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# Reactions of cationic carbyne complexes of manganese and rhenium with metal carbonyl anions

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Treatment of $[(\eta\text{-}C_5H_5)(OC)_2Mn{\equiv}CC_6H_5]BBr_4$ **1** and $[(\eta\text{-}C_5H_5)(OC)_2Re{\equiv}CC_6H_5]BBr_4$ **2** with the carbonyl monoanion $[Mn(CO)_5]^-$ **3** in THF at low temperature afforded the ketenyl bridged complexes $[Mn_2\{\mu\text{-}C(CO)C_6H_5\}(CO)_6(\eta\text{-}C_5H_5)]$ **6** and $[ReMn\{\mu\text{-}C(CO)C_6H_5\}(CO)_6(\eta\text{-}C_5H_5)]$ **7** respectively. The analogous reactions of complexes **1** and **2** with $[Co(CO)_4]^-$ **4** gave corresponding ketenyl bridged complexes $[MnCo\{\mu\text{-}C(CO)C_6H_5\}(CO)_5(\eta\text{-}C_5H_5)]$ **8** and $[ReCo\{\mu\text{-}C(CO)C_6H_5\}(CO)_5(\eta\text{-}C_5H_5)]$ **9** respectively. Complexes **1** and **2** reacted with the carbonyl dianion $[W(CO)_5]^{2-}$ **5** to give the dimetal carbene bridged complexes $[MnW\{\mu\text{-}C(H)C_6H_5\}(CO)_7(\eta\text{-}C_5H_5)]$ **10** and $[ReW\{\mu\text{-}C(H)C_6H_5\}(CO)_7(\eta\text{-}C_5H_5)]$ **11** respectively. The structures of complexes **6**, **9** and **11** have been established by X-ray diffraction studies.

## Introduction

There is currently considerable interest in the synthesis and study of a variety of metal–metal bonded transition metal cluster complexes, largely owing to their important role in many catalytic processes and their contribution to novel metal–metal bonds as well as the nature of metal reactions.[1] Some important metal–metal bonded systems are bridged binuclear complexes and these systems are suitable for studying the interaction between two metal reaction sites.[2] Since many transition metal carbene and carbyne bridged complexes are clusters themselves or are the precursors of transition metal cluster complexes, the chemistry of such complexes is an area of current interest. In this regard, we are interested in developing the methodology of the synthesis of transition metal carbene bridged complexes. A number of dimetal carbene bridged complexes reported by Stone and co-workers were synthesized by the reactions[3,4] of carbene complexes with low-valent metal species or by the reaction[5,6] of neutral carbyne complexes with metal hydrides. In our laboratory we employ highly electrophilic cationic carbyne complexes of manganese and rhenium, $[(\eta\text{-}C_5H_5)(OC)_2Mn{\equiv}CC_6H_5]BBr_4$ **1** and $[(\eta\text{-}C_5H_5)(OC)_2Re{\equiv}CC_6H_5]BBr_4$ **2**, with carbonyliron dianions, such as $Na_2[Fe(CO)]_4$, $[NEt_4]_2[Fe_2(CO)_8]$ and $Na_2[Fe_3(CO)_{11}]$, to form the dimetal carbene bridged complexes.[7,8] Recently, we showed that the reaction of the cationic carbyne complex of manganese with the carbonyliron anion $[FeH(CO)_4]^-$ afforded a novel Mn–Fe carbene bridged complex, eqn. (1).[9]

In order to examine the application range of this new synthetic method for dimetal carbene bridged complexes and the effects of different nucleophiles containing metal carbonyl anions on the reactivities of the cationic carbyne complexes and on the reaction products, we chose metal carbonyl monoanions of Groups 7 and 9, such as $Li[Mn(CO)_5]$ **3** and $Li[Co(CO)_4]$ **4**, and metal carbonyl dianions of Group 6, such as $Na_2[W(CO)_5]$ **5**, as nucleophiles for the reactions with cationic carbyne complexes of manganese and rhenium. In this paper we describe these reactions and the structural characterizations of the resulting products.

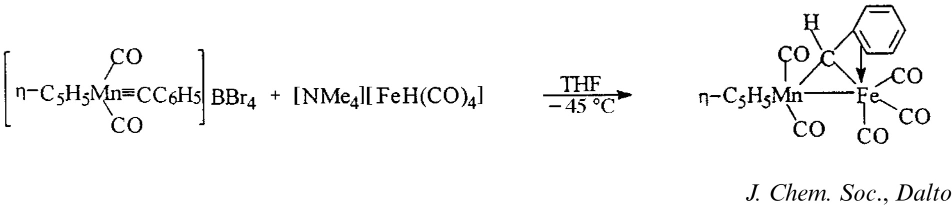
## Experimental

All procedures were performed under a dry, oxygen-free $N_2$ atmosphere by using standard Schlenk techniques. All solvents employed were reagent grade, dried by refluxing over appropriate agents and stored over molecular sieves under $N_2$. Tetrahydrofuran (THF) and diethyl ether ($Et_2O$) were distilled from sodium–benzophenone, while light petroleum (bp 30–60 °C) was distilled from $CaH_2$ and $CH_2Cl_2$ from $P_2O_5$. The neutral alumina ($Al_2O_3$) used for chromatography was deoxygenated at room temperature under high vacuum for 16 h, deactivated with 5% w/w $N_2$-saturated water and stored under $N_2$. The compounds $[(\eta\text{-}C_5H_5)(OC)_2Mn{\equiv}CC_6H_5]BBr_4$ **1**[10] and $[(\eta\text{-}C_5H_5)(OC)_2Re{\equiv}CC_6H_5]BBr_4$ **2**[11] were prepared as previously described, as were the metal carbonyl anions $Li[Mn(CO)_5]$ **3**,[12] $Li[Co(CO)_4]$ **4**[12] and $Na[W(CO)_5]$ **5**.[13]

The IR spectra were measured on a Shimadzu-IR-440 spectrophotometer, $^1H$ NMR spectra at ambient temperature in acetone-$d_6$ solution with TMS as the internal reference using a Bruker AM-300 spectrometer and electron ionization mass spectra (EIMS) on a Hewlett-Packard 5989A spectrometer. Melting points obtained on samples in sealed nitrogen-filled capillaries are uncorrected.

