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Oxygen and Chlorine Atom Transfer between Tungsten, Molybdenum, and Rhenium Complexes. Competition between One- and Two-Electron Pathways

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Inter-metal oxygen atom transfer reactions between molybdenum, tungsten, and rhenium complexes are described. With only chloride and $PMePh_2$ as supporting ligands, oxygen atom transfer is observed from rhenium to molybdenum and tungsten and from molybdenum to tungsten, but not in the reverse directions. For instance, $Re(O)Cl_3L_2$ reacts with $MoCl_2L_4$ or WCl_2L_4 to form $ReCl_3L_3$ and $M(O)Cl_2L_3$ ($M = W$, Mo, $L = PMePh_2$). These data suggest that the order of M–O bond strengths for the d^2 $M(O)Cl_xL_{5-x}$ complexes is W > Mo > Re. The above reactions also yield $MoCl_3L_3$ and WCl_3L_3, which result from chlorine atom transfer. Oxygen atom transfer is also observed from $Re(O)Cl_3L_2$ to MCl_3L_3 ($M = Mo$, W) to give $M(O)Cl_3L_2$ and $M(O)Cl_2L_3$, resulting from one- and two-electron oxygen atom transfers, as well as the chlorine atom transfer product, MCl_4L_2. Related reactions are described. Reactions between chloro–phosphine compounds also occur by chlorine atom transfer; for instance, WCl_3L_3 and $MoCl_4L_2$ give WCl_4L_2 and $MoCl_3L_3$. Reactions were followed by NMR, which is a very valuable technique despite the paramagnetic nature of the chloro–phosphine complexes. The spectra of MCl_xL_{6-x} ($M = Mo$, W, $x = 2$–4; $M = Re$, $x = 3$, 4) are reported, and 2-dimensional NMR has been used in the assignments. $MoO_2(S_2CNEt_2)_2$ also transfers an oxygen atom to $ReCl_3L_3$, WCl_2L_4, and $MoCl_2L_4$, although these reactions are quite complex. Even though the molybdenum oxidant has no chloride, the chlorine atom transfer product, e.g. WCl_3L_3, is also observed in each case. Oxygen atom transfer and chlorine atom transfer are competitive reaction paths in these systems, as are one- and two-electron pathways.

Transfer of an oxygen atom between a metal center and a substrate has been increasingly studied as attention has focused on metal–oxo complexes as selective oxidants, in laboratory, industrial, and enzymatic processes.[2] A comprehensive review[2a] details the range of metal complexes and substrates that have been studied, but also indicates that very few data are available for the transfer of an oxygen atom between two different metal centers.[3] Inter-metal oxygen atom transfer reactions are of particular interest as potential two-electron inner-sphere electron transfer processes. Inner-sphere reactions have not received the attention that outer-sphere processes have: for instance, it is only recently that there have been systematic studies of multielectron vs one-electron atom transfer reactions.[4] Inter-metal oxygen atom transfer can proceed with complete transfer of the oxygen or, more commonly, with the formation of oxo-bridged products, termed[2a] incomplete oxygen atom transfer.

We report here a number of complete inter-metal oxygen atom transfer reactions of molybdenum, tungsten, and rhenium complexes.[5] Most of the studies involve octahedral chloro–phosphine complexes of the form $M(O)Cl_xL_{5-x}$ and MCl_xL_{6-x} ($x = 2$, 3; $M = Mo$, W; $x = 3$, $M = Re$; $L = PMePh_2$); the bulky $PMePh_2$ ligand was chosen to ensure that ligand loss would not be rate limiting.[6] We began with the reactions of d^2 oxo complexes with d^4 non-oxo species, with the anticipation that these would proceed by clean two-electron oxygen atom transfer to give known, stable products. This is often the major pathway, allowing a direct comparison of the oxo transfer reactivities and the M–O bond strengths of the d^2 complexes. However, chlorine atom transfer always competes with oxygen atom transfer, even in cases where loss of $Cl^\bullet$ from the oxidant is expected to give an unstable product. Oxygen transfer with only one-electron redox change, formally transfer of O^- or O/Cl exchange, has also been observed. In order to probe these processes with one-electron redox change, some reactions of d^1 oxo and d^3 chloro–phosphine complexes have also been examined. The complex reactions of MCl_xL_{6-x} with $Mo(O)_2(dtc)_2$ ($dtc = S_2CNEt_2$), the most studied transition metal oxygen atom donor,[7] are also described.

