding band in the spectrum of (2).

Even though they are in very different environments, the two CO groups in [MoZr(μ-OCMe){μ-(σ:η^2-CO)}(CO)(η-C_5H_5)$_3$] give rise in the ^{13}C-{^1H} n.m.r. spectrum to two resonances which differ only by 2 p.p.m. in chemical shifts. As mentioned above, the ^{13}C-{^1H} spectrum of (2) at room temperature shows only a single CO environment, although at -80 °C two resonances are seen, albeit only 0.6 p.p.m. apart. It is known [12] that terminal CO ligands and μ-(σ:η^2-CO) groups give rise to similar chemical shifts. Indeed, in accord with this the two CO peaks in the spectrum of (1) differ by only *ca.* 5 p.p.m. Given that the chemical shifts of μ-(σ:η^2-CO) groups are not diagnostic, the spectral data for (2) raise a problem of interpretation. The appearance of one CO resonance at room temperature and two at -80 °C, but which have little chemical shift difference, could be interpreted in one of two ways. There is the possibility that at ambient temperatures the chemical shifts of the non-equivalent CO ligands happen to be coincident, the molecule is not fluxional, and the small separation at -80 °C is due to the chemical shifts changing with temperature. Alternatively, site exchange between the bridging and terminal CO groups is taking place at room temperature. Such scrambling occurs in [MoZr(Me){μ-(σ:η^2-CO)}$(CO)_2$(η-C_5H_5)$_3$] with a relatively low activation energy ($\Delta G_{T_c}^{\ddagger}$ 40 kJ mol^{-1}).[11]

Furthermore, although the i.r. data were strongly suggestive of the presence of a μ-(σ: η^2-CO) ligand, this evidence was not conclusive. Thus the compound [TiMo(Me)(μ-CO)$(CO)_2$(η-C_5H_5)(η-C_5Me_5)$_2$] has a band in its i.r. spectrum at 1 623 cm^{-1}, due to a bridging CO group, which is very similar in frequency to the band in the spectrum of (1). However, an *X*-ray crystallographic study [13] of [TiMo(Me)(μ-CO)$(CO)_2$(η-C_5H_5)(η-C_5Me_5)$_2$] revealed co-ordination of the titanium to the oxygen atom of a terminal CO on the molybdenum, *viz.* Ti$\leftarrow$O-C-Mo; the compound contains no Mo-Ti bond, and the interaction is of a Lewis base-acid type. In order, therefore, to establish the molecular structures of (1) and (2) with certainty, an *X*-ray diffraction study was carried out on the former, for which suitable crystals were available.

The molecular structure of (1) is illustrated in Figure 1 with the crystallographic numbering scheme. Selected bond lengths and angles are listed in Table 1. It is clear that one of the linear terminal carbonyl ligands on the tungsten atom is η^2-attached to the titanium atom, a mode of attachment for which, as mentioned above, there are several precedents.[10-12,14] In this case the W-C-O link is not quite linear (165°), but the Ti-C(1) and Ti-O(1) distances are closely similar [2.20(3) and 2.27(2) Å, respectively]. The four atoms W, Ti, C(1), and O(1) are not quite coplanar, however, O(1) being displaced some 0.24 Å from the plane of the other three. The rest of the molecule has the expected configuration, and in the carbyne bridging system [Ti-W 2.977(4), Ti-C(2) 2.19(3), and W-C(2) 1.91(2) Å] the tungsten-carbon bond length is appropriate for a bond order of two, as required by electron-counting rules. The planes of the two bridge systems Ti-C(1)-W and Ti-C(2)-W are nearly coincident (dihedral angle 1.5°), and the μ-CC_6H_4Me-4 ligand is twisted relative to the Ti-C(2)-W plane [torsion angle W-C(2)-C(3)-C(4) = $-104(2)$°]. It might have been expected that the two cyclopentadienyl ligands bound to the Ti atom [mean Ti-C 2.40(3) Å] would be symmetrically related to the plane of the bridging carbonyl [Ti-C(1)-W], and indeed the angles are closely similar [27.8° for the C(21)—(25) ring, 28.4° for the C(31)—(35) ring]. The rings are not, however, in a pseudo-mirror relationship because they are in a staggered orientation with respect to one

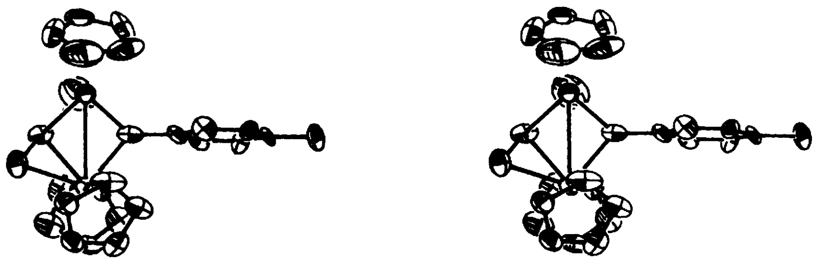

Figure 2. Stereoscopic view of complex (1)