### Reaction of $[(\eta\text{-}C_5H_5)(OC)_2Mn{\equiv}CC_6H_5]BBr_4$ 1 with $Li[Mn(CO)_5]$ 3 to give $[Mn_2\{\mu\text{-}C(CO)C_6H_5\}(CO)_6(\eta\text{-}C_5H_5)]$ 6

To a solution of 0.226 g (0.58 mmol) of $[Mn_2(CO)_{10}]$ in 40 mL of THF were slowly added 1.45 mmol of $LiBH(C_2H_5)_3$ (1.50 mL of 1.0 M THF solution). The mixture was stirred at room temperature for 15 min. The resulting brown-red solution of $Li[Mn(CO)_5]$ **3**[12] was cooled to −90 °C, then poured rapidly on to 0.691 g (1.02 mmol) of complex **1** in 50 mL of THF previously cooled to −90 °C. The mixture was stirred at −90 to



(1)

−60 °C for 5 h, during which time the blackish green solution gradually turned dark red. The resulting mixture was evaporated to dryness under high vacuum at −50 to −40 °C. The dark red residue was chromatographed on an alumina (neutral, 200–300 mesh) column (1.6 × 15 cm) at −25 °C with light petroleum–$CH_2Cl_2$ (15 : 1) as the eluant. The brown-red band was collected, the solvent removed *in vacuo*, and the residue recrystallized from light petroleum–$CH_2Cl_2$ solution at −80 °C to give 0.45 g (84%, based on **1**) of dark red crystals of **6**: mp 88–90 °C (decomp.); ($CH_2Cl_2$) $\nu$(CO) 2081s, 2055w, 2022vs, 1998 (sh), 1970vs and 1843m $cm^{-1}$; $^1$H NMR ($CD_3COCD_3$) $\delta$ 7.57 (d, 2 H, $C_6H_5$), 7.38 (t, 2 H, $C_6H_5$), 7.27 (t, 1 H, $C_6H_5$) and 4.94 (s, 5 H, $C_5H_5$); MS *m*/*z* 404 ($M^+ - 2CO$), 376 ($M^+ - 3CO$), 292 ($M^+ - 6CO$) and 204 [$C_5H_5Mn(CO)_3{}^+$] (Found: C, 49.25; H, 2.19. Calc. for $C_{19}H_{10}Mn_2O_7$: C, 49.59; H, 2.19%).

### Reaction of [($\eta$-$C_5H_5$)(OC)$_2$Re≡C$C_6H_5$]$BBr_4$ 2 with complex 3 to give [ReMn{$\mu$-C(CO)$C_6H_5$}(CO)$_6$($\eta$-$C_5H_5$)] 7

Compound **2** (0.459 g, 0.63 mmol) was treated, in a manner similar to that described above, with fresh Li[Mn(CO)$_5$] prepared by the reaction of 0.124 g (0.32 mmol) of [$Mn_2(CO)_{10}$] with 0.79 mmol of LiBH($C_2H_5$)$_3$ (0.80 mL of 1.0 M THF solution) in THF solution at −90 to −60 °C for 6 h, during which time the red solution gradually turned to dark red. Further treatment of the resulting mixture as described above gave 0.32 g (86%, based on **2**) of brown-red crystals of **7**: mp 70–72 °C (decomp.); IR ($CH_2Cl_2$) $\nu$(CO) 2081s, 2055w, 2022vs, 1994 (sh), 1953s and 1862m $cm^{-1}$; $^1$H NMR ($CD_3COCD_3$) $\delta$ 7.4 (d, 2 H, $C_6H_5$), 7.36 (t, 2 H, $C_6H_5$), 7.25 (t, 1 H, $C_6H_5$) and 5.63 (s, $C_5H_5$); MS *m*/*z* 592 ($M^+$), 480 ($M^+ - 4CO$), 452 ($M^+ - 5CO$), 424 ($M^+ - 6CO$), 396 ($M^+ - 7CO$) and 336 [$C_5H_5Re(CO)_3{}^+$] Found: C, 38.30; H, 1.69. Calc. for $C_{19}H_{10}MnO_7Re$: C, 38.59; H, 1.70%).