Experimental Section

All experiments were performed in a nitrogen or argon atmosphere using high-vacuum or Schlenk techniques and a standard glovebox. Solvents were degassed and dried by standard methods.[8] Ferrocene (Aldrich) was sublimed before use. All reactions were executed at ambient temperatures unless otherwise stated. Compounds were identified by NMR, using a Varian VXR-300 spectrometer. The chemical shifts in ^1H NMR spectra are given in ppm relative to the solvent peak (C_6D_6). ^{31}P NMR spectra were determined at 121.4 MHz and were internally referenced to $PMePh_2$, $\delta = -27.6$ ppm relative to H_3PO_4. A two-dimensional homonuclear Hartmann-Hahn (HOHAHA) experiment was performed on $MoCl_3L_3$ using the MLEV-17 mixing sequence on a 20 mM solution of molybdenum(III) in C_6D_6 on a Bruker AF-300

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spectrometer at 303 K.[9] The spectrum results from a 256 × 1K data matrix; zero-filling was used to yield a final 512 × 1K matrix. An acquisition time of 10.24 ms was used. Twenty-four scans were recorded for every value of t_1. The mixing time consisted of two MLEV-16 cycles, corresponding to a spin-lock time of 5 ms each. Off-line data processing was performed on a VAX 3100 using the software package FTNMR.[10] EPR spectra were obtained on a much modified Varian E4 spectrometer[11] at room temperature in a benzene solution. Elemental analyses were performed by Canadian Microanalytical Service Ltd. (Delta, BC, Canada).

Reactions were monitored by ^{1}H and ^{31}P NMR spectroscopy at 25 °C; at low temperatures the NMR signals for the paramagnetic compounds broadened substantially. In a typical procedure, a benzene-d_6 solution of 0.02 g (0.028 mmol) of $Re(O)Cl_3(PMePh_2)_2$ along with ferrocene as an internal standard was prepared in the glovebox and equally divided into two NMR tubes sealed to ground-glass joints. To one of the tubes was added 0.015 g (0.014 mmol) of $WCl_2(PMePh_2)_4$. The NMR tubes were then capped with Teflon valves and removed to a vacuum line where the reaction solutions were cooled to −196 °C; the tubes were then evacuated and flame-sealed. Concentrations were determined by integration of the $P(CH_3)Ph_2$ or $S_2CN(CH_2CH_3)_2$ protons relative to ferrocene.

$WCl_2(PMePh_2)_4$,[12] $WCl_4(PMePh_2)_2$,[12] $W(O)Cl_2(PMePh_2)_3$,[13] $MoCl_3(PMePh_2)_3$,[14] $ReCl_3(PMePh_2)_3$,[15] $ReCl_4(PMePh_2)_2$,[15] $MoO_2(dtc)_2$,[16] and $MoO(dtc)_2$[16] were prepared by following published procedures. The preparation of $MoCl_2(PMePh_2)_4$ by Hall will be reported presently.[17] $MoCl_4(PMePh_2)_2$,[18] $Mo(O)Cl_2(PMePh_2)_3$, and $W(O)Cl_3(PMePh_2)_2$ were prepared by using $PMePh_2$ instead of PMe_3 or PPh_3 and by following reported procedures.[19] NMR spectra for $MCl_x(PMePh_2)_{6-x}$ compounds are given in Table I.

$WCl_2(diphos)_2$.[20] To a solution of 0.2 g (0.19 mmol) of $WCl_2(PMePh_2)_4$ in 50 mL of toluene was added a 10-fold excess of dppe (0.75 g, 1.9 mmol). The reaction mixture was stirred at room temperature overnight. The solution was concentrated to 5 mL and pentane added to precipitate light yellow solids, which were washed with pentane and dried in vacuo, yielding 0.18 g, 90%. Anal. Calcd for $WCl_2P_4C_{52}H_{48}$: C, 59.38; H, 4.61. Found: C, 59.76; H, 4.65.

