Triadic coupling between hydride, acetylide and alkyne on the complex [WRe(η-C_5Me_5)O$(CO)_4$(μ-H)(CCPh)]. Crystal structures of complexes containing a substituted cyclopentadienylidene ligand or a folded metallacyclopentadienyl fragment

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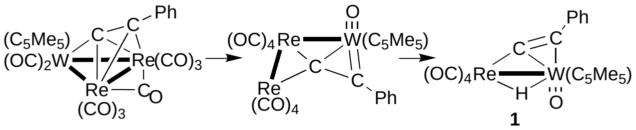
The reaction of the dinuclear oxoacetylide complex [WRe(η-C_5Me_5)O$(CO)_4$(μ-H)(μ-CCPh)] **1** with dimethyl acetylenedicarboxylate afforded the bis(alkylidene) complex [WRe(η-C_5Me_5)O$(CO)_3$(μ-CHPh){μ-$C_5(CO_2Me)_4$}] **2**, generated by formal co-ordination of two alkynes and cleavage of a C−C bond. In contrast, treatment of **1** with an excess of di-*p*-tolylacetylene in refluxing toluene gave three complexes [WRe(η-C_5Me_5)O$(CO)_3${CH(Ph)CC(C_6H_4Me-*p*)CH(μ-η^2-C_6H_3Me)}] **3**, [WRe(η-C_5Me_5)O$(CO)_3${μ-C_4Ph[C_2H(C_6H_4Me-*p*)$_2$](C_6H_4Me-*p*)$_2$}] **4** and [WRe(η-C_5Me_5)O$(CO)_3${μ-C_4[C_2H(C_6H_4Me-*p*)$_2$]Ph(C_6H_4Me-*p*)$_2$}] **5**. Compounds **4** and **5**, which possess a folded metallacyclopentadienyl fragment, are produced by hydride migration to alkyne, giving a *cis*-ditolylalkenyl substituent, followed by coupling with acetylide and a second ditolylacetylene molecule. Compound **3** is probably produced by a distinct sequence, involving initial formation of a C(C_6H_4Me-*p*)C(C_6H_4Me-*p*)CCHPh linkage, followed by orthometallation and hydrogen transfer. Single-crystal structural analyses of **2–5** have been performed and the possible reaction mechanisms leading to their isolation are presented.

Studies on organometallic oxo complexes[1] have intensified in recent years as a result of the implication of such species in catalytic oxidations, or as reagents in the oxidation of organic molecules.[2] We are interested in studying the chemistry of oxo-containing metal complexes or clusters as they may provide knowledge of the behaviour of organometallic compounds with metals in highly disparate oxidation states.[3] Therefore, elucidation of the reactivity and structural features of such complexes is crucial to a further understanding of how oxide ligands bond to the metal atoms,[4] and how they affect other ancillary ligands in the co-ordination sphere.[5]

For these reasons we prepared a trinuclear oxoacetylide cluster compound [WRe_2(η-C_5Me_5)O$(CO)_8$(μ-CCPh)] through treatment of the parent [WRe_2(η-C_5Me_5)$(CO)_9$(μ-CCPh)] with oxygen in solution, and investigated its degradation to a dinuclear analogue [WRe(η-C_5Me_5)O$(CO)_4$(μ-H)(μ-CCPh)] **1**, induced by treatment with benzenethiol under a carbon monoxide atmosphere (Scheme 1).[6a,b] Herein we report the reactions of **1** with disubstituted alkynes, such as dimethyl acetylenedicarboxylate (dmad) or di-*p*-tolylacetylene. Among the products generated from these reactions, we have characterised one complex [WRe(η-C_5Me_5)O$(CO)_3$(μ-CHPh){μ-$C_5(CO_2Me)_4$}] **2** which contains a unique bridging cyclopentadienylidene ligand, and a second dinuclear compound [WRe(η-C_5Me_5)O$(CO)_3${CH(Ph)CC(C_6H_4Me-*p*)CH(μ-η^2-C_6H_3Me)}] **3**, in which the organic ligand bridges to the non-bonded metal centres *via* a multisite interaction, as well as two ferrole-like derivatives [WRe(η-C_5Me_5)O$(CO)_3${μ-C_4Ph[C_2H(C_6H_4Me-*p*)$_2$](C_6H_4Me-*p*)$_2$}] **4** and [WRe(η-C_5Me_5)O$(CO)_3${μ-C_4[C_2H(C_6H_4Me-*p*)$_2$]Ph(C_6H_4Me-*p*)$_2$}] **5**. The last two complexes are unusual because they possess a rare, highly distorted metallacyclopentadienyl fragment[7] with the C_4 unit nearly perpendicular to the W−Re vector.