### Reaction of complex 1 with Li[Co(CO)$_4$] 4 to give [MnCo{$\mu$-C(CO)$C_6H_5$}(CO)$_5$($\eta$-$C_5H_5$)] 8

To a solution of 0.149 g (0.44 mmol) of [$Co_2(CO)_8$] dissolved in 40 mL of THF are slowly added 1.09 mmol of LiBH($C_2H_5$)$_3$ (1.10 mL of 1.0 M THF solution). The mixture was stirred for 15 min at room temperature. The resulting deep red solution of Li[Co(CO)$_4$] **4**[12] was cooled to −90 °C, then poured rapidly on to 0.518 g (0.87 mmol) of complex **1** in THF (50 mL) previously cooled to −90 °C. The mixture was stirred at −90 to −40 °C for 6 h, during which time the deep red solution gradually turned to dark green. The resulting solution was evaporated to dryness under vacuum at −50 to −40 °C, and the dark red residue chromatographed on $Al_2O_3$ at −25 °C with light petroleum–$CH_2Cl_2$ (10 : 1) as the eluent. The blackish green band was collected. The solvent was removed *in vacuo* and the residue recrystallized from light petroleum–$CH_2Cl_2$ solution at −80 °C to afford 0.31 g (82%, based on **1**) of dark green crystalline **8**: mp 108–110 °C (decomp.); IR($CH_2Cl_2$) $\nu$(CO) 2064s, 2025w, 1991vs (br), 1978 (sh) and 1894m $cm^{-1}$; $^1$H NMR ($CD_3COCD_3$) $\delta$ 7.83 (m, 2 H, $C_6H_5$), 7.56 (m, 3 H, $C_6H_5$) and 5.06 (s, 5 H, $C_5H_5$); MS *m*/*z* 436 ($M^+$), 408 ($M^+ - CO$), 324 ($M^+ - 4CO$), 296 ($M^+ - 5CO$) and 204 [$C_5H_5Mn(CO)_3{}^+$] (Found: C, 49.98; H, 2.35. Calc. for $C_{18}H_{10}CoMnO_6$: C, 49.57, H, 2.31%).

### Reaction of complex 2 with 4 to give [ReCo{$\mu$-C(CO)$C_6H_5$}(CO)$_5$($\eta$-$C_5H_5$)] 9

Similar to the reaction of complex **1** with **4**, 0.46 g (0.63 mmol) of **2** was added to fresh Li[Co(CO)$_4$] prepared by the reaction of 0.109 g (0.32 mmol) of [$Co_2(CO)_8$] with 0.78 mmol of LiBH($C_2H_5$)$_3$ (0.79 mL of 1.0 M THF solution) in THF solution at −90 to −40 °C for 6 h, during which time the solution gradually turned to blackish green. Further treatment of the resulting mixture as described in the reaction of **1** with **4** gave 0.29 g (81%, based on **2**) of **9** as blackish green crystals: mp 77–78 °C (decomp.); IR($CH_2Cl_2$) $\nu$(CO) 2069vs, 2015vs, 1979s, 1917s and 1804m $cm^{-1}$; $^1$H NMR ($CD_3COCD_3$) $\delta$ 7.35 (m, 3 H, $C_6H_5$), 7.19 (m, 2 H, $C_6H_5$) and 5.70 (s, 5 H, $C_5H_5$); MS *m*/*z* 568 ($M^+$), 484 ($M^+ - 3CO$), 456 ($M^+ - 4CO$), 428 ($M^+ - 5CO$), 400 ($M^+ - 6CO$) and 336 [$C_5H_5Re(CO)_3{}^+$] Found: C, 38.15; H, 1.84. Calc. for $C_{18}H_{10}CoO_6Re$: C, 38.10; H, 1.78%).

### Reaction of complex 1 with $Na_2$[W(CO)$_5$] 5 to give [MnW{$\mu$-C(H)-$C_6H_5$}(CO)$_7$($\eta$-$C_5H_5$)] 10

The compound [W(CO)$_6$] (0.168 g, 0.48 mmol) and sodium amalgam (1.08 mL of 0.8% Na in Hg) were stirred at room temperature in 20 mL of DME in a flask containing a stopcock on the side to facilitate the removal of amalgam. After approximately 2 h the solution was a deep red and infrared spectra in the $\nu$(CO) region indicated almost complete reduction to **5**.[13] The red solution was evaporated under vacuum to about 5 mL, 50 mL of THF were added; followed by cooling to −90 °C. This cooled red solution was poured rapidly on to a solution of **1** (0.518 g, 0.87 mmol) in THF (50 mL) previously cooled to −90 °C. The reaction proceeded rapidly to form a deep red solution. The mixture was stirred at −90 to −60 °C for 6 to 7 h then evaporated to dryness under vacuum at −50 to −40 °C and the dark red residue chromatographed on $Al_2O_3$ at −25 °C with light petroleum–$CH_2Cl_2$ (10 : 1) as the eluent. The red band was eluted and collected. After removal of the solvent *in vacuo*, the crude product was recrystallized from light petroleum–$CH_2Cl_2$ solution at −80 °C to give 0.20 g (78%, based on **1**) of dark red crystals of **10**: mp 73–74 °C (decomp.); IR($CH_2Cl_2$) $\nu$(CO) 2073s, 2050w, 1975vs (br), 1943s (br) and 1905m $cm^{-1}$; $^1$H NMR($CD_3COCD_3$) $\delta$ 16.35 (s, 1 H, $\mu$-CH), 7.78 (m, 2 H, $C_6H_5$), 7.47 (3 H, $C_6H_5$) and 5.36 (s, 5 H, $C_5H_5$); MS *m*/*z* 590 ($M^+$), 562 ($M^+ - CO$) and 204 [$C_5H_5Mn(CO)_3{}^+$] (Found: C, 38.78; H, 1.95. Calc. for $C_{19}H_{11}MnO_7W$: C, 38.67; H, 1.88%).