$WCl_3(PMePh_2)_3$. Toluene (25 mL) was added to a mixture of 0.25 g (0.23 mmol) of $WCl_2(PMePh_2)_4$ and 0.17 g (0.23 mmol) of $WCl_4(PMePh_2)_2$, and the reaction mixture was stirred for 5 h. The solution was concentrated to 5 mL and pentane added to precipitate pale yellow solids, which were washed with pentane and dried in vacuo, yielding 0.33 g, 80%. Anal. Calcd for $WCl_3P_3C_{39}H_{39}\cdot{}^1/_4C_5H_{12}$:[21] C, 53.18; H, 4.67. Found: C, 53.25; H, 4.51.

$Re(O)Cl_3(PMePh_2)_2$ was prepared by following the published procedure,[22] except the reaction mixture was not heated since the reaction results otherwise in the formation of $ReCl_3(PMePh_2)_3$. This reaction results in a mixture of the cis and trans isomers, which can be separated because of their different solubilities. The green trans isomer is soluble in toluene, while the blue cis isomer is not. ^{1}H NMR (C_6D_6): trans, 2.25 (t, 6 H); cis, 1.79 (d, 6 H). ^{31}P NMR (C_6D_6): trans, −21.5 (s); cis, 33.3 (s). Anal. Calcd for $ReOCl_3P_2C_{26}H_{26}$: C, 44.04; H, 3.70. Found: C, 44.12; H, 3.70.

$Mo_2O_3(dtc)_2(OPMePh_2)_2Cl_2\cdot C_6D_6$. Benzene-$d_6$ (0.5 mL) was added to a mixture of 0.006 g (0.019 mmol) of $Mo(O)_2(dtc)_2$ and 0.012 g of $Re(O)Cl_3(PMePh_2)_2$ in an NMR tube in the glovebox. The NMR tube was flame-sealed under vacuum. Over a 2-week period, black and yellow crystals were formed, which were physically separated. A yellow crystal gave triclinic unit cell parameters of a = 8.107 (4) Å, b = 9.262 (6) Å, c = 13.924 (10) Å, α = 107.7 (6)°, β = 101.4 (5)°, and γ = 94.4 (5)°, which match those for the known compound $Mo_2(O)_4(dtc)_2$.[23] An X-ray structure of a poorly diffracting black crystal showed it to be $Mo_2O_3(dtc)_2(OPMePh_2)_2Cl_2\cdot C_6D_6$.[24]

Results

Oxygen Atom Transfer between Chloro–Phosphine Compounds. The reaction between $Re(O)Cl_3L_2$ and WCl_2L_4 produces $ReCl_3L_3$ and the tungsten–oxo complex $W(O)Cl_2L_3$ as major products and goes to completion within hours (eq 1; L = $PMePh_2$ throughout

$$Re(O)Cl_3L_2 + WCl_2L_4 \rightarrow ReCl_3L_3 + W(O)Cl_2L_3 + WCl_3L_3 + W(O)Cl_3L_2 \quad (1)$$

this paper). This is the expected oxygen atom transfer process, with the d^2 rhenium–oxo complex reduced by two electrons to d^4 $ReCl_3L_3$ and the d^4 tungsten reactant oxidized to a d^2 oxo complex. In addition, a small amount of WCl_3L_3 (ca. 20% of the total tungsten) is formed initially, then diminishes in concentration, and disappears completely within the first hour. The tungsten(V)–oxo complex $W(O)Cl_3L_2$ is observed by EPR;[25] it is not visible by NMR because of its d^1 configuration. WCl_3L_3 is the result of chlorine atom transfer, and $W(O)Cl_3L_2$ is formed through both chlorine and oxygen atom transfer. In each case, the number of phosphines bound to the metal changes in order to keep the complex six-coordinate.

While reaction of $Re(O)Cl_3L_2$ and WCl_2L_4 occurs rapidly (eq 1), the opposite combination—the d^2 tungsten–oxo complex $W(O)Cl_2L_3$ plus the d^4 rhenium species $ReCl_3L_3$—do not react (eq 2): there is essentially no change in the NMR spectrum over 9 days at ambient temperatures. Equation 2 is essentially the reverse of eq 1, since the latter occurs primarily by oxygen atom transfer.

$$W(O)Cl_2L_3 + ReCl_3L_3 \nrightarrow Re(O)Cl_3L_2 + WCl_2L_4 \quad (2)$$

These reactions, and all the reactions discussed here, were carried out in C_6D_6 solutions in sealed NMR tubes. It is only quite recently that the utility of NMR spectra for the paramagnetic chloro–phosphine compounds MCl_xL_{6-x} has been recognized.[26] The spectra of MCl_xL_{6-x} are only mildly shifted, typically falling between δ −50 and δ +20, and 2-dimensional NMR techniques