Scheme 1

Experimental

General information and materials

Infrared spectra were recorded on a Perkin-Elmer 2000 FT-IR spectrometer, ^{1}H and ^{13}C NMR spectra on Bruker AM-400, Varian Gemini-300 or Varian Unity-400 instruments. The ^{1}H and ^{13}C NMR chemical shifts are quoted with respect to tetramethylsilane as internal standard. Mass spectra were obtained on a JEOL-HX110 instrument operating in fast atom bombardment (FAB) mode. The metal acetylide complex [WRe(η-C_5Me_5)O$(CO)_4$(μ-H)(μ-CCPh)][6a,b] and di-*p*-tolylacetylene[6c] were prepared according to literature procedures, dmad was purchased from Aldrich. All reactions were performed under a nitrogen atmosphere using deoxygenated solvents dried with an appropriate reagent. Reactions were monitored by analytical thin-layer chromatography (5735 Kieselgel 60 F_{254}, E. Merck) and the products separated on commercially available preparative thin-layer chromatographic plates (Kieselgel 60 F_{254}, E. Merck). Elemental analyses were carried out at the regional instrumentation centre at National Cheng Kung University, Tainan, Taiwan.

Reactions of compound 1

With dmad. A toluene solution (50 cm^3) of compound **1** (58 mg, 0.079 mmol) and dmad (15 μl) was heated to reflux for 3 h, during which it changed from orange to brown. After the removal of solvent, the residue was separated using thin-layer chromatography [dichloromethane–hexane (1 : 2)] giving [WRe(η-C_5Me_5)O$(CO)_3$(μ-CHPh){μ-$C_5(CO_2Me)_4$}] **2** (16.3 mg, 0.016

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mmol, 43%) and unchanged starting material (29 mg). Crystals of **2** suitable for X-ray diffraction study were obtained from dichloromethane–heptane at room temperature. FAB mass spectrum (^{184}W, ^{187}Re): *m/z* 991 (M^+). IR(C_6H_{12}): ν(CO) 2035vs, 1970s and 1937s cm^{-1}. NMR ($CDCl_3$, 294 K): ^{1}H (300 MHz), δ 7.42 (d, 2 H, $J_{HH} = 7.5$), 7.36 (t, 2 H, $J_{HH} = 7.5$), 7.04 (t, 1 H, $J_{HH} = 7.5$), 6.43 (s, C*H*Ph), 3.88 (s, 3 H, Me), 3.83 (s, 3 H, Me), 3.74 (s, 3 H, Me), 3.71 (s , 3 H, Me) and 1.77 (s, 15 H, C_5Me_5); ^{13}C (75.5 MHz), δ 198.2, 197.8, 191.6 (CO), 175.7, 170.5 (μ-*C*HPh, $J_{WC} = 43$ Hz), 168.1, 166.3, 164.5, 162.7, 149.1 (*ipso*-C of Ph), 133.1, 132.9, 132.0, 129.2 (2 C, *o*-C of Ph), 126.1 (2 C, *m*-C of Ph), 125.8 (*p*-C of Ph), 114.4 (C_5Me$_5$), 55.0 (Me), 52.5 (2 Me), 52.0 (Me) and 10.0 (C_5Me_5) (Found: C, 39.85; H, 3.4. Calc. for $C_{33}H_{32}O_{12}ReW$: C, 40.0; H, 3.25%).

With ditolylacetylene. A toluene solution (50 cm^3) of compound **1** (33 mg, 0.045 mmol) and ditolylacetylene (22 mg, 0.107 mmol) was refluxed for 7 h, during which it changed from yellow-orange to orange. After removal of solvent, the residue was separated using thin-layer chromatography [dichloromethane–hexane (1:1)] giving unchanged **1** (13 mg, 39%), orange [WRe(η-C_5Me_5)O(CO)$_3${μ-C_4[C_2H(C_6H_4Me-*p*)$_2$]Ph(C_6H_4Me-*p*)$_2$}] **5** (13.5 mg, 0.012 mmol, 27%), yellow-orange [WRe(η-C_5Me_5)O(CO)$_3${μ-C_4Ph[C_2H(C_6H_4Me-*p*)$_2$](C_6H_4Me-*p*)$_2$}] **4** (4.3 mg, 0.0038 mmol, 8%) and orange [WRe(η-C_5Me_5)O(CO)$_3${CH(Ph)CC(C_6H_4Me-*p*)CH(μ-η^2-C_6H_3Me)}] **3** (3.5 mg, 0.0038 mmol, 8%). Crystals **3–5** suitable for X-ray diffraction studies were recrystallised at room temperature from mixtures of CH_2Cl_2–heptane, CCl_4–hexane and acetone–heptane, respectively.

