Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 82.[1] Dimetallic Compounds prepared from the Complexes $[MR_2(\eta\text{-}C_5H_5)_2]$ (R = Cl or Bu^n; M = Ti or Zr)

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The bis(cyclopentadienyl)metal dihalides $[MCl_2(\eta\text{-}C_5H_5)_2]$ (M = Ti or Zr) are reduced by magnesium amalgam in tetrahydrofuran in the presence of the alkylidyne–tungsten complexes $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4 or C_6H_4OMe-2) to afford the dimetal compounds $[MW(\mu\text{-}CR)(\mu\text{-}\sigma{:}\eta^2\text{-}CO)(CO)(\eta\text{-}C_5H_5)_3]$. Alternatively, the reagents $[M(Bu^n)_2(\eta\text{-}C_5H_5)_2]$ (M = Ti or Zr), prepared *in situ* in diethyl ether, react with the complexes $[M'(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (M = Ti, M' = W, R = C_6H_4Me-4 or C_6H_4OMe-2; M = Zr, M' = W, R = Me, C_6H_4Me-4, C_6H_4OMe-2, or $C_6H_3Me_2$-2,6; M' = Mo, R = C_6H_4OMe-2) to give the compounds $[MM'(\mu\text{-}CR)(\mu\text{-}\sigma{:}\eta^2\text{-}CO)(CO)(\eta\text{-}C_5H_5)_3]$ in high yield. The n.m.r. data for the new complexes are reported and discussed.

In an earlier paper[2] we reported the synthesis of the compounds $[MW(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}\sigma{:}\eta^2\text{-}CO)(CO)(\eta\text{-}C_5H_5)_3]$ [M = Ti (**1a**) or Zr (**1b**)], obtained by displacing carbonyl groups in the titanium and zirconium complexes $[M(CO)_2(\eta\text{-}C_5H_5)_2]$ with $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$. Herein we describe alternative preparations for compounds of this class which are more convenient, and avoid the necessity to prepare the dicarbonyl species.

The synthesis of compounds containing metal–metal bonds between a late transition element and one belonging to the early or middle groups of the series is currently attracting attention. An interesting feature of these systems is their potential for activating substrates *via* processes facilitated by the different ligating properties of the metal centres involved. This ability has been demonstrated recently in studies on zirconium–ruthenium[3] and molybdenum–iron[4] compounds.

Attempts to prepare mixed-metal compounds of titanium or its congeners *via* elimination reactions with carbonyl metallates or hydrido-metal carbonyls often lead to the formation of isocarbonyl linkages, as in $[TiMo(\mu\text{-}\sigma,\sigma'\text{-}CO)(CO)_2(thf)(\eta\text{-}C_5H_4Me)(\eta\text{-}C_5H_5)_2]$ (thf = tetrahydrofuran),[5a] a result due to the high oxophilicity of these metals.[5]

Alternative approaches, based on using the reagents $[M(PEt_2)_2(\eta\text{-}C_5H_5)_2]$ (M = Zr or Hf) or $Li_2[W(PPh_2)_2(CO)_4]$ afford the species $[MM'(\mu\text{-}PR_2)_2(L_n)(\eta\text{-}C_5H_5)_2]$ [R = Ph, M'L$_n$ = $W(CO)_4$;[6a] R = Et, M'L$_n$ = $Mo(CO)_4$, $Fe(CO)_3$, Ni(cod) (cod = cyclo-octa-1,5-diene), or $Rh(\eta^5\text{-}C_9H_7)$ (C_9H_7 = indenyl)[6b]]. However, in these products the two metal centres are held together by μ-phosphido fragments, and the metal–metal interactions are either non-existent or weak. Moreover, the reactivity of the compounds seldom differs from that of the corresponding bis(phosphine) complexes $[M(PR_2CH_2PR_2)(L_n)]$. Evidently the development of new synthetic routes to compounds in which the elements of Group 4 (Ölander numbering) are bonded to other transition elements is desirable.