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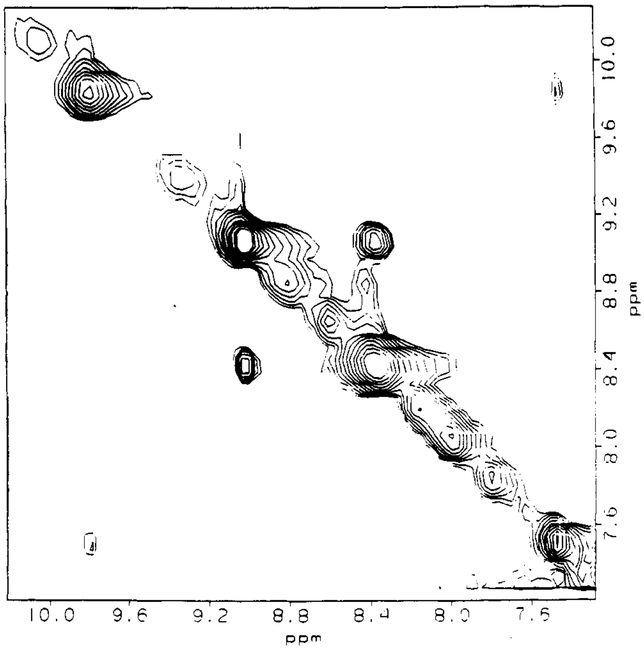

Figure 1. Homonuclear 2-dimensional ^1H NMR spectrum of paramagnetic $MoCl_3(PMePh_2)_3$, using a Hartmann–Hahn (HOHAHA) pulse sequence.

Table I. ^1H NMR Data for Molybdenum, Tungsten and Rhenium Chloro–Phosphine Complexes[a]

compound	phenyl resonances	methyl resonances
$WCl_2(PMePh_2)_4$	7.5–10, three br s, 40H	–0.5 to –3.5, br s, 12H
$WCl_3(PMePh_2)_3$	15.54, br s, 8H, ortho[b] 11.56, br s, 4H, ortho 9.83, d, 6 Hz, 4H, meta 9.45, d, 6 Hz, 8H, meta 7.37, s, 4H, para 5.01, s, 2H, para	–12.35, br s, 3H –24.59, br s, 6H
$WCl_4(PMePh_2)_2$	11.28, d, 7 Hz, 8H, ortho 7.95, t, 7 Hz, 8H, meta 7.56, t, 7 Hz, 4H, para	–27.62, br s, 6H
$WCl_2(diphos)_2$	15.85, s, 16H, ortho or meta 9.69, s, 16H, ortho or meta 7.91, s, 8H, para (or CH_2)	21.26, s, 8H, CH_2 (or para)[c]
$MoCl_2(PMePh_2)_4$	5 to 10, br m, 40H	–11 to –16, br s, 12H
$MoCl_3(PMePh_2)_3$	11.00–15.5, 12H, br m, ortho[d] 9.79, s, 4H, meta 9.05, s, 4H, para 8.40, s, 8H, meta 7.49, s, 2H, para	–19.5, br s, 3H –39.5, br s, 6H
$MoCl_4(PMePh_2)_2$	15.31, br s, 8H, ortho[b] 9.65, s, 4H, para 7.95, d, 4 Hz, 8H, meta	–28.0, br s, 6H
$ReCl_3(PMePh_2)_3$	14.13, d, 7 Hz, 8H, ortho or meta 9.83, d, 8 Hz, 4H, ortho or meta 8.87, t, 8 Hz, 2H, para 8.35, m, 8 Hz, 8H + 4H, ortho and meta 7.57, t, 8 Hz, 4H, para	–0.15, s, 6H –2.84, s, 3H
$ReCl_4(PMePh_2)_2$	23.93, s, 8H, ortho 11.32, t, 7 Hz, 4H, para 8.98, d, 4 Hz, 8H, meta	–48.69, s, 6H

[a] In C_6D_6 solution at 25 °C. Chemical shifts in ppm are referenced to TMS, ferrocene, or residual protons in the solvent. br = broad; s = singlet; d = doublet; m = multiplet. [b] The doublets were assigned meta because they collapsed upon decoupling of the resonances for the para hydrogens. [c] Methylene resonance of the diphos ligand. [d] Assignment of the four singlets between 9.79 and 7.49 ppm was possible through integration and location of cross peaks in a 2-dimensional experiment (Figure 1).

