

Net [2 + 2] Cycloaddition of the Metal–Oxo Bonds of $\text{Cp}_2\text{M}=\text{O}$ ($\text{Cp} = \text{C}_5\text{H}_5$; $\text{M} = \text{Mo}, \text{W}$) across the Carbon–Oxygen Bond of Carbonyl Ligands to form $\mu_2, \eta^3\text{-CO}_2$ Complexes

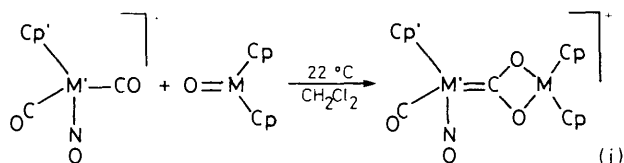
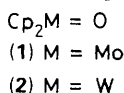
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A new family of bimetallic $\mu_2, \eta^3\text{-CO}_2$ complexes have been prepared by net [2 + 2] cycloaddition of the metal–oxo bond of $\text{Cp}_2\text{M}=\text{O}$ ($\text{M} = \text{Mo}, \text{W}$) across the carbon–oxygen bond of the CO ligands of $[\text{Cp}'\text{M}(\text{CO})_2(\text{NO})][\text{BF}_4]$ ($\text{M} = \text{Mn}, \text{Re}$) and $[\text{Cp}'\text{M}(\text{CO})_3]\text{BF}_4$ ($\text{M} = \text{Fe}, \text{Ru}$) ($\text{Cp} = \text{C}_5\text{H}_5$; $\text{Cp}' = \text{C}_5\text{H}_4\text{Me}$ or C_5Me_5); the crystal structure of $[(\text{C}_5\text{Me}_5)\text{Re}(\text{CO})(\text{NO})(\mu\text{-CO}_2)\text{W}(\text{C}_5\text{H}_5)_2][\text{BF}_4]$ has been determined.

The transfer of an oxygen atom from a metal to an organic molecule is a key step in many practiced and envisaged catalytic oxidation reactions,¹ but many aspects of this reaction step are still poorly understood. One way to probe such transformations on a fundamental level is to study the interaction of oxo ligands on model compounds with organic substrates, either co-ordinated or free.² Attractive oxo complexes for such studies are $\text{Cp}_2\text{Mo}=\text{O}$, (1),³ and $\text{Cp}_2\text{W}=\text{O}$, (2),³ since they are sterically unencumbered and the oxo ligand uses only two of its six valence electrons for bonding to the metal. Evidence for the nucleophilicity of the oxo ligand in these complexes comes from their [2 + 2]cycloaddition across



(3); $\text{M} = \text{Mn}$, $\text{Cp}' = \text{C}_5\text{H}_4\text{Me}$

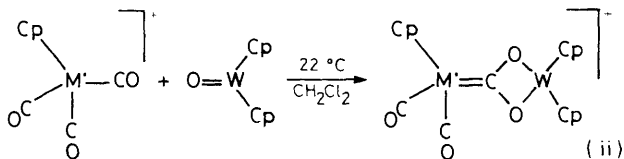
(4); $\text{M} = \text{Re}$, $\text{Cp}' = \text{C}_5\text{Me}_5$

(7); $\text{M} = \text{W}$, $\text{M}' = \text{Re}$ (92%)

(8); $\text{M} = \text{W}$, $\text{M}' = \text{Mn}$ (83%)

(9); $\text{M} = \text{Mo}$, $\text{M}' = \text{Re}$ (77%)

(10); $\text{M} = \text{Mo}$, $\text{M}' = \text{Mn}$ (62%)



(5); $\text{M} = \text{Fe}$

(6); $\text{M} = \text{Ru}$

(11); $\text{M}' = \text{Fe}$ (95%)

(12); $\text{M}' = \text{Ru}$ (95%)

the $\text{N}=\text{C}$ and $\text{C}=\text{O}$ bonds of PhNCO and Ph_2CCO to form metallacycles.⁴ Here we show that these oxo complexes also undergo an unusual cycloaddition across the $\text{C}=\text{O}$ bond of co-ordinated carbonyls to yield bimetallic CO_2 complexes with the rare μ_2, η^3 bonding mode.