Results and Discussion

Treatment of a mixture of $[TiCl_2(\eta\text{-}C_5H_5)_2]$ and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ in thf (tetrahydrofuran) with magnesium amalgam affords in high yield the previously characterised compound $[TiW(\mu\text{-}CC_6H_4Me\text{-}4)(\mu\text{-}\sigma{:}\eta^2\text{-}CO)(CO)(\eta\text{-}C_5H_5)_3]$ (**1a**).[2] A similar synthesis using the reagents $[ZrCl_2(\eta\text{-}C_5H_5)_2]$ and $[W(\equiv CC_6H_4OMe\text{-}2)(CO)_2(\eta\text{-}C_5H_5)]$ gives the complex $[ZrW(\mu\text{-}CC_6H_4OMe\text{-}2)(\mu\text{-}\sigma{:}\eta^2\text{-}CO)(CO)(\eta\text{-}C_5H_5)_3]$ (**1c**) (*ca.* 65% yield), data for which are given in Tables 1 and 2. Compounds of type (**1**) show two strong CO stretching bands in

Table 1. Analytical[a] and physical data for the complexes

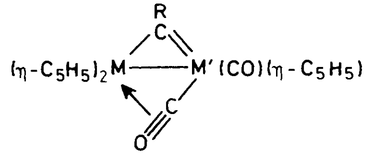
Compound	Colour	Yield[b] (%)	$\nu_{max.}(CO)$[c]/cm^{-1}	Analysis (%) C	H	M[d]
(**1c**) $[ZrW(\mu\text{-}CC_6H_4OMe\text{-}2)(\mu\text{-}CO)(CO)(\eta\text{-}C_5H_5)_3]$	Orange	80	1 965vs, 1 572s	46.1 (46.5)	3.6 (3.4)	646 (646)
(**1d**) $[ZrMo(\mu\text{-}CC_6H_4OMe\text{-}2)(\mu\text{-}CO)(CO)(\eta\text{-}C_5H_5)_3]$	Orange	73	1 966vs, 1 579s	52.1 (53.8)	4.3 (4.0)	558 (558)
(**1e**) $[TiW(\mu\text{-}CC_6H_4OMe\text{-}2)(\mu\text{-}CO)(CO)(\eta\text{-}C_5H_5)_3]$	Red	70	1 941vs, 1 632s	49.7 (49.8)	3.6 (3.7)	602 (602)
(**1f**) $[ZrW(\mu\text{-}CMe)(\mu\text{-}CO)(CO)(\eta\text{-}C_5H_5)_3]$	Yellow	76	1 937vs, 1 561s	41.4 (41.2)	2.8 (3.3)	554 (554)
(**1g**) $[ZrW(\mu\text{-}CC_6H_3Me_2\text{-}2,6)(\mu\text{-}CO)(CO)(\eta\text{-}C_5H_5)_3]$	Red	84	1 950vs, 1 583s	48.6 (48.5)	3.8 (3.8)	644 (644)

[a] Calculated values are given in parentheses. [b] Based on alkylidyne–metal complex *via* method (*i*), see Experimental section. [c] In CH_2Cl_2. [d] Molecular ion from mass spectrum, with isotope pattern consistent with formulation. Peak due to $(M - 2CO)^+$ also evident.