### Reaction of complex 2 with 5 to give [ReW{$\mu$-C(H)$C_6H_5$}(CO)$_7$($\eta$-$C_5H_5$)] 11

Similarly compound **2** (0.383g, 0.53 mmol) dissolved in 50 mL of THF was treated with fresh $Na_2$[W(CO)$_5$] prepared by the reaction of [W(CO)$_6$] (0.102 g, 0.29 mmol) with sodium amalgam (0.65 mL of 0.8% Na in Hg) at −90 °C. The reaction solution turned immediately purple-red. After stirring at −90 to −60 °C for 6 h, further treatment of the resulting mixture in a manner similar to that described in the reaction of **1** with **5** yielded 0.145 g (76%, based on **2**) of red crystalline **11**: mp 121–122 °C (decomp); IR($CH_2Cl_2$) $\nu$(CO) 2078s, 1981s, 1961vs (br), 1947s (br) and 1904w $cm^{-1}$; $^1$H NMR ($CD_3COCD_3$) $\delta$ 11.07 (s, 1 H, $\mu$-CH), 7.26 (m, 3 H, $C_6H_5$), 7.00 (m, 2 H, $C_6H_5$) and 5.90 (s, 5 H, $C_5H_5$); MS *m*/*z* 582 ($M^+ - 5CO$), 336 [$C_5H_5Re(CO)_3{}^+$] and 308 [$C_5H_5Re(CO)_2{}^+$] (Found: C, 31.57; H, 1.49. Calc. for $C_{19}H_{11}O_7ReW$: C, 31.64; H, 1.54%).

### Crystal structure determination of complexes 6, 9 and 11

Single crystals of complexes **6**, **9** and **11** suitable for X-ray diffraction study were obtained by recrystallization from light petroleum–$CH_2Cl_2$ solution at −80 °C, mounted on a glass fibre and sealed with epoxy glue.

The structures were solved by the direct method and expanded using Fourier techniques. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was respectively based on 1503, 2066 and 3324 observed reflections [$I > 3.00\sigma(I)$] and 262, 236 and 253 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.059$ and $R' = 0.072$ for complex **6**, 0.026 and 0.030 for **9**, and 0.029 and 0.040 for **11**. All the calculations were performed using the TEXSAN software package.

The details of the crystallographic data and the procedures used for data collection and reduction are given in Table 1. Selected bond lengths and angles listed in Tables 2 and 3, respectively.

CCDC reference number 186/1183.

## Results and discussion

The complex $[(\eta\text{-}C_5H_5)(OC)_2Mn{\equiv}CC_6H_5]BBr_4$ **1** was treated with equimolecular amounts of freshly prepared (*in situ*) carbonylmanganese monoanion $[Mn(CO)_5]^-$ **3** in THF at −90 to −60 °C for 6 h. After removal of the solvent *in vacuo*, the residue was chromatographed on an alumina column at low temperature and the crude product recrystallized from light petroleum–$CH_2Cl_2$ solution at −80 °C to give deep red crystalline complex $[Mn_2\{\mu\text{-}C(CO)C_6H_5\}(CO)_6(\eta\text{-}C_5H_5)]$ **6** in 84% yield, eqn. (2). The compound **2** similarly reacted with **3** under the same conditions to afford $[ReMn\{\mu\text{-}C(CO)C_6H_5\}(CO)_6(\eta\text{-}C_5H_5)]$ **7**, a known compound,[15] eqn. (3), in 86% yield.

The analogous reactions of complexes **1** and **2** with carbonylcobalt monoanion $[Co(CO)_4]^-$ **4** under the similar conditions produced dark green crystals of $[MnCo\{\mu\text{-}C(CO)C_6H_5\}(CO)_5(\eta\text{-}C_5H_5)]$ **8**, eqn. (4), and blackish crystals of $[ReCo\{\mu\text{-}C(CO)C_6H_5\}(CO)_5(\eta\text{-}C_5H_5)]$ **9**, eqn. (5), in 82 and 81% yields, respectively.

On the basis of elemental analyses, spectroscopic evidence, and X-ray crystallography, compounds **6**, **8** and **9** are formulated as possessing a ketenyl ligand bonded to a carbene atom, similar to complex **7** reported by Fischer and co-workers[15] by the reaction of $[(\eta\text{-}C_5H_5)(OC)_2Mn{\equiv}CC_6H_5]BCl_4$ with $Na[Re(CO)_5]$. Complexes **6**, **8** and **9** are readily soluble in polar organic solvents but sparingly soluble in non-polar solvents. They are air-sensitive in solution but relatively stable as the solid. X-Ray diffraction studies for **6** and **9** were carried out in order firmly to establish their structures. The salient results are summarized in Table 1, and the molecular structures are shown in Figs. 1 and 2, respectively.

The structure of complex **6** (Fig. 1) resembled that of analogous complexes **7**[15] and $[Mn_2\{\mu\text{-}C(CO)C_6H_5Me\text{-}p\}(CO)_6(\eta\text{-}C_5H_5)]$.[16] The Mn–Mn bond [2.726(3) Å], similar in length to that found [2.735(1) Å] in $[Mn_2\{\mu\text{-}C(CO)C_6H_5Me\text{-}p\}(CO)_6(\eta\text{-}C_5H_5)]$,[15] is symmetrically bridged by the α-carbon atom of a phenyl ketenyl group [Mn(1)–C(8) 2.13(1), Mn(2)–C(8) 2.12(1) Å] and semi-bridged by a CO group [Mn(1)–C(2)