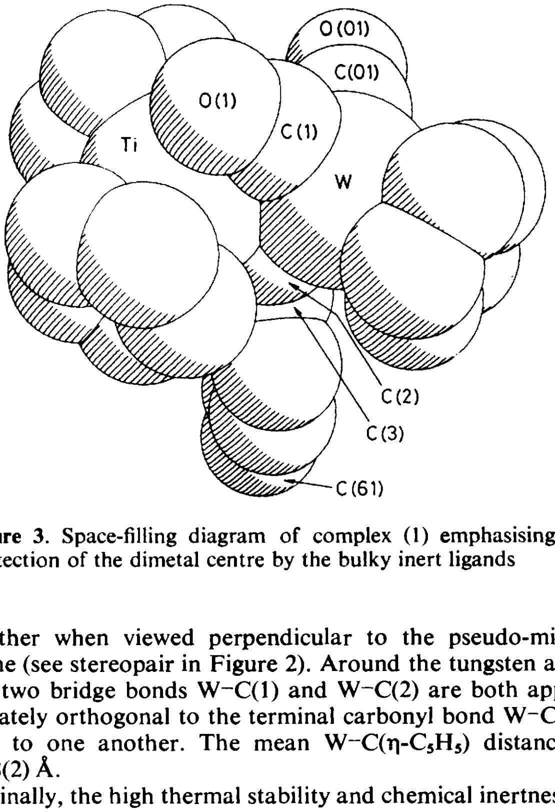

Figure 3. Space-filling diagram of complex (1) emphasising the protection of the dimetal centre by the bulky inert ligands

another when viewed perpendicular to the pseudo-mirror plane (see stereopair in Figure 2). Around the tungsten atom the two bridge bonds W–C(1) and W–C(2) are both approximately orthogonal to the terminal carbonyl bond W–C(01) and to one another. The mean W–C(η-C_5H_5) distance is 2.38(2) Å.

Finally, the high thermal stability and chemical inertness of the molecule, mentioned earlier, may arise, at least in part, from the compact arrangement of the inert bulky ligands around the metal centres (see Figure 3). Inspection of intramolecular contact distances shows that there are contacts approximately equal to the sum of van der Waals radii (Table 2) between * cp^a and cp^b, cp^a and tol, cp^b and tol, cp^a and both CO ligands, and tol and cp^c. Indeed, the only non-contact distance is between cp^c and the terminal carbonyl ligand on the tungsten atom.

Experimental

The techniques used, and the instrumentation employed, have been previously described.[2,4] The compounds [W($\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)],[15] [M(CO)$_2$(η-C$_5$H$_5$)$_2$],[8,16] and [Ti(C$_6$H$_4$Me-4)$_2$(η-C$_5$H$_5$)$_2$] [17] were made by methods previously reported. Light petroleum refers to that fraction of b.p. 40—60 °C.

Synthesis of the Complexes [MW(μ-CC$_6$H$_4$Me-4)(μ-CO)(CO)(η-C$_5$H$_5$)$_3$] (M = Ti *or* Zr).—(*a*) A toluene (15 cm^3) solution of [W($\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] (0.50 g, 1.23 mmol) and [Ti(CO)$_2$(η-C$_5$H$_5$)$_2$] (0.284 g, 1.21 mmol) was heated at 55 °C for 15 h in an evacuated Schlenk tube fitted with a Young's high-pressure stopcock. Solvent was then removed *in vacuo*, the residue dissolved in toluene–heptane (1 : 1), and chromatographed on a Florisil column. With toluene–heptane (1 : 1) as eluant, a trace of [W($\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] was recovered first, followed by a red product. Evaporation of solvent, and crystallisation from toluene–hexane (1 : 3), gave red-mauve *crystals* of [TiW(μ-CC$_6$H$_4$Me-4)(μ-CO)(CO)(η-C$_5$H$_5$)$_3$] (1) (0.57 g, 80%) [Found: C, 50.8; H, 3.8%; *M* (mass spectrum) 586. C$_{25}$H$_{22}$O$_2$TiW requires C, 51.2; H, 3.7%; *M* 586], m.p. 170 °C, $\nu_{max.}$(CO) at 1 921s and 1 638s cm^{-1} (tetrahydrofuran), and at 1 930s and 1 628s cm^{-1} (Nujol). N.m.r.: ^{1}H ([^{2}H$_6$]acetone), δ 2.24 (s 3 H, Me-4), 5.32 (s, 5 H, TiC$_5$H$_5$), 5.44 (s, 5 H, TiC$_5$H$_5$), 5.70 (s, 5 H, WC$_5$H$_5$), and 7.12 (m, 4 H, C$_6$H$_4$); ^{13}C-{^{1}H} ([^{2}H$_2$]dichloromethane-CH$_2$Cl$_2$), δ 391.4 (μ-C), 227.2 (CO), 222.5 (CO), 161.1 [C(1) (C$_6$H$_4$)], 135.3, 129.1, 123.7 (C$_6$H$_4$), 109.5, 109.4, 93.9 (η-C$_5$H$_5$), and 21.4 p.p.m. (Me-4).