Compound **3**: FAB mass spectrum (^{184}W, ^{187}Re) *m/z* 914 (M^+). IR(C_6H_{12}): ν(CO) 2022vs, 1942s and 1925s; ν(W≡O) 920 (br) cm^{-1}. NMR ($CDCl_3$, 294 K): ^{1}H (300 MHz), δ 7.85–7.83 (m, 3 H), 7.40 (d, 1 H, $J_{HH} = 8.7$), 7.33–7.28 (m, 4 H), 7.11–7.05 (m, 4 H), 6.00 (s, 1 H, CH), 2.41 (s, 3 H, Me), 2.34 (s, 3 H, Me), 2.21 (s, 1 H, CH) and 1.62 (s, 15 H, C_5Me_5); ^{13}C (75.5 MHz), δ 194.4 (3 CO), 148.6, 148.0, 139.6, 136.3, 133.5, 132.7, 129.0 (2 C), 128.8 (2 C), 128.0 (2 C), 127.8, 127.6 (2 C), 125.8, 121.5, 118.2, 112.9 (C_5Me$_5$), 97.7, 92.6, 73.5 (CH), 38.6 ($J_{WC} =$ 38 Hz, CH), 21.2 (Me), 21.0 (Me) and 10.7 (C_5Me_5) (Found: C, 48.45; H, 3.9. Calc. for $C_{37}H_{35}O_4ReW$: C, 48.65; H, 3.85%).

Compound **4**: FAB mass spectrum (^{184}W, ^{187}Re) *m/z* 1120 (M^+). IR(C_6H_{12}): ν(CO) 2015vs, 1936s (br) and 1906s (br) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 294 K): δ 7.64–6.48 (m, 20 H), 5.72 (d, br, 2 H), 2.31 (s, 3 H, Me), 2.16 (s, 3 H, Me), 2.13 (s, 6 H, 2 Me) and 1.76 (s, 15 H, C_5Me_5) (Found: C, 46.7; H, 3.55. Calc. for $C_{53}H_{49}O_4ReW{\cdot}2CCl_4$: C, 46.25; H, 3.45%).

Compound **5**: FAB mass spectrum (^{184}W, ^{187}Re) *m/z* 1120 (M^+). IR(C_6H_{12}): ν(CO) 2012vs, 1930s (br) and 1908s (br) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, 294 K): δ 7.20–6.43 (m, 22 H), 2.30 (s, 3 H, Me), 2.24 (s, 3 H, Me), 2.18 (s, 3 H, Me), 2.07 (s, 15 H, C_5Me_5) and 1.86 (s, 3 H, Me) (Found: C, 56.7; H, 4.5. Calc. for $C_{53}H_{49}O_4ReW$: C, 56.85; H, 4.4%).

X-Ray crystallography

The X-ray diffraction measurements were carried out on a Nonius CAD-4 diffractometer. Lattice parameters were determined from 25 randomly selected high-angle reflections. Three standard reflections were monitored every 3600 s. No significant change in intensities, due to crystal decay, was observed over the course of all data collection. Intensities of the diffraction signals were corrected for Lorentz-polarisation and absorption effects (ψ scans). The structure was solved by using the NRCC-SDP-VAX package.[8] All the non-hydrogen atoms had anisotropic thermal parameters, and the hydrogen atoms were placed at idealised positions with $U_H = U_C + 0.1$ Å^2. The crystallographic refinement parameters of complexes **2–5** are given in Table 1, while selected bond distances and angles are presented in Tables 2–5 respectively.

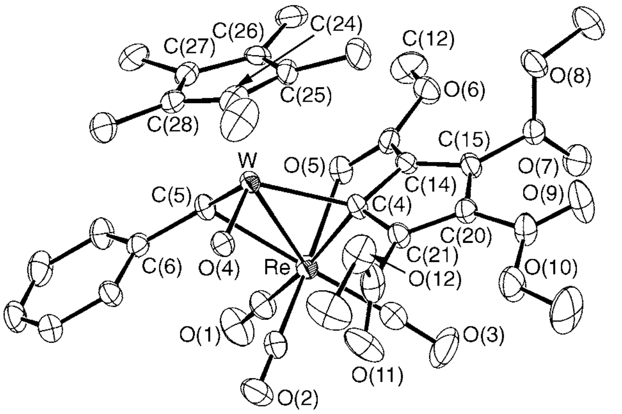


Fig. 1 Molecular structure of [WRe(η-C_5Me_5)O(CO)$_3$(μ-CHPh)-{μ-C_5(CO_2Me)$_4$}] **2** showing the atomic labelling scheme and the thermal ellipsoids at 30% probability

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/461.