This cycloaddition chemistry is illustrated by the reactions shown in equations (i) and (ii) which give complexes (7)–(12) in excellent yields. These compounds have been spectroscopically characterized[†] and complex (7) has been fully defined by a crystallographic study, Figure 1.[‡] Complexes (7)–(12) have a co-ordinated CO_2 ligand that is formed by cycloaddition of the $\text{M}=\text{O}$ bond of the $\text{Cp}_2\text{M}=\text{O}$ fragment across a carbonyl $\text{C}=\text{O}$ bond of (3)–(6). These reactions are likely to occur by initial attack of the nucleophilic oxo ligands on the carbonyl carbons of (3)–(6) since the CO ligands in these complexes are known to be highly susceptible to nucleophilic attack.⁵ The structural data indicate that the CO_2 moiety is best viewed as a dimetallated dioxycarbene ligand with a $\text{Re}=\text{C}$ double bond [$\text{Re}-\text{C}(21)$ 2.041(38) Å] and with $\text{C}(21)-\text{O}$ and $\text{W}-\text{O}$ single bonds. Consistent with this formulation is the typical carbene-

[†] Spectroscopic data for (7): i.r. (CH_2Cl_2) ν_{CO} 1990, ν_{NO} 1727 cm^{-1} ; m/z fast atom bombardment (f.a.b.) 738; ^1H n.m.r. (CD_2Cl_2) δ 5.96 (s, Cp, 10H), 2.06 (s, Cp', 15H); ^{13}C n.m.r. (CD_2Cl_2) δ 247.4 (s, CO_2), 202.8 (s, CO), 106.1 (s, C_5Me_5), 98.0 (s, Cp), 10.2 (s, C_5Me_5). For (11): i.r. (acetone) ν_{CO} 2047 (vs), 1996 (vs); m/z (f.a.b.) 534; ^1H n.m.r. ($[\text{C}_5\text{H}_5]$ acetone) δ 6.13 (s, C_5H_5 , 10H), 5.21 (s, C_5H_5 , 5H); ^{13}C n.m.r. ($[\text{C}_5\text{H}_5]$ acetone) δ 259.5 (s, CO_2), 211.9 (s, CO), 98.4 (s, C_5H_5), 87.7 (s, C_5H_5).

[‡] Crystal data: $\text{C}_{22}\text{H}_{25}\text{BF}_4\text{NO}_4\text{ReW}$, monoclinic, space group $\text{C}2/c$, $a = 49.764(5)$, $b = 29.561(5)$, $c = 13.607(2)$ Å, $\beta = 95.73(1)^\circ$, $U = 19917(5)$ Å³, $Z = 32$, $D_c = 2.242$ g cm^{-3} , $\mu(\text{Mo}-K_\alpha) = 100.6$ cm^{-1} , $R = 6.83\%$, $R'_{\text{w}} = 7.16\%$ for 5297 absorption corrected reflections [298 K, $4^\circ \leq 2\theta \leq 42^\circ$, $F_o \geq 5\sigma(F_o)$], Nicolet diffractometer, $\text{Mo}-K_\alpha$ ($\lambda = 0.71073$ Å)]. Maximum residual electron density = 3.17 e \AA^{-3} [1.23 Å from $\text{Re}(b)$] followed by peaks below 1 e \AA^{-3} . Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