are applicable despite the paramagnetism (see Figure 1).[9] We report here (Table I) the ^1H NMR spectra of nine chloro–phosphine complexes, including two series of d^2, d^3, and d^4 complexes (MCl_xL_{6-x}, $x = 2$–4, M = Mo, W). These give remarkably similar spectra, with phenyl peaks shifted downfield and methyl resonances upfield. In general, spectra for the rhenium compounds are quite sharp, with line widths often as low as a few hertz so that spin–spin coupling could be observed. The molybdenum compounds give comparatively broad NMR spectra, with line widths often reaching hundreds of hertz. The spectra of the tungsten compounds are intermediate. We have been unable to observe ^{31}P NMR spectra for these complexes, despite a recent report on the related $WCl_3(PMe_2Ph)_3$ complex.[27] The NMR spectra of the reaction mixtures allow definitive identification of highly air-sensitive components of complex reaction mixtures, by comparison of ^1H and ^{31}P NMR spectra with those of authentic samples. Yields were determined by integration versus a standard, typically ferrocene, although the accuracy is often not very good due to broad or overlapping peaks; quantitative interpretation of the data has not been attempted. From mass balance considerations, it is also clear that some of the products (typically 0–25% of the material) are not visible by NMR.

The reaction of $Re(O)Cl_3L_2$ with $MoCl_2L_4$ (eq 3) is similar to the tungsten case except that $MoCl_3L_3$ is the dominant initial product, requiring many hours to disappear completely, and no

$$Re(O)Cl_3L_2 + MoCl_2L_4 \rightarrow ReCl_3L_3 + Mo(O)Cl_2L_3 + MoCl_3L_3 \quad (3)$$

$Mo(O)Cl_3L_2$ is observed.[28] The reverse reaction between $Mo(O)Cl_2L_3$ and $ReCl_3L_3$ does not occur. $Mo(O)Cl_2L_3$ oxidizes WCl_2L_4 to give $W(O)Cl_2L_3$, $W(O)Cl_3L_2$ (by EPR), and WCl_3L_3 (eq 4). The likely molybdenum product, $MoCl_2L_4$, has not been conclusively identified in this reaction because of its very broad NMR spectrum; very little, if any $MoCl_3L_3$ is produced. Again,

$$Mo(O)Cl_2L_3 + WCl_2L_4 \rightarrow W(O)Cl_2L_3 + WCl_3L_3 + W(O)Cl_3L_2 \quad (4)$$

no reactions are observed for the opposite combination of reactants, for $Mo(O)Cl_2L_3 + ReCl_3L_3$ or for $W(O)Cl_2L_3 + MoCl_2L_4$.

Following reaction 4 over time (Figure 2A) illustrates the complexity of these processes. In the initial stage, both $W(O)Cl_2L_3$ and WCl_3L_3 are formed. Once all of the WCl_2L_4 is consumed, WCl_3L_3 is consumed by reaction with $Mo(O)Cl_2L_3$. Calculating the mass balance in the reaction (Figure 2B) shows the quantity of material not observed by NMR. A large percentage of the oxo groups are accounted for, so there is not much $W(O)Cl_3L_2$ formed in the reaction (because tungsten(V) is NMR silent, it has not been quantified and is not included in Figures 2 and 3). There are, however, unobserved molybdenum and tungsten chloro–phosphine complexes produced (the initial rise in total tungsten is due to the difficulty in quantifying the paramagnetic WCl_2L_4).

In the above reactions, the chlorine atom transfer product, d^3 MCl_3L_3, appears and then decays. This is because it too can act as an oxygen or chlorine atom acceptor, as has been shown by its reaction with oxo complexes. $Re(O)Cl_3L_2$ rapidly oxidizes WCl_3L_3 (eq 5, Figure 3A) with stoichiometric formation of $ReCl_3L_3$. Three tungsten products are formed: $W(O)Cl_3L_2$, WCl_4L_2, and $W(O)Cl_2L_3$, the products of net oxygen atom

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[28] This reaction is particularly difficult to monitor by NMR because (i) $MoCl_2L_4$ exhibits very broad peaks, (ii) the *cis* isomer of $Re(O)Cl_3L_2$ is not very soluble and dissolves slowly as the *trans* isomer is consumed, and (iii) the NMR peaks for $Mo(O)Cl_2L_3$ are obscured by those of $Re(O)Cl_3L_2$. The presence of substantial amounts of $Mo(O)Cl_2L_3$ is indicated by ^{31}P NMR.