Table 2. Significantly short intramolecular contacts (Å) for [TiW(μ-CC$_6$H$_4$Me-4)(μ-CO)(CO)(η-C$_5$H$_5$)$_3$] (1)

H(8)–H(32)	2.51	C(8)–H(32)	2.49
O(01)–H(21)	2.71	H(8)–H(31)	2.55
C(1)–H(22)	2.80	C(33)–H(24)	2.60
H(33)–H(24)	2.13	H(33)–C(24)	2.65
H(8)–H(13)	2.13	O(1)–H(35)	2.72
H(4)–H(21)	2.20	O(01)–H(21)	2.75

Compound (1) was also prepared (33 mg, 25%) by heating a mixture of [W($\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] (90 mg, 0.22 mmol) and [Ti(C$_6$H$_4$Me-4)$_2$(η-C$_5$H$_5$)$_2$] (80 mg, 0.22 mmol) in toluene (15 cm^3) at 100 °C for 30 h.

(*b*) In a similar manner to that described above, the compounds [W($\equiv$CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] (0.48 g, 1.18 mmol) and [Zr(CO)$_2$(η-C$_5$H$_5$)$_2$] (0.32 g, 1.16 mmol) in toluene (20 cm^3) were heated at 70 °C for 24 h. The product was isolated by chromatography on Florisil using toluene–heptane (1 : 3) as eluant to remove a trace of the mononuclear tungsten compound, and eluting with toluene to give a red solution. Evaporation of the latter and crystallisation of the residue (hexane–toluene, 3 : 1) gave red *crystals* of [WZr(μ-CC$_6$H$_4$Me-4)(μ-CO)(CO)(η-C$_5$H$_5$)$_3$] (2) (0.30 g, 40%) [Found: C, 47.6; H, 3.7%; *M* (mass spectrum) 629. C$_{25}$H$_{22}$O$_2$WZr requires C, 47.7; H, 3.5%; *M* 629], m.p. 130 °C (decomp.), $\nu_{max.}$(CO) at 1 937s and 1 578s cm^{-1} (tetrahydrofuran), and at 1 937s and 1 567s cm^{-1} (Nujol). N.m.r.: ^{1}H ([^{2}H$_2$]dichloromethane), δ 2.27 (s, 3 H, Me-4), 5.37 (s, 5 H, ZrC$_5$H$_5$), 5.39 (s, 5 H, ZrC$_5$H$_5$), 5.42 (s, 5 H, WC$_5$H$_5$), and 6.90 (m, 4 H, C$_6$H$_4$); ^{13}C-{^{1}H} ([^{2}H$_2$]dichloromethane-CH$_2$Cl$_2$), δ 391.2 [μ-C, *J*(WC) 129], 222.7 [CO, *J*(WC) 198 Hz], 161.8 [C(1) (C$_6$H$_4$)], 134.2, 129.1, 121.1 (C$_6$H$_4$), 108.3, 108.1, 94.0 (η-C$_5$H$_5$), and

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* cp = Cyclopentadienyl ligand, tol = *p*-tolylidyne ligand; cp^a = C(21)—C(25), cp^b = C(31)—C(35), and cp^c = C(11)—C(15).