Results and Discussion

Reaction of compound 1 with dmad

The synthesis of compound **2** was effected by the reaction of **1** with dmad in refluxing toluene solution. Addition of 1 equivalent of Me_3NO to an acetonitrile solution of **1**, followed by heating of the resulting acetonitrile-substituted complex [WRe(η-C_5Me_5)O(CO)$_3$(NCMe)(μ-H)(μ-CCPh)][6b] with dmad also affords **2**, with no formation of any reaction intermediate. Elemental analysis and mass spectroscopy indicated that **2** was a 1:2 adduct of **1** and alkyne ligands. The IR spectrum showed, in addition to the terminal Re–CO stretching bands, two bands at 1738 and 1716 cm^{-1} due to the pendant CO_2Me groups and one weak band at 1575 cm^{-1}, assigned to the CO_2Me group with its oxygen co-ordinated to a metal atom.[9] The ^{1}H NMR spectrum suggests that the hydride has transferred to hydrocarbyl fragments, resulting in a signal at δ 6.43. The ^{13}C NMR data are likewise consistent with this formulation, showing three Re–CO resonances, four signals due to the phenyl substituent and three methyl signals for four CO_2Me functional groups with ratio 1:2:1. The CH group was observed at δ 170.5 and showed the presence of tungsten satellites ($J_{WC} = 43$ Hz), while the assignment of other resonance signals is less obvious. In order to identify **2**, particularly with regard to the identity of the hydrocarbyl groups, a single-crystal X-ray diffraction study was undertaken.

An ORTEP[10] diagram of the molecular structure of compound **2** is depicted in Fig. 1. Compound **2** possesses a (C_5Me_5)WO and a Re(CO)$_3$ unit linked by a W–Re bond, which is bridged by an alkylidene μ-CHPh ligand on one side and a cyclopentadienylidene group C(CCO$_2$Me)$_4$ on the other. The cyclopentadienylidene ligand seems to be planar and exhibits a configuration perpendicular to the triangular plane defined by the W, Re and C(4) atoms. In addition, the carboxylate substituent on C(14) is co-ordinated to the Re atom by its carbonyl oxygen atom. As the result, the Re–CO(1) distance, which is *trans* to this oxygen atom, becomes substantially shorter than the other two Re–CO distances. Thus, the molecular geometry of **2** resembles that found in the heterodinuclear complex [FeRe(η-C_5H_5)CC(CO_2Me)$_2$C(S)N(C_6H_4Me)C(O)}(CO)$_5$],[11] which contains one bridging CO ligand and a pentagonal C_4N carbene fragment bridging the Fe–Re bond, with one carboxylate group co-ordinated to the Re atom by its oxygen atom.

Table 1 Experimental data for the X-ray diffraction studies of complexes **2**–**5***

	2	**3**	**4**	**5**
Formula	$C_{33}H_{32}O_{12}ReW{\cdot}CH_2Cl_2$	$C_{37}H_{35}O_4ReW$	$C_{53}H_{49}O_4ReW{\cdot}2CCl_4$	$C_{53}H_{49}O_4ReW$
M	1075.61	913.73	1427.66	1120.01
Crystal system	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	Cc	$P\bar{1}$	$P2_1/n$
a/Å	9.725(3)	9.861(3)	13.872(3)	16.528(2)
b/Å	21.105(4)	16.053(5)	14.391(3)	11.400(1)
c/Å	18.767(4)	20.020(4)	14.777(6)	23.678(2)
α/°			103.07(4)	
β/°	103.29(2)	91.10(2)	95.56(3)	92.517(9)
γ/°			97.87(2)	
U/Å^3	3749(2)	3169(2)	2821(1)	4457(1)
Z	4	4	2	4
D_c/g cm^{-3}	1.900	1.915	1.681	1.669
F(000)	2068	1752	1392	2192
h k l Ranges	−11 to 11, 0–25, 0–22	−13 to 13, 0–22, 0–28	−16 to 16, 0–17, −17 to 17	−19 to 19, 0–13, 0–28
Crystal size/mm	0.05 × 0.08 × 0.40	0.15 × 0.25 × 0.55	0.30 × 0.60 × 0.60	0.30 × 0.50 × 0.50
μ(Mo-Kα)/cm^{-1}	64.56	75.98	44.77	54.28
Maximum, minimum transmission	1.00, 0.73	1.00, 0.60	1.00, 0.67	1.00, 0.73
No. unique data	6597	4571	9913	7841
data with $I > 2\sigma(I)$	4630	4049	7349	6170
No. atoms and parameters	82, 461	78, 387	118, 623	108, 533
g	0.000 07	Unit weight	Unit weight	0.000 05
Maximum Δ/σ ratio	0.0014	0.009	0.044	0.011
R, *R′*	0.030, 0.030	0.030, 0.025	0.035, 0.039	0.028, 0.028
Goodness of fit	1.32	1.83	1.08	1.43
Maximum, minimum residual electon density/e Å^{-3}	0.97, −0.73	1.05, −1.17	1.17, −0.87	0.83, −0.66

* Features common to all determinations: λ(Mo-Kα) = 0.7107 Å; $2\theta_{max} = 50°$; function minimised $\Sigma (w|F_o - F_c|^2)$; weighting scheme $w^{-1} = \sigma^2(F_o) + |g| F_o^2$; goodness of fit $= [\Sigma w|F_o - F_c|^2/(N_o - N_v)]^{\frac{1}{2}}$ (N_o = number of observations, N_v = number of variables).