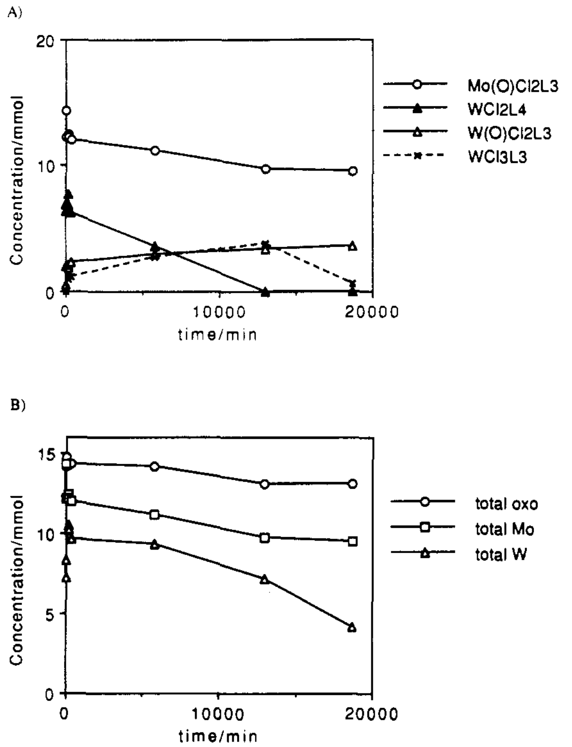

Figure 2. Time course of the reaction of $Mo(O)Cl_2L_3$ and WCl_2L_4 as determined from ^1H NMR spectra: (A) concentrations of starting materials and products; (B) total observed molybdenum, tungsten, and oxo compounds. $MoCl_2L_4$ and $W(O)Cl_3L_2$ are not observed in the NMR spectra; the latter is observed by EPR (see text; L = $PMePh_2$).

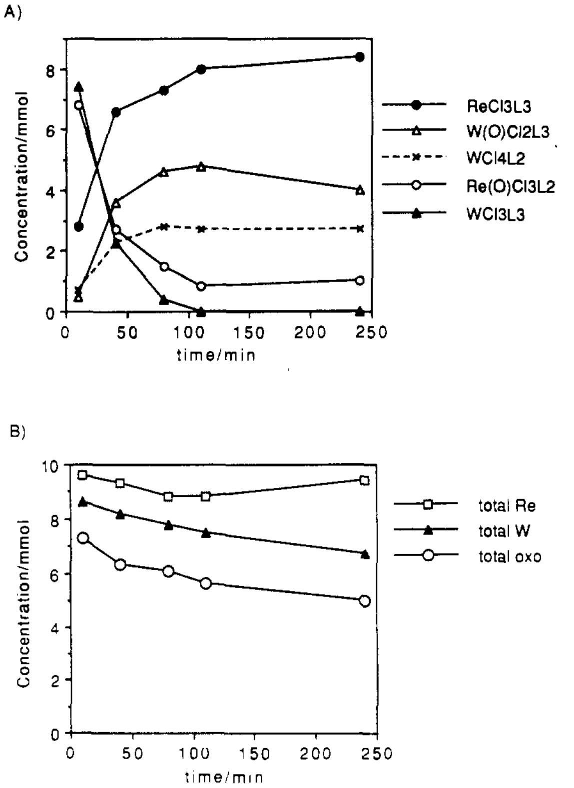

Figure 3. Time course of the reaction of $Re(O)Cl_3L_2$ and WCl_3L_3 as determined from ^1H NMR spectra: (A) concentrations of starting materials and products; (B) total concentrations of rhenium, tungsten, and oxo compounds. $W(O)Cl_3L_2$ is present (by EPR) but not observed by NMR (see text; L = $PMePh_2$).