Table 2. Hydrogen-1 and carbon-13 n.m.r. data[a] for the complexes

Compound	$^1H(\delta)$[b]	$^{13}C(\delta)$[c]
(1c)	3.81 (s, 3 H, OMe), 5.50, 5.61, 5.67 (s × 3, 15 H, C_5H_5), 6.93—6.67 (m, 4 H, C_6H_4)	388.0 (μ-C), 223.0, 222.0 (CO), 158.2 [$C^1(C_6H_4)$], 143.9, 122.8, 119.7, 114.1, 110.2 (C_6H_4), 108.7, 108.2 (ZrC_5H_5), 94.3 (WC_5H_5), 55.2 (OMe)
(1d)	3.67 (s, 3 H, OMe), 5.31, 5.45, 5.54 (s × 3, 15 H, C_5H_5), 5.94—6.85 (m, 4 H, C_6H_4)	423.4 (μ-C), 230.2, 229.0 (CO), 156.2 [$C^1(C_6H_4)$], 144.0, 123.4, 119.9, 114.7, 110.4 (C_6H_4), 108.5, 108.1 (ZrC_5H_5), 95.6 (MoC_5H_5), 54.4 (OMe)
(1e)	3.69 (s, 3 H, OMe), 5.23 (s, 5 H, WC_5H_5), 5.48 (s, 10 H, TiC_5H_5), 6.8—7.2 (m, 4 H, C_6H_4)	384.9 (μ-C), 226.5, 222.8 (CO), 156.7 [$C^1(C_6H_4)$], 146.2, 124.3, 119.8, 116.6, 110.8 (C_6H_4), 109.8, 109.0 (TiC_5H_5), 94.4 (WC_5H_5), 54.9 (OMe)
(1f)	3.80 (s, 3 H, Me), 5.38, 5.53, 5.70 (s × 3, 15 H, C_5H_5)	406.1 (μ-C), 223.9, 222.8 (CO), 107.6, 107.3 (ZrC_5H_5), 93.2 (WC_5H_5), 53.6 (Me)
(1g)	2.24, 2.81 (s × 2, 6 H, Me-2,6), 5.62 (s, 5 H, WC_5H_5), 5.73, 5.75 (s × 2, 10 H, ZrC_5H_5), 6.73—7.79 (m, 3 H, C_6H_3)	399.0 (μ-C), 226.9, 224.3 (CO), 168.4 [$C^1(C_6H_4)$], 128.7, 127.5, 121.9, 121.3, 119.3 (C_6H_3), 108.9, 108.5 (ZrC_5H_5), 95.2 (WC_5H_5), 23.1, 22.2 (Me-2,6)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz, measurements at room temperature. [b] Measured in $(CD_3)_2CO$. [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of $SiMe_4$. Measurements in CD_2Cl_2–CH_2Cl_2.



	M	M′	R
(1a)	Ti	W	C_6H_4Me-4
(1b)	Zr	W	C_6H_4Me-4
(1c)	Zr	W	C_6H_4OMe-2
(1d)	Zr	Mo	C_6H_4OMe-2
(1e)	Ti	W	C_6H_4OMe-2
(1f)	Zr	W	Me
(1g)	Zr	W	$C_6H_3Me_2$-2,6

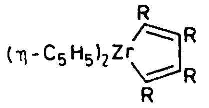
their i.r. spectra. Those for (**1c**) occur at 1 965 and 1 572 cm^{-1}, and may be compared with those seen in the spectrum of (**1b**)[2] at 1 937 and 1 578 cm^{-1}. The band at lowest frequency in these spectra is due to the CO ligand adopting the μ-σ:η^2 bonding mode; a structural feature confirmed for (**1a**) by an *X*-ray diffraction study.[2] Also structurally diagnostic are the resonances for the bridging alkylidyne carbon nuclei in the ^{13}C-{^1H} n.m.r. spectra. For compound (**1c**) the signal occurs at δ 388.0 p.p.m. (Table 2). The corresponding peak in the spectrum of (**1b**) is at 391.2 p.p.m.[2]

For the synthesis of titanium complexes of type (**1**) the use of [$TiCl_2(\eta$-$C_5H_5)_2$] and magnesium amalgam has little advantage over the route described previously.[2] However, for zirconium complexes the more direct synthesis from [$ZrCl_2(\eta$-$C_5H_5)_2$] is advantageous since the alternative precursor [$Zr(CO)_2(\eta$-$C_5H_5)_2$] is obtained in only moderate yield.[7] Moreover, treatment of the latter with [$W(\equiv CC_6H_4Me$-4$)(CO)_2(\eta$-$C_5H_5)$] gives (**1b**) in relatively low yield.[2]