Table 2 Selected bond distances (Å) and angles (°) for compound **2** with estimated standard deviations (e.s.d.s) in parentheses

W–Re	2.7757(8)	W–O(4)	1.703(5)
W–C(4)	2.149(7)	W–C(5)	2.065(7)
Re–O(5)	2.234(5)	Re–C(4)	2.258(7)
Re–C(5)	2.277(8)	O(5)–C(13)	1.262(9)
C(4)–C(14)	1.47(1)	C(4)–C(21)	1.44(1)
C(14)–C(15)	1.37(1)	C(15)–C(20)	1.42(1)
C(20)–C(21)	1.37(1)		
W–C(4)–Re	78.0(2)	W–C(5)–Re	79.3(2)
Re–C(1)–O(1)	179.7(8)	Re–C(2)–O(2)	178.7(7)
Re–C(3)–O(3)	176.1(8)		

Table 3 Selected bond distances (Å) and angles (°) for compound **3** with e.s.d.s in parentheses

W···Re	3.383(1)	W–O(4)	1.760(6)
W–C(4)	2.189(9)	W–C(5)	2.022(9)
W–C(27)	2.261(8)	Re–C(5)	2.200(8)
Re–C(6)	2.290(9)	Re–C(7)	2.274(9)
Re–C(21)	2.362(9)	Re–C(27)	2.497(8)
C(4)–C(5)	1.42(1)	C(5)–C(6)	1.44(1)
C(6)–C(7)	1.40(1)	C(7)–C(21)	1.47(1)
C(21)–C(27)	1.40(1)		
Re–C(1)–O(1)	176.4(8)	Re–C(2)–O(2)	175.0(9)
Re–C(3)–O(3)	179.5(9)		

Reaction of compound 1 with di-*p*-tolylacetylene

Treatment of compound **1** with di-*p*-tolylacetylene leads to the formation of three complexes identified as orange [WRe(η-C_5Me_5)O(CO)$_3${CH(Ph)CC(C_6H_4Me-*p*)CH(μ-η^2-C_6H_3Me)}] **3** and the metallacyclopentadienyl complexes [WRe(η-C_5Me_5)-O(CO)$_3${μ-C_4Ph[C_2H(C_6H_4Me-*p*)$_2$](C_6H_4Me-*p*)$_2$}] **4** and [WRe-(η-C_5Me_5)O(CO)$_3${μ-C_4[C_2H(C_6H_4Me-*p*)$_2$]Ph(C_6H_4Me-*p*)$_2$}] **5**. Complex **3** can be easily separated by thin-layer chromatography, followed by recrystallisation from CH_2Cl_2 and heptane at room temperature. Complexes **4** and **5** exhibit very similar R_f values on the TLC plates; therefore, their purification is more laborious. Two distinctive crystals of yellow-orange **4** and orange **5** were obtained by carrying out the recrystallisation of this mixture in a solution of CH_2Cl_2 and diethyl ether at −20 °C. After the separation by hand picking, single crystals suitable for X-ray diffraction studies were obtained by further recrystallisation from CCl_4 and hexane, and in acetone and heptane, at room temperature, respectively.

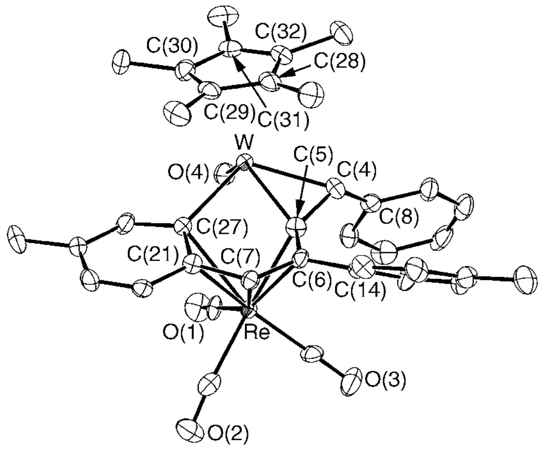


Fig. 2 Molecular structure of [WRe(η-C_5Me_5)O(CO)$_3${CH(Ph)-CC(C_6H_4Me-*p*)CH(μ-η^2-C_6H_3Me)}] **3**. Details as in Fig. 1

The molecular structure of compound **3** is depicted in Fig. 2. The W–Re distance [3.383(1) Å] is far beyond the expected M–M single-bond interaction.[12] The W atom is linked to an *o*-carbon atom of the tolyl fragment *via* a σ interaction and to the C=CHPh terminus *via* π bonding, thus the local environment of the (C_5Me_5)WO fragment resembles that found in the oxoalkyne complexes [Mo(η-C_5H_5)O(PhC$_2$Ph){Ru(η-C_5H_5)-(CO)$_2$}], [W(η-C_5H_5)O(HC$_2$Ph)(CH$_2$CO$_2$Et)] and [Mo(η-C_5H_5)O(CF$_3$C$_2$CF$_3$)(SC$_6$F$_5$)].[13] On the contrary, the Re atom is co-ordinated to the U-shaped C(5)–C(6)–C(7)–C(21)–C(27) unit *via* an η^5 interaction. The Re–C distances deviate substantially and span a large range, with Re–C(21) 2.362(9) and