$$2Re(O)Cl_3L_2 + 3WCl_3L_3 \rightarrow 2ReCl_3L_3 + W(O)Cl_3L_2 + WCl_4L_2 + W(O)Cl_2L_3 \quad (5)$$

transfer, chlorine atom transfer, and O/Cl exchange, respectively. O/Cl exchange is a net one-electron oxidation, equivalent to O^- addition and Cl^- loss. The rhenium mass balance in the reaction is good (Figure 3B), but there is a parallel loss of tungsten and oxo intensity in the NMR spectrum, which is most likely due to the formation of $W(O)Cl_3L_2$. It was at first surprising that the major product is $W(O)Cl_2L_3$, the product of O/Cl exchange. There appear to be two routes to this product, both by direct exchange and by comproportionation of $W(O)Cl_3L_2$ and WCl_3L_3 (eq 6). This comproportionation reaction proceeds rapidly at ambient temperature in independent experiments. It is another example of O/Cl exchange and appears to be a major route to WCl_4L_2 in reaction 5.

$$W(O)Cl_3L_2 + WCl_3L_3 \rightarrow W(O)Cl_2L_3 + WCl_4L_2 \quad (6)$$

The d^3 molybdenum(III) complex $MoCl_3L_3$ is also oxidized by $Re(O)Cl_3L_2$ to $Mo(O)Cl_3L_2$[29] and $Mo(O)Cl_2L_3$ (eq 7). This reaction is not as clean as the tungsten analog and light green solids precipitate, but the dominant pathways are still oxygen atom transfer and O/Cl exchange. Although the broad signals for $MoCl_4L_2$ are not observed in the NMR spectrum, the brick red color of the solution indicates its presence. In a control experiment, a solution of blue-green $Re(O)Cl_3L_2$ and red $MoCl_4L_2$ showed no reaction (there was no change in the $Re(O)Cl_3L_2$ concentration), but it was almost impossible to observe the NMR signals for the paramagnetic $MoCl_4L_2$.

$$Re(O)Cl_3L_2 + MoCl_3L_3 \rightarrow ReCl_3L_3 + Mo(O)Cl_3L_2 + Mo(O)Cl_2L_3 + MoCl_4L_2 \quad (7)$$

WCl_3L_3 is oxidized by $Mo(O)Cl_2L_3$ in a slower reaction to give $W(O)Cl_3L_2$ and roughly equimolar amounts of $W(O)Cl_2L_3$ and WCl_4L_2 (eq 8). $MoCl_2L_4$ is presumably formed but was not clearly seen due to its broad NMR spectrum.

$$Mo(O)Cl_2L_3 + WCl_3L_3 \rightarrow W(O)Cl_3L_2 + W(O)Cl_2L_3 + WCl_4L_2 \quad (8)$$

None of the reactions described above show the formation of phosphine oxide. The tungsten- and molybdenum-oxo complexes are not reduced by phosphines, and reduction of $Re(O)Cl_3L_2$ by the metal complexes is faster than reaction with $PMePh_2$. The addition of 2 or 10 equivalents of phosphine to the reaction between $Re(O)Cl_3L_2$ and WCl_2L_4 (eq 1) does not appreciably change the rate of initial reaction, but the decay of WCl_3L_3 is slowed and, with 10 equiv, $OPMePh_2$ is observed. In contrast, added phosphine substantially inhibits the reaction of $Re(O)Cl_3L_2$ and WCl_3L_3 (eq 5), 2 equiv increasing the approximate half-life from 30 to 100 min. No phosphine oxide is observed even when 10 equiv of L is added.

Chlorine Atom Transfer between Chloro-Phosphine Compounds. In order to understand some of the secondary reactions mentioned above, we have examined reactions of chloro-phosphine complexes without any oxo ligands. WCl_3L_3 and $MoCl_4L_2$ react slowly to form WCl_4L_2 and $MoCl_3L_3$ as the major products (eq 9): chlorine atom transfer occurs from the d^2 molybdenum to the d^3 tungsten center. The mass balance of this reaction shows that the total metal concentration diminishes over time, suggesting the formation of other, NMR-silent compounds. No reaction is observed in the reverse direction, between WCl_4L_2 and $MoCl_3L_3$. Chlorine atom transfer also occurs in the reaction between d^4 WCl_2L_4 and

$$WCl_3L_3 + MoCl_4L_2 \rightarrow WCl_4L_2 + MoCl_3L_3 \quad (9)$$

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(29) A *g* value of 1.89 was found for $Mo(O)Cl_3L_2$. While this species does not appear to have been reported,[29a,b] the spectrum is similar to those of other $MoOCl_3L'_2$ complexes and the tungsten analogue. (a) Garner, D. C.; Charnock, J. M. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: New York, 1987; Vol. 3, p 1329. (b) Stiefel, E. I. *Prog. Inorg. Chem.* **1977**, *22*, 1.