A third route to complexes of type (**1**) was suggested by the recent employment by Negishi *et al.*[8] of the compound [$Zr(Bu^n)_2(\eta$-$C_5H_5)_2$] as a reagent in organic syntheses. The zirconium compound acts as a source of the $Zr(\eta$-$C_5H_5)_2$ fragment *via* elimination of n-butane and but-1-ene. Treatment of Et_2O solutions of [$Zr(Bu^n)_2(\eta$-$C_5H_5)_2$] at 0 °C with [$W(\equiv CC_6H_4OMe$-2$)(CO)_2(\eta$-$C_5H_5)$] affords compound (**1c**) in yields of *ca.* 80%. The reagent [$Zr(Bu^n)_2(\eta$-$C_5H_5)_2$] appears to be stable at 0 °C in Et_2O, and is only consumed slowly upon addition of the alkylidyne–tungsten complex. Thus butane elimination would appear to follow co-ordination of the C≡W bond of the tungsten species to the zirconium centre, so that an 18-electron zirconium intermediate [$ZrW(Bu^n)_2(\mu$-CC_6H_4-OMe-2$)(CO)_2(\eta$-$C_5H_5)_3$] may be mechanistically important, rather than a 16-electron zirconocene–but-1-ene complex [$Zr(\eta$-$CH_2{=}CHEt)(\eta$-$C_5H_5)_2$].

The zirconium–molybdenum compound [$ZrMo(\mu$-CC_6H_4-OMe-2$)(\mu$-$\sigma{:}\eta^2$-$CO)(CO)(\eta$-$C_5H_5)_3$] (**1d**) was prepared by treating [$Zr(Bu^n)_2(\eta$-$C_5H_5)_2$] with [$Mo(\equiv CC_6H_4OMe$-2$)$-$(CO)_2(\eta$-$C_5H_5)$]. Preparation of (**1d**) by this method involves very mild conditions, and is an important result since alkylidyne–molybdenum precursors are less robust than their tungsten analogues, and the former species tend to decompose when used in the other synthetic routes employed for compounds of type (**1**). The corresponding reaction between [$W(\equiv CC_6H_4OMe$-2$)(CO)_2(\eta$-$C_5H_5)$] and [$Ti(Bu^n)_2(\eta$-$C_5H_5)_2$] gave [$TiW(\mu$-CC_6H_4OMe-2$)(\mu$-$\sigma{:}\eta^2$-$CO)(CO)(\eta$-$C_5H_5)_3$] (**1e**). However, it was observed that if thf was used as solvent instead of Et_2O in the synthesis of (**1e**), none of the desired product was obtained. This may be due to the formation of 'titanocene' [$Ti_2(\mu$-$H)_2(\mu$-$\eta^5{:}\eta^{5'}$-$C_{10}H_8)(\eta$-$C_5H_5)_2$][9] which is green in colour and inert to the alkylidyne–metal reagents. We observed that treatment of [$TiCl_2(\eta$-$C_5H_5)_2$] in thf with $LiBu^n$ produced a green material whereas species of the type [$TiR_2(\eta$-$C_5H_5)_2$] (R = alkyl or aryl) are orange. Also if thf is used as solvent elimination of butane and occupation of sites on titanium might be favoured thereby inhibiting access of the tungsten reagent. In this context it has recently been shown[10] that [$Zr(Bu^n)_2(\eta$-$C_5H_5)_2$] reacts with PMe_3 to give the but-1-ene complex [$Zr(\eta$-$CH_2{=}CHEt)(PMe_3)(\eta$-$C_5H_5)_2$].