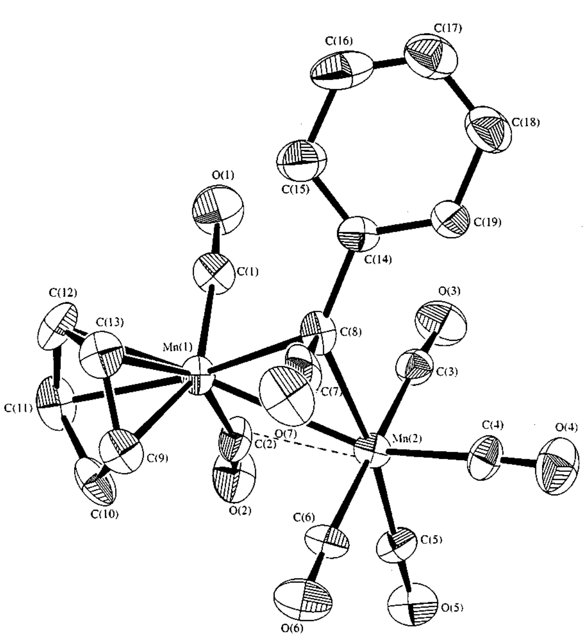
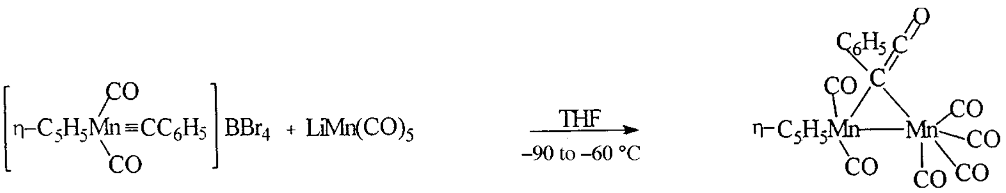
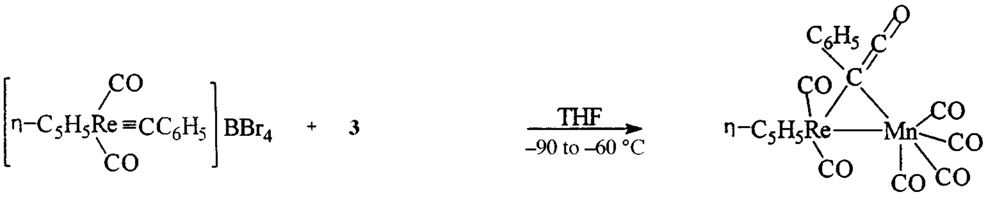


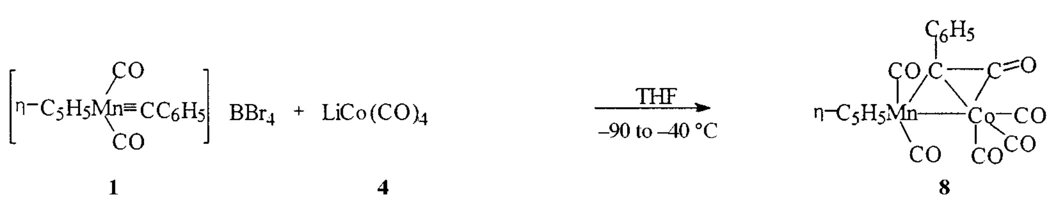
**Fig. 1** Molecular structure of complex **6**, showing the atom-numbering scheme.



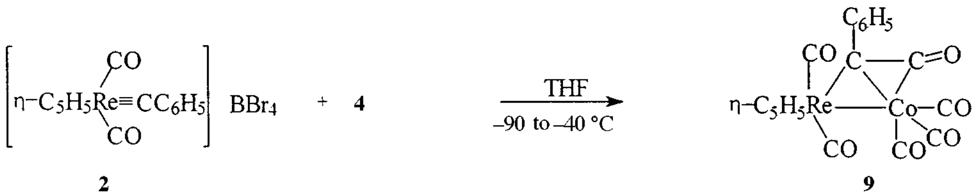
**1** **6** (2)



**2** **7** (3)



**1** **4** **8** (4)



**2** **9** (5)

1.80(1), Mn(2)–C(2) 2.48(1) Å, Mn(1)–C(2)–O(2) 161(1)°]. The $C(7)\cdots Mn(2)$ distance of 2.76(1) Å is much longer than the similar bond [C(7)–Co 1.983(8) Å] in **9** (see below), which indicates the different ways in which the ketenyl ligand is bridged to the metal–metal bonds, as seen in the structures shown in eqns. (2)–(5). A unique structural feature is the presence of the C(7)O(7) group bonded to C(8) with C(7)–O(7) 1.16(2) and C(8)–C(7) 1.37(2) Å. The former distance might correspond either to a C≡O or a C=O bond. The latter distance suggests C=C character so that the μ-$C(C_6H_5)CO$ group is regarded as a one-electron ketene bridge $C_6H_5C{=}C{=}O$.[16]

The structure of complex **9** (Fig. 2) resembled that of **6**, except that the CO moiety of the phenylketenyl group is linked to the Co atom through the carbon atom [C(7)] in **9**. In contrast to that of **6**, the Re–Co bond of **9** is asymmetrically bridged by the $C(CO)C_6H_5$ group [Re–C(8) 2.135(9), Co–C(8) 2.021(7) Å], and the Co–C(7) distance of 1.983(8) Å is much shorter than the corresponding bonds in **6**, indicating a stronger bond between the C(7) and Co atom. The μ-C(8)–Re bond length of 2.135(9) Å in **9** is somewhat shorter than that found [2.24(3) Å] in $[ReMn\{\mu\text{-}C(CO)C_6H_5\}(CO)_6(\eta\text{-}C_5H_5)]$,[15] while the μ-C(8)–Co distance of 2.021(7) Å is significantly shorter than the corresponding bond distance in **6**.