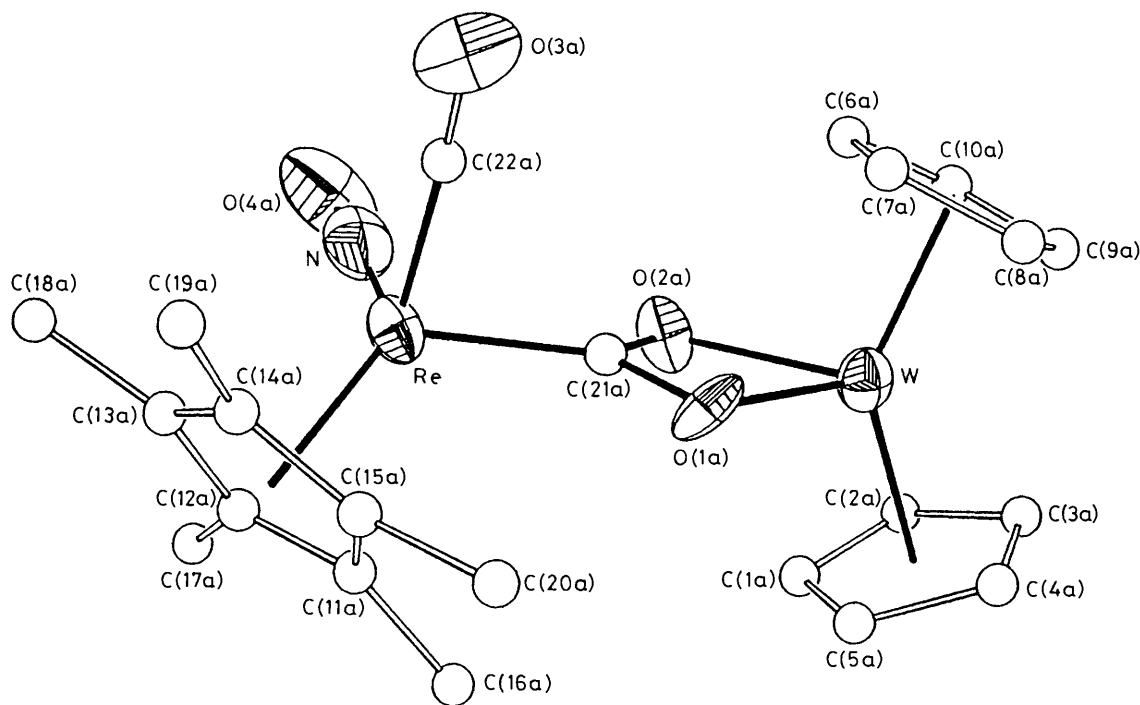
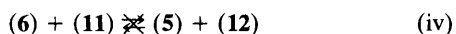
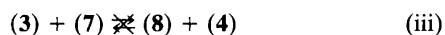


Figure 1. An ORTEP drawing of one of the four cations in the asymmetric unit of $[\text{Cp}_2\text{W}(\mu_2, \eta^3\text{-CO}_2)\text{Re}(\text{CO})(\text{NO})(\text{C}_5\text{Me}_5)]^+$, (**7**). Important bond lengths (Å) and angles ($^\circ$) for this cation are representative of all four independent cations: W–O(1) 2.09(2), W–O(2) 2.08(2), W–Cnt(1) 1.99(3), W–Cnt(2) 1.96(3), Re–N 1.79(4), Re–C(22a) 1.88(4), Re–Cnt(3) 1.95(2), Re–C(21a) 2.04(4), O(1a)–C(21a) 1.34(4), O(2a)–C(21a) 1.32(4); Cnt(1)–W–Cnt(2) 139.0(9), O(2a)–C(21a)–O(1a) 106(3), O(2a)–W–O(1a) 60.9(9). (Cnt = centroid of Cp ring.)

like ^{13}C n.m.r. signal observed for the CO_2 carbon [*e.g.*, (**7**) δ 247.4; (**11**) δ 259.5]. The CO_2 ^{13}C n.m.r. signals for these compounds are further downfield than those of all other complexes possessing a CO_2 moiety (the typical range is δ 195–225),⁶ emphasizing the importance of the carbene formulation. This specific type of CO_2 co-ordination has been well-defined previously only in the compounds $\text{Cp}(\text{CO})(\text{NO})\text{Re}=\text{C}(\text{O})_2\text{ZrCp}_2\text{Cl}^{7a}$ and $\text{Cp}(\text{PPh}_3)(\text{NO})\text{Re}=\text{C}(\text{O})_2\text{SnR}_3$,^{7b} which were prepared by routes quite different from that described here. To our knowledge, the reactions described above are the first examples of cycloaddition of metal–oxo bonds across metal carbonyl ligands, although in related work OsO_4 has been shown to react with $\text{Ir}(\text{PPh}_3)_2(\text{CO})(\text{Cl})$ to give a binuclear OsIr species possessing a CO_2 ligand with a significantly different bonding mode than that found in (**7**)–(**12**).⁸