The two zirconium–tungsten compounds [$ZrW(\mu$-$CR)(\mu$-$\sigma{:}\eta^2$-$CO)(CO)(\eta$-$C_5H_5)_3$] [R = Me (**1f**) or $C_6H_3Me_2$-2,6 (**1g**)] were prepared by treating [$Zr(Bu^n)_2(\eta$-$C_5H_5)_2$] with [$W(\equiv CMe)(CO)_2(\eta$-$C_5H_5)$] and [$W(\equiv CC_6H_3Me_2$-2,6$)(CO)_2$-$(\eta$-$C_5H_5)$], respectively. Data characterising the complexes (**1d**)—(**1g**) are given in Tables 1 and 2. All the compounds show molecular ions in their mass spectra, followed by a peak corresponding to the loss of two CO ligands. The latter give rise to two bands in the i.r. spectra, as mentioned above. The n.m.r. spectra (Table 2) are structurally informative displaying the expected signals. In particular, the ^{13}C-{^1H} n.m.r. spectra show characteristic peaks for the μ-*C* nuclei. These occur in the range δ 384.9—423.4 p.p.m., but are relatively deshielded for dimetal compounds with bridging alkylidyne ligands. Such species are known to show resonances in the range 300—390 p.p.m., but for most compounds the peaks are located between 300 and 350 p.p.m.[11] There are many factors which affect these shifts. For example, signals for μ-*C*Me groups tend to be more deshielded than those of μ-*C*C_6H_4Me-4 ligands [*e.g.*, δ 406.1 for (**1f**) *versus* 388.0 p.p.m. for (**1c**)], and the resonances for the ligating carbon atoms in chromium- or molybdenum-containing species are more deshielded than those in the corresponding tungsten compounds[11a,d] [*e.g.*, δ 423.4 for (**1d**) *versus* 388.0 p.p.m. for (**1c**)]. Moreover, in dimetal compounds which are electronically unsaturated, with 32 valence electrons, the signals for the μ-C nuclei are *ca.* δ 50—120 p.p.m. more deshielded than those in



(**2**) R = Me, Et or Ph

related complexes which are electronically saturated with 34 valence electrons.[11e] The presence of the μ-σ:η^2-CO ligand in the compounds (**1**) formally confers an 18-electron configuration at titanium or zirconium, and hence in these dimetal compounds both metal centres are apparently electronically saturated. However, if electron-pair donation from the μ-CO group to Ti or Zr is weak, it is possible that the π electrons in the C=M′ fragment also interact with a vacant orbital on the Group 4 metal, resulting in a shift to low-field of the μ-C ^{13}C-{^{1}H} n.m.r. signal.

During the course of the work it was observed that although [HfCl$_2$(η-C$_5$H$_5$)$_2$] reacted with two equivalents of LiBu^n, the resulting mixture failed to combine with [W(≡CC$_6$H$_4$OMe-2)(CO)$_2$(η-C$_5$H$_5$)] to afford a hafnium–tungsten complex analogous to (**1c**) or (**1e**). In other studies it was found that the compound [Mo(≡CC$_6$H$_4$OMe-2)(CO)$_2${HB(pz)$_3$}] [HB(pz)$_3$ = hydrotris(pyrazol-1-yl)borate] reacts with [Zr(Bu^n)$_2$(η-C$_5$H$_5$)$_2$] to give an orange product with an i.r. spectrum similar to (**1d**). However this species was very air sensitive, and decomposed in solution at room temperature. It therefore could not be characterised. It is likely that the low stability is due to the steric problems associated with the bulky HB(pz)$_3$ ligand. It should also be mentioned that we were unable to prepare titanium or zirconium–chromium compounds using [Cr(≡CC$_6$H$_4$OMe-2)(CO)$_2$(η-C$_5$H$_5$)] as a precursor.

In view of the isolobal relationship between alkynes and the reagents [M(≡CR)(CO)$_2$(η-C$_5$H$_5$)] (M = Mo or W, R = alkyl or aryl)[12] it is interesting to compare the syntheses described herein with analogous reactions involving alkynes. Thus treatment of thf solutions of [ZrCl$_2$(η-C$_5$H$_5$)$_2$] with magnesium in the presence of alkynes affords the bis(η-cyclopentadienyl)zirconacyclopentadiene complexes (**2**).[13] We obtained no evidence in our work with the alkylidyne–molybdenum or tungsten compounds for the formation of products containing trimetallacyclopentadiene ring systems structurally akin to the complexes (**2**). Indeed, previous work[14] suggests that if such species were formed reductive elimination would occur to yield μ-alkyne dimetal compounds [M$_2$(μ-RC$_2$R)(CO)$_4$(η-C$_5$H$_5$)$_2$]. However, no evidence for the formation of these complexes was obtained.