The complexes **6**–**9** are postulated to form *via* CO transfer in the carbene intermediate $[(\eta\text{-}C_5H_5)(OC)_2M{=}C(C_6H_5)\text{-}M'(CO)_n]$ (M = Mn or Re, M′ = Mn or Co, $n$ = 5 or 4)[17] or *via* transfer of a CO group from $M'(CO)_n$ to a metal–carbyne centre.[16] The analogous bridging ketenyl complexes $[Mn_2\{\mu\text{-}C(CO)C_6H_5Me\text{-}p\}(CO)_6(\eta\text{-}C_5H_5)]$[16] and $[Me(\eta\text{-}C_5H_5)(OC)_2Mn\{\mu\text{-}C(R)CO\}Mn(CO)_4]$ (R = $C_6H_5$ or CpFeCp)[17] have been synthesized by the reactions of cationic carbyne complex $[(\eta\text{-}C_5H_5)(OC)_2M{\equiv}CC_6H_5Me\text{-}p]BF_4$ (M = Mn or Re) or $[Me(\eta\text{-}C_5H_5)(OC)_2MnCR]BCl_4$ (R = $C_6H_5$ or CpFeCp)[17] with $[(Ph_3P)_2N][Mn(CO)_5]$ or $K[Mn(CO)_5]$. Interestingly, the reaction of $[Me(\eta\text{-}C_5H_5)(OC)_2MnCR]BCl_4$ (R = $C_6H_5$ or CpFeCp) with $[Co(CO)_4]^-$ reported Fischer *et al.*[17] produced the neutral carbene complexes $[Me(\eta\text{-}C_5H_5)(OC)_2Mn{=}C(R)Co(CO)_4]$. However, in the present reaction of the cationic carbyne complex **1** or **2** with $[Co(CO)_4]^-$ the product is the ketenyl bridged complex instead of the neutral carbene.

