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A molecular model for the reductive cleavage of carbon monoxide to carbide and oxide on reduced metal oxides

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Abstract

In an attempt to model the initial step in Fischer–Tropsch chemistry, the reductive cleavage of carbon monoxide to carbide and oxide, we have examined the interactions between CO and alkoxides of molybdenum and tungsten in their middle oxidation states. At low CO/M ratios $M_2(\mu\text{-CO})$ compounds may be isolated and their characterization data reveal extensive M-to-CO π^* bonding in the order M = W > Mo. For tungsten a further reaction sequence is observed involving the head-to-tail dimerization of two $W_2(\mu\text{-CO})$ units and ultimate cleavage to a carbido-oxide-W_4 cluster. The molecular structure of the latter compound is inferred from ^{13}C NMR spectroscopy and is proposed to be isostructural to the isoelectronic and structurally characterized compound $W_4(C)(NMe)(O\text{-i-Pr})_{12}$.

Introduction

Metal alkoxides [1] often provide molecular models for metal oxides [2,3]. Specifically for molybdenum and tungsten in their middle oxidation states (2, 3, 4) one finds that the basic repeating subunits in the oxides contain metal–metal bonds. These are normally used to form clusters which may be separated from one another by oxo bridges or may be fused along common edges or faces [4,5]. The same cluster units may also be found in discrete molecular alkoxide clusters. For example, the M_4O_{16} unit in $W_4(OEt)_{16}$ [6] is seen in $Ba_{1.14}Mo_8O_{16}$ [5]. The alkoxide has 8 cluster bonding electrons and in the oxide two Mo_4O_{16} units are seen differing principally in their M–M distances. These are assignable to 8 and 10 electron clusters. The ability of these reduced metal oxides to act as heterogeneous catalysts for a wide variety of reactions involving C–H and C–C bond forming and breaking reactions led us to speculate (i) that the surface effects of metal oxides might be modeled by alkoxides where coordinative unsaturation could be introduced by steric factors associated with the alkoxide and (ii) that the small discrete alkoxide clusters should be capable of supporting an extensive organometallic chemistry [3].

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Alkoxides and oxo ligands share a number of attractive common features as ancillary ligands for organometallic chemistry of metals which are in high formal oxidation states and have low d^n electron counts [7]. They are π-donors and may readily move between bridging and terminal sites. This flexibility in coordination chemistry allows for response to substrate uptake or release. In mononuclear chemistry the role of the oxo ligand in the olefin metathesis reaction has been noted and its influence on the reaction has been termed the spectator ligand effect [8]. It is not unreasonable to expect that similar effects will be operating on metal oxide surfaces and in metal alkoxide cluster compounds. We review here our studies of the activation of carbon monoxide by alkoxides of reduced molybdenum and tungsten.

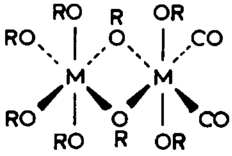
Carbonylation of $M_2(OR)_6$ compounds

The addition of carbon monoxide to hydrocarbon solutions of $M_2(OR)_6$ leads to the formation of $M(CO)_6$ and higher valent metal alkoxides of molybdenum and tungsten [9–12]. The cleavage of the M≡M bond occurs at room temperature and 1 atm CO. Since the $M(CO)_6$ compounds are relatively insoluble in pentane, this carbonylation employing ^{13}CO provides an easy preparative route to the labelled compounds $M(^{13}CO)_6$. It is an efficient reaction in terms of the labelled ^{13}CO. The detailed course of the reaction depends on the metal and the alkoxide.

Carbonylation of $Mo_2(O\text{-t-Bu})_6$ proceeds according to the stoichiometry shown in eq. 1 [9].