The ^{17}O n.m.r. spectra of complexes (**7**) and (**11**) prepared using $\text{Cp}_2\text{W}=\text{O}$ showed resonances for both the CO_2 [(**7**) δ 143; (**11**) δ 168] and the CO [(**7**) δ 394; (**11**) δ 369] oxygens but not for the NO oxygen in (**7**). The observation of ^{17}O n.m.r. signals for the CO ligands implies that oxygen exchange has occurred between these and the co-ordinated CO_2 ligands. Such exchange could take place *via* reversible dissociation of the $\text{Cp}_2\text{W}=\text{O}$ molecule from the binuclear complexes followed by re-addition to the adjacent carbonyl. However, cross-over experiments of the type illustrated in equations (iii) and (iv) show that completely free $\text{Cp}_2\text{W}=\text{O}$ is never liberated since no exchange occurs when these equilibria are approached from either direction using a 10-fold excess of the mononuclear reagent. Exchange must thus occur *via* dissociation and re-addition of the $\text{Cp}_2\text{M}=\text{O}$ fragment within the solvent cage or by an intramolecular process.



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References

- R. A. Sheldon and J. K. Kochi, 'Metal-catalyzed Oxidations of Organic Compounds,' Academic Press, New York, 1981.
- F. Bottomley and L. Sutin, *Adv. Organomet. Chem.*, 1988, **28**, 339; W. A. Herrmann, *J. Organomet. Chem.*, 1986, **300**, 111; R. H. Holm, *Chem. Rev.*, 1987, **87**, 1401.
- M. L. H. Green, A. H. Lynch, and M. G. Swanswick, *J. Chem. Soc., Dalton Trans.*, 1972, 1445.
- P. Jernakoff, G. L. Geoffroy, A. L. Rheingold, and S. J. Geib, *J. Chem. Soc., Chem. Commun.*, 1987, 1610; R. S. Pilato and G. L. Geoffroy, unpublished results.
- C. P. Casey, M. A. Andrew, and J. E. Rinz, *J. Am. Chem. Soc.*, 1979, **101**, 741; W. Tam, W. K. Wong, and J. Gladysz, *J. Am. Chem. Soc.*, 1979, **101**, 1589; R. P. Stewart, N. Okamoto, and W. A. G. Graham, *J. Organomet. Chem.*, 1972, **42**, C32; L. Busetto, A. Palazzi, D. Pietropaolo, and G. Dolcetti, *J. Organomet. Chem.*, 1974, **66**, 453; A. E. Kruse and R. J. Angelici, *J. Organomet. Chem.*, 1970, **24**, 231; R. J. Angelici and L. Busetto, *J. Am. Chem. Soc.*, 1969, **91**, 3197.
- R. Alvarez, E. Carmona, J. M. Marin, M. L. Poveda, E. Gutierrez-Puebla, and A. Monge, *J. Am. Chem. Soc.*, 1986, **108**, 2286; G. S. Bristow, P. B. Hitchcock, and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, 1981, 1145; G. R. Lee, J. M. Maher, and N. J. Cooper, *J. Am. Chem. Soc.*, 1987, **109**, 2956.
- (a) C. T. Tso and A. R. Cutler, *J. Am. Chem. Soc.*, 1986, **108**, 6069; (b) D. R. Senn, J. A. Gladysz, K. Emerson, and R. D. Larsen, *Inorg. Chem.*, 1987, **26**, 2737.
- J. D. Audett, T. J. Collins, B. D. Santarsiero, and G. H. Spies, *J. Am. Chem. Soc.*, 1982, **104**, 7352.