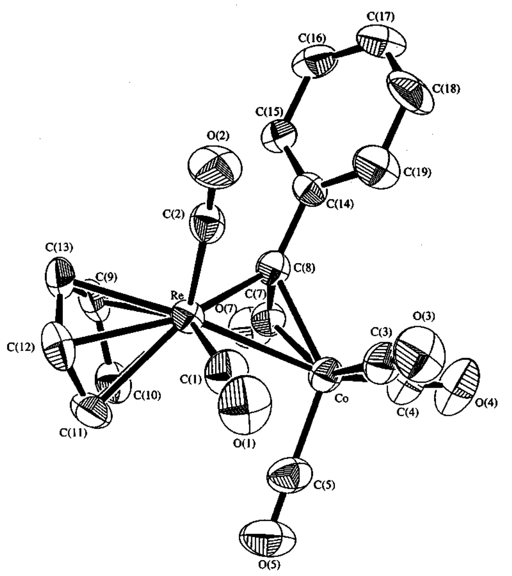


**Fig. 2** Molecular structure of complex **9**, showing the atom-numbering scheme.

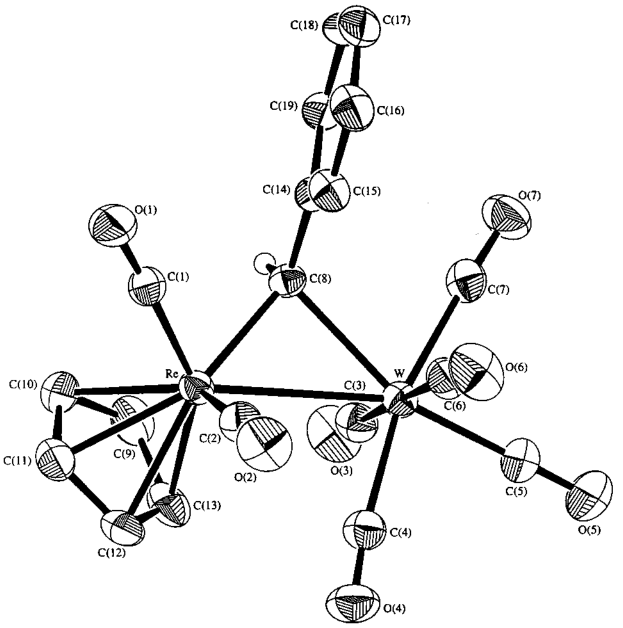


**Fig. 3** Molecular structure of complex **11**, showing the atom-numbering scheme.

**Table 1** Crystal data and experimental details for complexes **6**·$H_2O$, **9** and **11**[a]

| | **6**·$H_2O$ | **9** | **11** |
|---|---|---|---|
| Formula | $C_{19}H_{12}Mn_2O_8$ | $C_{18}H_{10}CoO_6Re$ | $C_{19}H_{11}O_7ReW$ |
| Formula weight | 478.18 | 567.41 | 721.35 |
| Space group | $P\bar{1}$(no. 2) | $P2_1/n$(no. 14) | $C2/c$(no. 15) |
| $a$/Å | 8.161(8) | 15.073(6) | 16.628(2) |
| $b$/Å | 16.46(1) | 8.477(2) | 7.6569(7) |
| $c$/Å | 7.653(5) | 15.782(6) | 30.118(4) |
| $\alpha$/° | 96.39(6) | | |
| $\beta$/° | 106.10(6) | 116.15(2) | 93.50(1) |
| $\gamma$/° | 85.27(7) | | |
| $V$/Å$^3$ | 980(1) | 1810(1) | 3827.4(8) |
| $Z$ | 2 | 4 | 8 |
| $D_c$/g cm$^{-3}$ | 1.620 | 2.082 | 2.504 |
| Crystal size/mm | 0.20 × 0.20 × 0.30 | 0.25 × 0.30 × 0.30 | 0.20 × 0.30 × 0.30 |
| $\mu$(Mo-K$\alpha$)/cm$^{-1}$ | 13.31 | 76.31 | 123.74 |
| Data collection range, $2\theta$/° | 5–45 | 5–50 | 5–55 |
| No. unique data, total | 2428 | 3220 | 4231 |
| $[I > 3.00\sigma(I)]$ | 1503 | 2066 | 3324 |
| $R^a$ | 0.059 | 0.026 | 0.029 |
| $R'$ | 0.072 | 0.030 | 0.040 |
| Maximum, minimum/e Å$^{-3}$ | 0.62, −0.55 | 0.75, −0.42 | 1.29, −1.30 |

[a] Details in common: monochromated Mo-K$\alpha$ radiation ($\lambda$ 0.71069 Å); Rigaku AFC7R diffractometer; 20 °C.

Interestingly, carbonyltungsten dianion $[W(CO)_5]^{2-}$ **5** reacted with complexes **1** and **2** to afford bridging carbene complexes $[MnW\{\mu\text{-}C(H)C_6H_5\}(CO)_7(\eta\text{-}C_5H_5)]$ **10**, eqn. (6), and $[ReW\{\mu\text{-}C(H)C_6H_5\}(CO)_7(\eta\text{-}C_5H_5)]$ **11**, eqn. (7), in 78 and 76% isolated yields, respectively, similar to those reactions[7] of carbonyliron dianion $Na_2[Fe(CO)_4]$ or $[NEt_4]_2[Fe_2(CO)_8]$ and $Na_2[Fe_3(CO)_{11}]$ with complex **2**.

The formulation of complexes **10** and **11** is supported by microanalytical and spectroscopic data (Experimental section) and crystallography. Their $^1H$ NMR spectra had a resonance at $\delta$ 16.35 and 11.07, respectively, characteristic for a μ-CHR ($R = C_6H_5$) group.[18] Surprisingly, this chemical shift has moved downfield dramatically by comparison with that for analogous carbene bridged complexes $[ReFe\{\mu\text{-}C(H)C_6H_5\}(CO)_6(\eta\text{-}C_5H_5)]$ ($\delta$ 9.03)[7] and $[N(PPh_3)_2][ReW\{\mu\text{-}CH(C_6H_4Me\text{-}p)\}(CO)_9]$ ($\delta$ 8.09).[19]

**Table 2** Selected bond lengths (Å) and angles (°) for complex **6** with estimated standard deviations in the least significant figure in parentheses

| | | | |
|---|---|---|---|
| Mn(1)–Mn(2) | 2.726(3) | Mn(2)–C(4) | 1.80(1) |
| Mn(1)–C(8) | 2.13(1) | Mn(2)–C(5) | 1.81(1) |
| Mn(2)–C(8) | 2.12(1) | Mn(2)–C(6) | 1.86(1) |
| Mn(1)–C(1) | 1.78(1) | Mn(2)···C(7) | 2.76(1) |
| Mn(1)–C(2) | 1.80(1) | C(7)–C(8) | 1.37(2) |
| Mn(2)–C(2) | 2.48(1) | C(7)–O(7) | 1.16(2) |
| Mn(2)–C(3) | 1.88(1) | C(8)–C(14) | 1.53(2) |
| Mn(1)–Mn(2)–C(8) | 50.3(3) | Mn(2)–C(3)–O(3) | 174(1) |
| Mn(2)–Mn(1)–C(8) | 50.0(3) | Mn(2)–C(4)–O(4) | 177(1) |
| Mn(1)–C(8)–Mn(2) | 79.6(4) | Mn(2)–C(5)–O(5) | 179(1) |
| Mn(2)–C(7)–C(8) | 48.8(7) | Mn(2)–C(6)–O(6) | 176(1) |
| Mn(2)–C(8)–C(7) | 102.2(8) | Mn(2)–C(7)–O(7) | 134(1) |
| C(7)–Mn(2)–C(8) | 29.0(4) | C(8)–C(7)–O(7) | 177(1) |
| Mn(1)–C(1)–O(1) | 175(1) | Mn(1)–C(8)–C(14) | 126.0(8) |
| Mn(1)–C(2)–O(2) | 161(1) | Mn(2)–C(8)–C(14) | 127.8(8) |
| Mn(2)–C(2)–O(2) | 122.0(9) | Mn(1)–C(2)–Mn(2) | 77.5(4) |