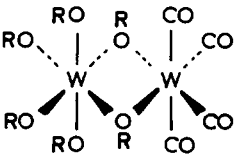
$$2Mo_2(O\text{-t-Bu})_6 + 6CO \xrightarrow[\text{hexane}]{22^\circ C} Mo(CO)_6 + 3Mo(O\text{-t-Bu})_4 \qquad (1)$$

Reactions employing isopropoxides lead, in addition to $M(CO)_6$, to carbonyl adducts of higher valent metal alkoxides. Specifically for M = Mo to $Mo_2(O\text{-i-Pr})_8(CO)_2$ (I) [11], and for M = W to $W_2(O\text{-i-Pr})_6(CO)_4$ (II) [13]. Both I and II can be formulated as edge-shared bioctahedra as shown diagrammatically below. Compound II has, in fact, been shown to be so by a single crystal X-ray study [13]. Based on the M-to-M distance, 3.4 Å, and the asymmetric M–O distances in the μ-OR bridges, 1.95 versus 2.25 Å, compound II may be formulated as a $W(O\text{-i-Pr})_6$ molecule ligated to a $W(CO)_4$ fragment. A similar Mo(6 +)---Mo(2 +) dimer may be formulated for I.



M = Mo , R = i-Pr

(I)

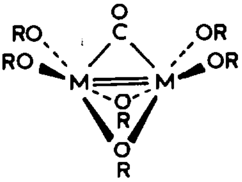


R = i-Pr

(II)

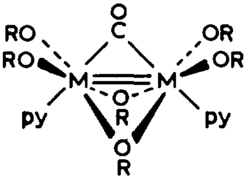
The facile disruption of the M≡M bond in these carbonylations arises because of the ability of facile alkoxy and carbonyl group transfer reactions. If a model for an oxide surface is to be obtained cluster fragmentation must be suppressed and the ratio of the substrate of interest to the metal must be small and, in general, less than one.

Under more controlled additions of CO wherein one equivalent of CO was added to the $M_2(OR)_6$ compounds 1/1 adducts were formed [9,10,12]. In the case of the bulky t-butoxy ligands $M_2(O\text{-}t\text{-}Bu)_6(\mu\text{-}CO)$ compounds III were isolated and structurally characterized [9,12]. In the presence of pyridine the isopropoxy compounds $M_2(O\text{-}i\text{-}Pr)_6(py)_2(\mu\text{-}CO)$ (IV) were similarly isolated [11].



M = Mo or W , R = t-Bu

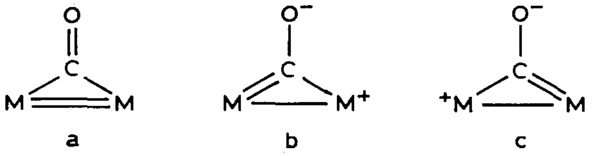
(III)



M = Mo or W , R = i-Pr or CH_2-t-Bu

(IV)

These compounds show extremely low values for $\bar{\nu}(CO)$ in their infrared spectra ca. 1650 cm^{-1} for M = Mo and 1570 cm^{-1} for M = W. These values are unprecedentedly low for μ_2-CO ligands for neutral organometallic compounds. Typical $\bar{\nu}(CO)$ values for μ_2-CO are in the range 1850–1700 cm^{-1} [14]. In part, the low stretching frequencies can be understood in terms of the resonance structures Va, Vb and Vc. The compounds are inorganic analogues of cyclopropenone [15].



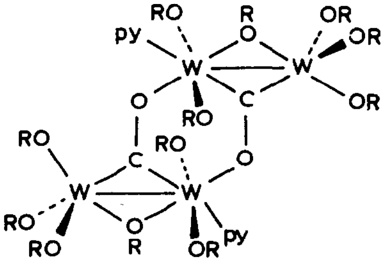
(V)

The oxyalkylidyne resonance contributions lead one to anticipate that the carbonyl oxygen should be nucleophilic and this is seen in the formation of the tetranuclear compounds $W_4(O\text{-}i\text{-}Pr)_{12}(CO)_2(py)_2$ (VI) [16] and $W_4(O\text{-}i\text{-}Pr)_{12}(CO)_2$ (VII) [12], according to eq. 2 and 3, respectively.