Table 4 Selected bond distances (Å) and angles (°) of compound **4** with e.s.d.s in parentheses

W–Re	3.075(1)	W–O(4)	1.736(5)
W–C(4)	2.048(7)	W–C(5)	2.445(7)
W–C(6)	2.446(7)	W–C(7)	2.038(7)
Re–C(4)	2.266(7)	Re–C(5)	2.317(7)
Re–C(6)	2.318(7)	Re–C(7)	2.257(7)
C(4)–C(5)	1.47(1)	C(5)–C(6)	1.46(1)
C(6)–C(7)	1.463(9)	C(6)–C(14)	1.51(1)
C(14)–C(15)	1.33(1)		
Re–C(1)–O(1)	177.4(1)	Re–C(2)–O(2)	177.9(7)
Re–C(3)–O(3)	178.7(9)	C(4)–C(5)–C(6)	119.5(6)
C(5)–C(6)–C(7)	118.8(6)	C(6)–C(14)–C(15)	117.4(6)
C(6)–C(14)–C(30)	117.4(6)	C(14)–C(15)–C(37)	130.3(7)

Table 5 Selected bond distances (Å) and angles (°) for compound **5** with e.s.d.s in parentheses

W–Re	3.1055(5)	W–O(4)	1.732(4)
W–C(4)	2.049(5)	W–C(5)	2.466(5)
W–C(12)	2.451(5)	W–C(13)	2.059(5)
Re–C(4)	2.292(5)	Re–C(5)	2.284(5)
Re–C(12)	2.299(5)	Re–C(13)	2.242(5)
C(4)–C(5)	1.466(7)	C(5)–C(12)	1.476(7)
C(12)–C(13)	1.443(7)	C(4)–C(28)	1.500(7)
C(28)–C(29)	1.334(8)		
Re–C(1)–O(1)	176.1(7)	Re–C(2)–O(2)	175.3(5)
Re–C(3)–O(3)	176.5(7)	C(4)–C(28)–C(29)	118.3(5)
C(4)–C(28)–C(30)	120.7(5)	C(28)–C(29)–C(37)	131.2(5)

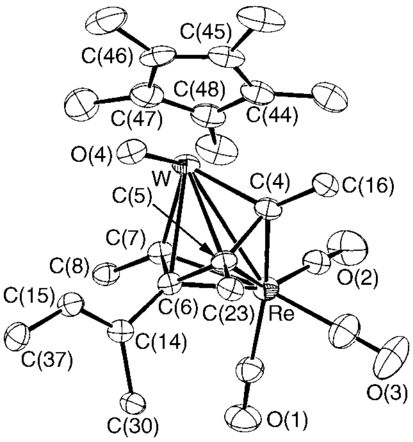
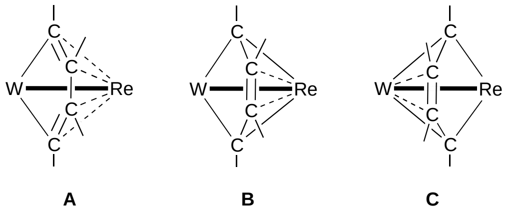


Fig. 3 Molecular structure of [WRe(η-C$_5$Me$_5$)O(CO)$_3${μ-C$_4$Ph[C$_2$H(C$_6$H$_4$Me-*p*)$_2$](C$_6$H$_4$Me-*p*)$_2$}] **4** with the phenyl and the tolyl substituents, except for the *ipso*-carbon, deleted for clarity



Scheme 2

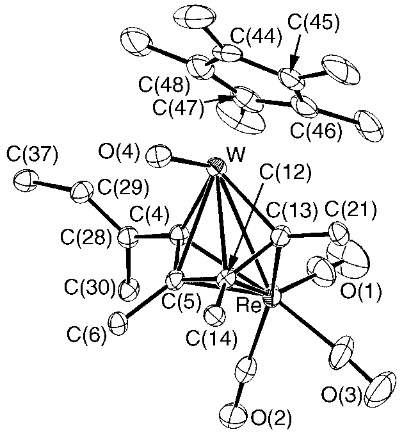


Fig. 4 Molecular structure of [WRe(η-C$_5$Me$_5$)O(CO)$_3${μ-C$_4$[C$_2$H(C$_6$H$_4$Me-*p*)$_2$]Ph(C$_6$H$_4$Me-*p*)$_2$}] **5**. Details as in Fig. 3