Experimental

The experimental procedures used and the instrumentation employed in spectroscopic measurements have been described earlier.[1] The compound [W(≡CC$_6$H$_4$OMe-2)(CO)$_2$(η-C$_5$H$_5$)] was prepared by the method used to obtain its molybdenum analogue,[11e] whilst the complexes [W(≡CR)(CO)$_2$(η-C$_5$H$_5$)] (R = Me, C$_6$H$_4$Me-4,[15] or C$_6$H$_3$Me$_2$-2,6 [11e]) were prepared as reported previously. Light petroleum refers to that fraction of b.p. 40–60 °C. Analytical and other data for the new compounds are given in Table 1.

Synthesis of the Dimetal Compounds.—The complexes were prepared using two different methods and only one example of each procedure is given. Yields listed in Table 1 refer to preparations *via* the di-n-butylmetallocenes, these being in general higher than the method using magnesium.

(*i*) Finely ground [ZrCl$_2$(η-C$_5$H$_5$)$_2$] (1.0 g, 3.4 mmol) was suspended in Et$_2$O (50 cm^3) and cooled to −40 °C. A hexane solution of LiBu^n (4.3 cm^3, 6.9 mmol) was added dropwise, and the mixture was stirred for 30 min, during which time a homogeneous pale yellow solution formed, followed by precipitation of LiCl. The mixture was warmed to −10 °C and treated with [W(≡CC$_6$H$_4$OMe-2)(CO)$_2$(η-C$_5$H$_5$)] (1.0 g, 2.34 mmol), and the reactants were allowed to warm to room temperature. After stirring for 3 h, or until all of the alkylidyne–tungsten complex had been consumed (monitored by i.r.), solvent was removed *in vacuo*. The residue was extracted with CH$_2$Cl$_2$ (3 × 5 cm^3) and the extract was chromatographed on an alumina column (3 × 45 cm, at −35 °C), eluting with the same solvent. An orange-red eluate [yellow in the case of compound (**1f**)] was collected, and the solvent was removed *in vacuo*. The residue was triturated with light petroleum (10 cm^3), and the latter was removed by decantation from the resulting suspension affording orange *microcrystals* of [ZrW(μ-CC$_6$H$_4$OMe-2)(μ-σ:η^2-CO)(CO)(η-C$_5$H$_5$)$_3$] (**1c**) (1.22 g), which were dried *in vacuo*. The complex may be crystallised from CH$_2$Cl$_2$–light petroleum (1:5) at *ca.* −80 °C.

For the titanium–tungsten compound (**1e**), addition of LiBu^n to [TiCl$_2$(η-C$_5$H$_5$)$_2$] was carried out at −80 °C, and the resulting orange solution was warmed to −40 °C and treated with [W(≡CC$_6$H$_4$OMe-2)(CO)$_2$(η-C$_5$H$_5$)]. The mixture was stirred for 5 h at 0 °C. Subsequent work-up and isolation of product was as for (**1c**).

(*ii*) Magnesium turnings (0.50 g) were flame dried in a Schlenk tube *in vacuo*. A dry nitrogen atmosphere was admitted, followed by HgCl$_2$ (0.05 g) and thf (50 cm^3). The mixture was stirred for 1 h and then treated with [ZrCl$_2$(η-C$_5$H$_5$)$_2$] (1.0 g, 3.4 mmol) followed by [W(≡CC$_6$H$_4$OMe-2)(CO)$_2$(η-C$_5$H$_5$)] (1.0 g, 2.3 mmol). The reactants were stirred for 1 d, the reaction time being dependent on the activity of the magnesium–mercury surface. Accordingly, the progress of the reaction should be monitored by i.r. spectroscopy (2 000—1 500 cm^{-1}). Solvent was removed *in vacuo*, and the residue was worked up following a similar procedure to that described above, yielding 1.09 g of desired product, (**1c**).

Acknowledgements

We thank the S.E.R.C. for support and the Deutscher Akademischer Austauschdienst for award of a grant (to H. D. H.).

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Received 11*th January* 1988; *Paper* 8/00119G