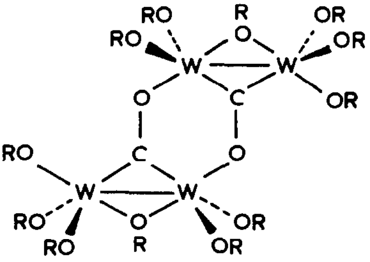
$$2W_2(O\text{-}i\text{-}Pr)_6(py)_2(CO)\xrightarrow[\text{hexane}]{22^\circ C}[W_2(O\text{-}i\text{-}Pr)_6(py)(CO)]_2+2py \qquad (2)$$

$$2W_2(O\text{-}t\text{-}Bu)_6(\mu\text{-}CO)+i\text{-}PrOH(\text{excess})\xrightarrow[\text{hexane}]{22^\circ C}[W_2(O\text{-}i\text{-}Pr)_6(CO)]_2+t\text{-}BuOH \qquad (3)$$

The structures of VI and VII are shown diagrammatically below and can be viewed as head-to-tail dimers of Vb and Vc.



(VI)



(VII)

The transformation of III to VII (M = W) has several noteworthy structural changes in terms of the central $M_2(\mu\text{-CO})$ moiety. In III the M–M, M–C and C–O distances are 2.52, 2.04 and 1.22 Å, respectively [12]. In VII the M–M, M–C and C–O distances are 2.66, 1.95 and 1.34 Å, respectively [12]. Clearly, the dimerization of the two $W_2(\mu\text{-CO})$ units occurs with reduction of M–M bonding, reduction of C–O bonding and an increase in M–C bonding. Of further note is the carbonyl oxygen-to-tungsten distance in VII, 1.98 Å, which is shorter than that expected for a O-to-W single bonds implying some supplemental oxygen-to-tungsten π-bonding [17].

The bonding in these μ-CO containing compounds has been investigated by MO calculations employing the Fenske–Hall method [18,19]. In VII it is seen that the C–O ligand is being reduced by extensive tungsten-to-CO π^* bonding and by carbonyl oxygen-to-tungsten π-donation. This is clearly evident from examinations of the Mulliken populations of the carbonyl orbitals. See Table 1. Furthermore using a frozen orbital technique [20], the effect of RO-to-W π-donation can be seen to assist in this reduction of the CO ligand. The greater reducing power of tungsten relative to molybdenum can be traced to the better orbital energy match. Tungsten filled $5d$ orbitals are closer in energy to the CO π^* orbitals than are molybdenum's $4d$.

In compound VII the metal atoms are five coordinate, i.e. formally unsaturated, and we have tried to reduce the CO ligand further by the addition of more reducing agent in the form of $W_2(\text{O-i-Pr})_6$. Two reactions have been studied, namely those shown in eq. 4 and 5 [21]. In reaction 5, compound VII is formed competitively with [A], the unknown. By employing the use of ^{13}CO compound [A] can be seen to be formed in roughly 50% yield based on CO, with the remaining ^{13}CO containing compound being VII. Compound [A] is a dark greeen crystalline compound and can be separated from VII by careful crystal packing using tweezers. Regrettably a crystalline sample suitable for a single crystal X-ray study has not yet been obtained.

$$[W_2(\text{O-i-Pr})_6(\mu\text{-CO})]_2 + W_2(\text{O-i-Pr})_6(\text{py})_2 \xrightarrow[\text{hexane}]{22^\circ\text{C}} [\text{A}] \tag{4}$$

$$W_2(\text{O-t-Bu})_6(\mu\text{-CO}) + W_2(\text{O-t-Bu})_6 \xrightarrow[\text{i-PrOH/hexane}]{22^\circ\text{C}} \text{VII} + \underset{[\text{A}]}{W_4(\text{C})(\text{O})(\text{O-i-Pr})_{12}} \tag{5}$$

Our formulation of the unknown compound [A] as $W_4(\text{C})(\text{O})(\text{O-i-Pr})_{12}$ rests on its ^{13}C NMR spectrum, a comparison with that for VII and the observed structure of the isoelectronic and structurally characterized compound $W_4(\text{C})(\text{NMe})(\text{O-i-Pr})_{12}$ [22].