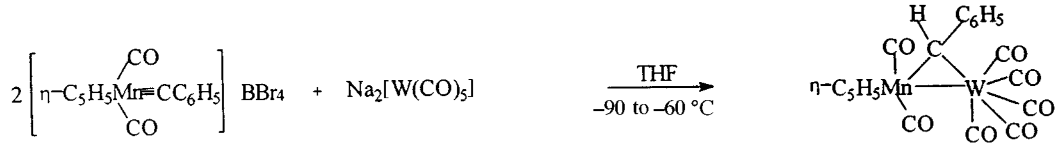
The crystal structure of complex **11** is shown in Fig. 3. As expected, five terminal carbonyl groups are attached to the tungsten and two to the rhenium. The metal–metal bond is bridged by the $C(H)C_6H_5$ group. The Re–W distance [3.0233(5) Å] could be compared with that in the Re–W carbene bridged complex $[N(PPh_3)_2][ReW\{\mu\text{-}CH(C_6H_4Me\text{-}p)\}(CO)_9]$ [3.033(1) Å].[19] The alkylidene carbon asymmetrically bridges the metal–metal bond [μ-C–Re 2.126(7), μ-C–W 2.355(7) Å], but this asymmetry is less marked than that in $[N(PPh_3)_2][ReW\{\mu\text{-}CH(C_6H_4Me\text{-}p)\}(CO)_9]$ [μ-C–Re 2.155(8), μ-C–W 2.404(6) Å].[19] The μ-C–Re distance in **11** is comparable with that in complexes $[N(PPh_3)_2][ReW\{\mu\text{-}CH(C_6H_4Me\text{-}p)\}(CO)_9]$[μ-C–Re 2.155(8) Å],[19] $[Re_2(\mu\text{-}H)_2(\mu\text{-}CHBu^t)(\eta\text{-}C_6H_6)_2]$ [2.13(3) Å][20] and $[ReFe\{\mu\text{-}C(H)C_6H_5\}(CO)_6(\eta\text{-}C_5H_5)]$ [2.120(5) Å].[7]

The possible reaction pathway to complexes **10** and **11** might involve initial formation of an anionic carbene intermediate $[(\eta\text{-}C_5H_5)(OC)_2M{=}C(C_6H_5)W(CO)_5]^-$ (M = Mn or Re), where the $W(CO)_5{}^{2-}$ moiety is bonded to the carbene carbon through the W atom, by attack of the $[W(CO)_5]^{2-}$ anion on the cationic carbyne carbon of **1** or **2**. There are analogous precedents for this type of intermediate in the reaction[7] of **2** with $Na_2[Fe(CO)_4]$ or $[NEt_4]_2[Fe_2(CO)_8]$ and in the literature.[6,21] The protonation of the anionic carbene intermediate then afforded the bridging carbene complex **10** or **11**. The source of the hydrogen atom could be either THF or water. The latter is a trace contaminant in solvent THF as that in the reaction[7] of **2** with $Na_2[Fe(CO)_4]$ or $[NEt_4]_2[Fe_2(CO)_8]$ to form $[ReFe\{\mu\text{-}C(H)C_6H_5\}(CO)_6(\eta\text{-}C_5H_5)]$.

Complexes **10** and **11**, as heteronuclear dimetal carbene bridged complexes, were synthesized by the reaction of cationic carbyne complexes with metal carbonyl anions. Thus, the cationic carbyne complexes of manganese and rhenium not only reacted with the carbonyliron anions but also with the carbonyltungsten dianion to yield the dimetal carbene bridged complexes. This offers a convenient and useful method for the preparation of such complexes.

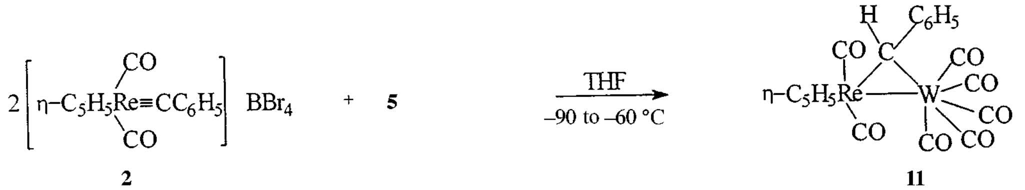
**Table 3** Selected bond lengths (Å) and angles (°) for complexes **9** and **11**

| | **9** M = Co | **11** M = W | | **9** M = Co | **11** M = W |
|---|---|---|---|---|---|
| Re–M | 2.716(2) | 3.0233(5) | M–C(5) | 1.798(9) | 2.00(9) |
| Re–C(8) | 2.135(9) | 2.126(7) | M–C(6) | | 2.052(9) |
| M–C(8) | 2.021(7) | 2.355(7) | M–C(7) | 1.983(8) | 2.050(8) |
| Re–C(2) | 1.911(8) | 1.896(8) | C(7)–C(8) | 1.41(1) | |
| M–C(3) | 1.838(9) | 2.042(8) | C(7)–O(7) | 1.173(9) | 1.137(9) |
| M–C(4) | 1.76(1) | 2.049(8) | C(8)–C(14) | 1.467(10) | 1.482(10) |
| Re–M–C(8) | 51.0(2) | 44.5(2) | M–C(6)–O(6) | | 174.9(8) |
| M–Re–C(8) | 47.4(2) | 50.9(2) | M–C(7)–O(7) | 140.5(6) | 177.2(7) |
| Re–C(8)–M | 81.6(3) | 84.7(2) | M–C(7)–C(8) | 70.9(4) | |
| Re–C(1)–O(1) | 175.4(9) | 177.0(7) | M–C(8)–C(7) | 68.0(4) | |
| Re–C(2)–O(2) | 176.6(8) | 177.6(7) | C(7)–M–C(8) | 41.1(3) | 74.1(3) |
| M–C(3)–O(3) | 178.3(9) | 178.2(7) | Re–C(8)–C(14) | 132.1(5) | 127.2(5) |
| M–C(4)–O(4) | 177.4(9) | 174.1(8) | M–C(8)–C(14) | 128.6(6) | 117.2(5) |
| M–C(5)–O(5) | 178.6(8) | 179.4(8) | | | |



**1** **5** **10**

(6)



**2** **11**

(7)

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