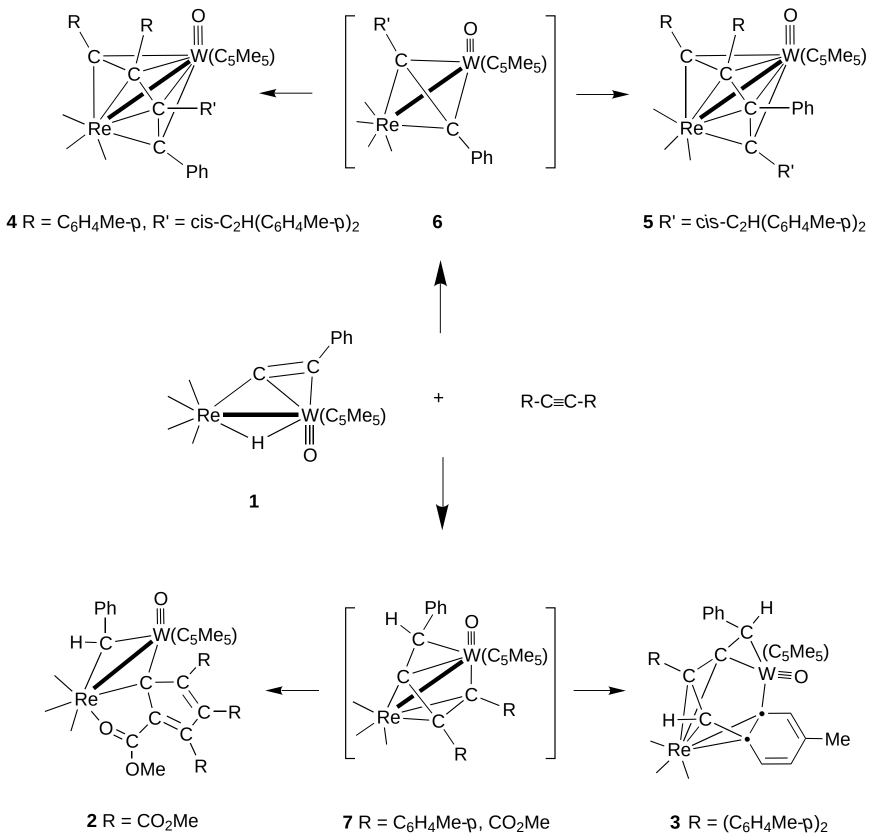
Re–C(27) 2.497(8) Å being significantly longer than those to C(5)–C(7), which are in the range 2.200(8)–2.290(9) Å. Such a large deviation is due to the resonance stabilisation of the π orbitals within the C$_6$ ring of the tolyl group which reduces the donor interaction to the Re atom. The elongation of M–C distances to an aromatic hexagonal ring has been observed for the mononuclear benzyl complexes of Re and W[14] and clusters containing an orthometallated phenyl substituent.[15]

An ORTEP diagram of compound **4** is shown in Fig. 3 with the distances listed in Table 4. The central C$_4$ fragment contains one phenyl group located at atom C(7) and two tolyl substituents at atoms C(4) and C(5) and a *cis*-ditolylalkenyl functional group, C(C$_6$H$_4$Me-*p*)=CH(C$_6$H$_4$Me-*p*), at atom C(6). All C–C distances within this C$_4$ fragment are essentially equal. The C$_4$ fragment forms a folded tungstacyclopentadienyl fragment and is linked to the Re(CO)$_3$ fragment in a manner similar to that of the ferrole-like molecules.[16] In agreement with this description, the calculated bent angle between the C$_4$ plane and the Re–C(4)–C(7) triangle is 87.7(4)°. The Re–C distances show a pattern of two long and two short [Re–C(4) 2.266(7), Re–C(5) 2.317(7), Re–C(6) 2.318(7) and Re–C(7) 2.257(7) Å], indicating that the Re atom is bonded much closer to two terminal carbon atoms and is slightly off the centre of the C$_4$W ring.

However, it is noteworthy that the bent angle between the W–C(4)–C(7) triangle and the C$_4$ plane is 117.9(4)°, with the W atom 1.276(9) Å above the C$_4$ extension. As a result, the presence of substantial π bonding between the W atom and the inner carbon atoms C(5) and C(6) of the C$_4$ fragment is confirmed, W–C(5) 2.445(7) and W–C(6) 2.446(7) Å. This unique bonding mode is in contrast to that of the typical metallacyclopentadienyl complexes which always contain one metal atom in the C$_4$ plane,[16] but is related to that of the isostructural bicapped-tetrahedral complex [{Mo(η-C$_5$H$_5$)Cl}$_2${μ-C$_4$(C$_6$H$_4$Me)$_4$}],[7] in which both Mo atoms are linked to all four carbon atoms, giving the so-called folded metallacyclopentatriene geometry.