The ^{13}C NMR spectrum of VII shows a single resonance at δ 306 ppm flanked by two sets of tungsten satellites of equal intensity $^1J(^{183}\text{W}-^{13}\text{C})$ 189 and 164 Hz [12]. This is readily reconcilable with the observed structure given that the three bond coupling J(W–O–C) is very small [23 *]. The ^{13}C spectrum of the unknown compound [A] is shown in Fig. 1. The central resonance at δ ca. 350 ppm is flanked by four satellites due to coupling to ^{183}W, two having large coupling constants, 177 and 160 Hz, and two with small values, 37 and 24 Hz. The chemical shift of the

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* This and other references marked with asterisks indicate notes occurring in the list of references.

Table 1

Mulliken populations of the canonical orbitals of free CO and the CO moiety in CO, $W_2(OH)_6(\mu\text{-}CO)$, $M_2(OH)_6L_2(\mu\text{-}CO)$, and $[W_2(OH)_6(\mu\text{-}CO)]_2$ compounds, where $L = NH_3$ (from ref. 19)

Compound	3σ	4σ	1π	1π	5σ	2π	2π	6σ
CO	2.000	2.000	2.000	2.000	2.000	0.000	0.000	0.000
$Mo_2(OH)_6(\mu\text{-}CO)$	2.038	1.938	2.017	1.975	1.266	0.428	0.732	0.009
$Mo_2(OH)_6L_2(\mu\text{-}CO)$	2.038	1.936	2.017	1.972	1.334	0.394	0.846	0.009
$W_2(OH)_6(\mu\text{-}CO)$	2.055	1.950	2.019	1.971	1.343	0.530	0.835	0.007
$W_2(OH)_6L_2(\mu\text{-}CO)$	2.057	1.955	2.019	1.967	1.412	0.492	0.975	0.007
$[W_2(OH)_6(\mu\text{-}CO)]_2$	2.053	1.734	1.907	1.841	1.381	0.914	1.174	0.014

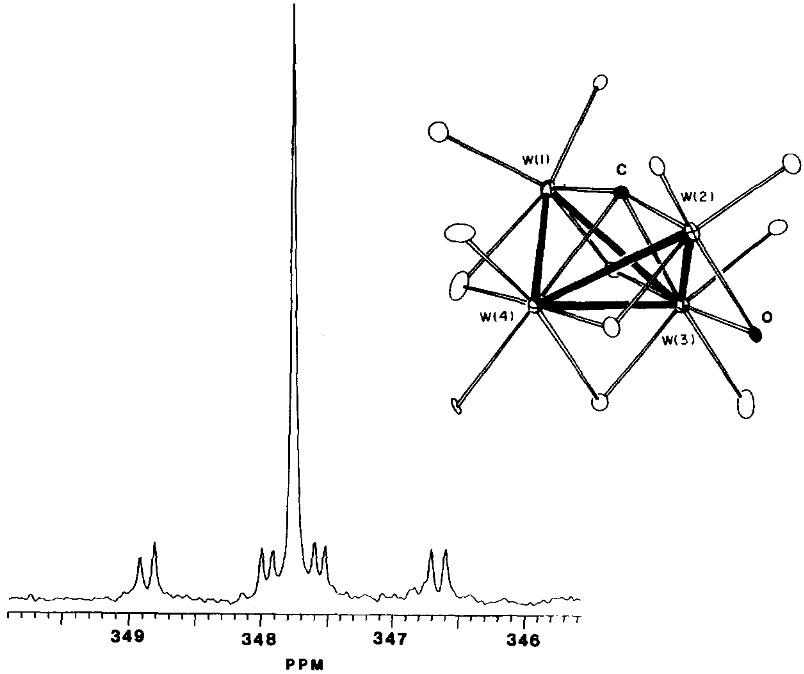

Fig. 1. $^{13}C\{^{1}H\}$ NMR spectrum of the carbido carbon resonance in the labelled compound $W_4(^*C)(O)(O\text{-}i\text{-}Pr)_{12}$ where $^*C$ represents 92 mole % ^{13}CO. The spectrum was recorded in toluene-d_8 at 75 MHz, 22° C (from ref. 21).

carbide carbon in $W_4(C)(NMe)(O\text{-}i\text{-}Pr)_{12}$ was found at 367 ppm but at natural abundance ^{13}C no satellite information could be obtained [22]. The observed structure involves a W_4 butterfly as shown in Fig. 2. The wingtip W–C bond distances are notably shorter, 1.94 Å, than the backbone W–C distances, 2.22 Å (av), as has been found in other $M_4(\mu_4\text{-}C)$ clusters supported by carbonyl ligands