Table 3. Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses for [TiW(μ-CC$_6$H$_4$Me-4)(μ-CO)(CO)(η-C$_5$H$_5$)$_3$] (1)

Atom	*x*	*y*	*z*
W	0.225 04(7)	0.268 69(10)	0.004 50(5)
Ti	0.207 6(3)	0.011 3(5)	−0.104 6(2)
C(11)	0.240 9(12)	0.463(3)	0.100 4(12)
C(12)	0.289 9(12)	0.519(3)	0.041 9(12)
C(13)	0.374 6(12)	0.422(3)	0.037 0(12)
C(14)	0.378 1(12)	0.306(3)	0.092 6(12)
C(15)	0.295 4(12)	0.332(3)	0.131 8(12)
C(21)	0.047 8(13)	0.109(3)	−0.174 6(12)
C(22)	0.023 3(12)	0.007(3)	−0.121 8(11)
C(23)	0.055 6(15)	−0.136(3)	−0.140 0(15)
C(24)	0.099(2)	−0.118(3)	−0.203 0(15)
C(25)	0.095 8(2)	0.034(3)	−0.223 9(14)
C(31)	0.395 5(12)	0.010(3)	−0.075 3(13)
C(32)	0.364 8(13)	0.020(3)	−0.154 3(14)
C(33)	0.316 5(14)	−0.117(3)	−0.177 0(12)
C(34)	0.313 3(13)	−0.208(3)	−0.114 3(11)
C(35)	0.363 1(15)	−0.132(3)	−0.050 8(12)
C(01)	0.073(2)	0.321(3)	−0.027(2)
O(01)	−0.009 3(14)	0.349(3)	−0.045 8(13)
C(1)	0.185(2)	0.063(4)	0.010 9(14)
O(1)	0.180 3(11)	−0.075(2)	0.009 3(9)
C(2)	0.239 0(12)	0.256(3)	−0.099 3(9)
C(3)	0.271 0(14)	0.355(3)	−0.157 3(11)
C(4)	0.203 7(13)	0.425(3)	−0.216 8(12)
C(5)	0.234 5(13)	0.512(3)	−0.269 9(11)
C(6)	0.336 4(13)	0.543(3)	−0.269 5(10)
C(61)	0.370(2)	0.642(3)	−0.329 3(13)
C(7)	0.407 5(14)	0.478(3)	−0.211 3(10)
C(8)	0.377 1(15)	0.390(3)	−0.156 4(13)

21.5 p.p.m. (Me-4); ^{13}C-{^{1}H} at −80 °C, δ(CO) 222.9 and 222.3 p.p.m., with *J*(WC) 196 and 199 Hz, respectively.

Crystal-structure Determination of [TiW(μ-CC$_6$H$_4$Me-4)(μ-CO)(CO)(η-C$_5$H$_5$)$_3$] (1).—Crystals of (1) grow as red-mauve prisms from toluene–hexane. Diffracted intensities were recorded at room temperature for a crystal of dimensions 0.25 × 0.225 × 0.15 mm mounted in a Lindemann capillary tube under solvent and sealed in with low-temperature epoxy-resin. Of the 5 273 reflections measured for $2.9 \leqslant 2\theta \leqslant 60°$ on a Nicolet $P2_1m$ diffractometer, 2 269 had $I \geqslant 2.0\sigma(I)$, where $\sigma(I)$ is the estimated standard deviation based on counting statistics, and only these were used in the refinement of the structure. Corrections were applied for Lorentz, polarisation, anomalous-dispersion, and, semi-empirically, for *X*-ray absorption effects; the maximum and minimum transmission coefficients were 0.101 and 0.048. Two check reflections (11$\bar{3}$ and 424) were remeasured every 50 reflections, and showed no significant decay over 170 h of exposure to *X*-rays. Computations were carried out in the laboratory on an Eclipse (Data General) computer with the SHELXTL system of programs.[18]

Crystal data. C$_{25}$H$_{22}$O$_2$TiW, $M = 586.2$, Monoclinic, $a = 13.194(7)$, $b = 8.798(3)$, $c = 17.971(6)$ Å, $\beta = 100.61(3)°$, $U = 2\,050(2)$ Å^3, $Z = 4$, $D_c = 1.90$ g cm^{-3}, $F(000) = 1\,136$, space group $P2_1/c$ (no. 14), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 61.3 cm^{-1}.

The structure was solved by heavy-atom methods, and was refined by blocked-cascade least squares with anisotropic thermal parameters for all non-hydrogen atoms. The carbon atoms of the cyclopentadienyl ligand on the tungsten atom were constrained to ideal pentagonal geometry, but all other atoms were refined freely. Hydrogen atoms were incorporated at calculated (' riding ') positions with C–H 0.96 Å and with isotropic thermal parameters restrained to 1.2 times that of the attached carbon atom. Those of the methyl group on the tolyl ligand were constrained to ideal tetrahedral geometry. Individual weights were ascribed according to the scheme $w = (\sigma^2|F_o| + 0.0002|F_o|^2)^{-1}$. Scattering factors and corrections for anomalous dispersion were from ref. 19. A final electron-density difference synthesis showed a maximum of 2.4 and a minimum of −3.6 e Å^{-3} in the region of the tungsten atom but much lower values elsewhere. The final atom co-ordinates are listed in Table 3.

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