Based on these structural data, although complex **4** can be considered to inherit some bonding features from the ferrole-like molecule **A** as discussed earlier,[16] it is even more likely that both structures **B** and **C** are important contributing forms (Scheme 2). The key feature of **B** and **C** includes a bridging alkylidene interaction between the terminal carbon atoms and the W–Re edge. In addition, they contain alkene to metal π bonding through the remote C=C double bond in a manner related to that in the metallacyclopentatriene complex [{Mo(η-C$_5$H$_5$)Cl}$_2${C$_4$(C$_6$H$_4$Me)$_4$}],[7,17] and early transition-metal butadiene complexes,[18] which is indicated by the longer M–C distances to two inner carbon atoms with respect to the terminal M–C distances. Parallel to this argument, the resonance form **C** appears to be less important than **B**, as the W–C distances to the inner carbon atoms are much longer than the respective Re–C distances, and the bent angle is greater.

The structural drawing of compound **5** is depicted in Fig. 4, showing that the *cis*-ditolylalkenyl substituent has now switched with the phenyl substituent at the terminal position. The angles between the W–C(4)–C(13) and the C$_4$ plane



Scheme 3

[118.3(3)°] and between the Re−C(4)−C(13) and the C_4 plane [89.5(3)°] are identical to those of **4** as expected. If we consider that the oxide ligand in these complexes serves as a four-electron donor *via* formation of W≡O bonding and the C_4 group of the metallacyclopentadienyl fragment donates six electrons, electron counting gives 34 valence electrons, which is consistent with the prediction of the effective atomic number rule.

Discussion

The reactions of compound **1** with alkynes lead to the formation of three classes of products. Complex **2** is produced by the addition of two alkynes and cleavage of the acetylide C−C bond. On the other hand, formation of **3** involves orthometallation of a tolyl substituent on the incoming alkyne, while **4** and **5** are each produced by sequential coupling with two alkynes, forming the highly distorted metallacyclopentadienyl framework.

With respect to the possible mechanism (Scheme 3), we believe that complexes **4** and **5** are produced through the prior formation of a μ-η^2-alkyne complex **6** with a dimetallatetrahedrane core.[19] This intermediate is probably produced through formation of a *cis*-ditolylalkenyl *via* insertion of di-*p*-tolylacetylene into the metal–hydride linkage, followed by coupling with the acetylide fragment. The subsequent reaction between **6** and di-*p*-tolylacetylene would generate **4** and **5**, as they comprise two distinctive orientations of introducing the second alkyne molecule. The formation of a metallacyclopentadienyl fragment through the addition of an alkyne to a M_2C_2 dimetallatetrahedrane framework similar to that of **6** is well documented.[19] Nevertheless, the geometry for the metallacyclopentadienyl fragment formed in this study is highly distorted. Such an unusual arrangement is presumably caused by the presence of the oxide ligand on the electron-deficient, high-oxidation-state W atom. We believed that the oxide ligand is ineffective in forming O→W back bonding, which would generate some co-ordinative unsaturation, and thus requires partial overlap with the olefinic π orbital of the C_4 fragment to compensate the deficiency in valence electrons. Fenske–Hall non-empirical MO calculations on the isostructural *cis*[{Mo(η-C_5H_5)Cl}$_2$(C_4H_4)] molecule, however, suggest that the stability is derived from the large gap between the highest occupied and lowest unoccupied orbitals.[20]

In contrast, complexes **2** and **3** were produced through a distinct pathway as their structural analyses revealed the possession of a CHPh terminus, in the form of a bridging alkylidene ligand μ-CHPh and an alkenyl group C=CHPh, respectively. This observation implies that they are probably produced *via* prior hydride migration to the β-carbon of the acetylide, followed by coupling with the alkyne to give the intermediate **7** with a μ-CR=CRC=CHPh linkage, R = CO_2Me or C_6H_4Me-*p*. The orthometallation and transfer of hydrogen to the adjacent carbon atom would give **3** as expected. In addition, as the tolyl substituents in **3** adopt a *trans* configuration, the participation of **6** which is the intermediate to **4** and **5** was unambiguously eliminated. This is because both **4** and **5** possess a *cis*-$C_2H(C_6H_4Me$-*p*$)_2$ group.

Finally, reactions of compound **1** with dmad also passed through **7** as intermediate. Cleavage of the C_4 fragment of **7** and the addition of a second dmad molecule affords **2** with two bridging alkylidene ligands. This reaction resembles that observed for condensation of acetylide complexes [WL-$(CO)_3$(CCPh)] (L = η-C_5H_5 or η-C_5Me_5) and osmium alkyne clusters [$Os_3(C_2R_2)(CO)_{10}$] (R = Me or Ph).[21] Cleavage of the C_4 fragment was reported in the latter case, and the products were found to contain both an alkylidyne ligand μ_3-CPh and a C_3 fragment μ_4-C_3R_2.

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