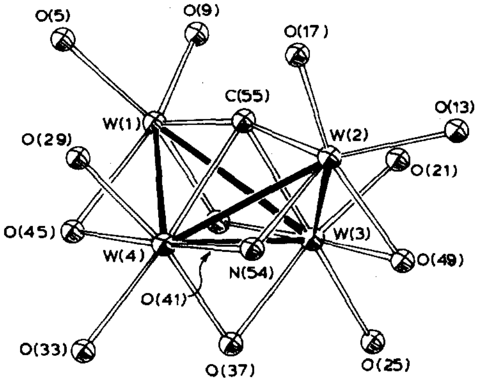

Fig. 2. A ball-and-stick drawing of the central W_4CNO_{12} unit of the $W_4(C)(NMe)(O\text{-}i\text{-}Pr)_{12}$ molecule (from ref. 22).

[24 *]. The virtual C_{2v} symmetry of the $W_4(\mu\text{-}C)$ moiety is destroyed by the imido ligand which bridges between a backbone and a wingtip tungsten atom. It is not unreasonable to anticipate a related structure for the isoelectronic compound $W_4(C)(O)(O\text{-i-Pr})_{12}$ in which the oxo group substitutes for the μ-NMe ligand.

Concluding remarks

It is regrettable that at this time the formulation of the unknown compound [A] as $W_4(C)(O)(O\text{-i-Pr})_{12}$ rests on mere spectroscopic evidence. However, the principals of $C{\equiv}O$ reduction are clearly evident in this molecular approach. (1) The M–M bonds provide a reservoir of electrons for extensive back-bonding to CO π^* orbitals. (2) The alkoxide ligands assist as π-donors and offer flexibility in terms of their bonding modes. In the former capacity one should note that in $M_2(OR)_6(\mu\text{-}CO)$ compounds there are six π-donor ligands and one π-acceptor. The facile terminal-bridge interconversions can be controlled, at least to some extent, by steric factors but may in some instances lead to unwanted disproportionation reactions. (3) The substrate of interest, CO, to metal ratio must be small. (4) The $[W_2(\mu\text{-}CO)]_2$ containing compound [12], which shows $\bar{\nu}(CO)$ at 1242 cm^{-1} (deduced from ^{13}CO labelling) parallels $\bar{\nu}(CO)$ values for "side-on chemisorbed CO on metal surfaces such as recently noted for Cr(110) [25 *]. (5) The cooperative bonding effects of tungsten atoms provide an excellent example of the advantages of metal cluster chemistry in the activation of a small molecule.

Finally the ultimate C–O cleavage to carbide and oxide may well have a parallel with the reductive cleavage of C=O bonds noted previously for the reaction between acetone and $W_2(O\text{-i-Pr})_6(py)_2$, eq. 6 [26].

$$2W_2(O\text{-i-Pr})_6(py)_2 + 2Me_2C{=}O \xrightarrow[\text{hexane}]{22^\circ C} W_4(O)_2(O\text{-i-Pr})_{12} + Me_2C{=}CMe_2 \qquad (6)$$

In the present case the addition of one $W_2(\mu\text{-}CO)$ moiety across the W=W bond of a $W_2(O\text{-i-Pr})_6$ molecule could lead to C–O cleavage in a manner not dissimilar to the cleavage of $C{\equiv}C$ and $C{\equiv}N$ bonds in the reactions with $W_2(OR)_6$ compounds [27–30]. In each instance the $C{\equiv}X$ bond requires a six electron reduction.

Finally it is worth noting that the Fischer–Tropsch reaction [31 *] which provides for the conversion of $CO + H_2$ to alkanes and water is not limited to reactions employing metal surfaces. Many reduced metal oxides show this type of chemical reaction and the reduced oxides of molybdenum either in bulk form or dispersed on silica or alumina have, for example, provided a wealth of catalytic reactivity [32 *]. It is toward this end that we are examining the reactivity of reduced metal alkoxide clusters of molybdenum and tungsten.

Acknowledgements

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