d^3 $MoCl_3L_3$ to give WCl_3L_3 and $MoCl_2L_4$ (eq 10). Measurement

$$WCl_2L_4 + MoCl_3L_3 \rightarrow WCl_3L_3 + MoCl_2L_4 \quad (10)$$

$$WCl_3L_3 + MoCl_3L_3 \rightarrow WCl_4L_2 \quad (11)$$

$$WCl_2L_4 + MoCl_4L_2 \rightarrow WCl_3L_3 + MoCl_3L_3 \rightarrow WCl_4L_2 \quad (12)$$

$$ReCl_4L_2 + WCl_3L_3 \rightarrow ReCl_3L_3 + WCl_4L_2 \quad (13)$$

$$ReCl_4L_2 + MoCl_3L_3 \rightarrow ReCl_3L_3 + MoCl_4L_2 \quad (14)$$

of the NMR integrals is difficult, however, because the NMR resonances for $MoCl_2L_4$ are very broad and overlap with those of WCl_3L_3. In the reaction of $MoCl_3L_3$ with WCl_3L_3 (eq 11), the tungsten complex is oxidized to WCl_4L_2 while the broad peaks for reduced molybdenum product, $MoCl_2L_4$, cannot be distinguished. The d^4 complex WCl_2L_4 reacts quickly with d^2 $MoCl_4L_2$ (eq 12) to form initially d^3 WCl_3L_3 and d^3 $MoCl_3L_3$, which then react further to produce d^2 WCl_4L_2 and presumably d^4 $MoCl_2L_4$, which was not observed. Similarly, $ReCl_4L_2$ reacts with WCl_3L_3 and $MoCl_3L_3$ by transfer of a chlorine atom, forming $ReCl_3L_3$, WCl_4L_2, and $MoCl_4L_2$, respectively (eqs 13 and 14). In the reverse direction, only small amounts of oxidized products are observed in the reactions of $WCl_3L_3 + MoCl_2L_4$ and $ReCl_3L_3 + MoCl_4L_2$; mixtures of $ReCl_3L_3$ + WCl_4L_2 show no reaction by NMR. In all of these reactions, mass balance considerations indicate that there are also NMR-silent products. With the same metal, however, comproportionation of d^2 WCl_4L_2 and d^4 WCl_2L_4 cleanly yields WCl_3L_3; this is our preferred method of synthesis of WCl_3L_3.

Oxygen Atom Transfer from $Mo(O)_2(dtc)_2$. The molybdenum(VI)–dioxo complex $Mo(O)_2(dtc)_2$ (dtc = S_2CNEt_2) reacts readily with $ReCl_3L_3$, WCl_2L_4, and $MoCl_2L_4$ (eqs 15–17). Among

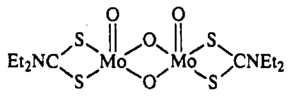
$$Mo(O)_2(dtc)_2 + ReCl_3L_3 \rightarrow Mo(O)(dtc)_2 + Re(O)Cl_3L_2 + OPMePh_2 + ReCl_4L_2 \quad (15)$$

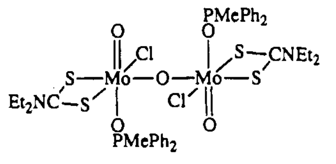
$$Mo(O)_2(dtc)_2 + WCl_2L_4 \rightarrow Mo(O)(dtc)_2 + W(O)Cl_2L_3 + WCl_3L_3 \quad (16)$$

$$Mo(O)_2(dtc)_2 + MoCl_2L_4 \rightarrow Mo(O)(dtc)_2 + Mo(O)Cl_2L_3 + MoCl_3L_3 \quad (17)$$

the compounds formed are $Mo(O)(dtc)_2$, $Mo_2(O)_3(dtc)_4$, and the expected oxygen atom transfer products, $Re(O)Cl_3L_2$, $W(O)Cl_2L_3$, and $Mo(O)Cl_2L_3$, as well as other diamagnetic and paramagnetic products which have not been identified. $OPMePh_2$ was only observed in the reaction of $Mo(O)_2(dtc)_2$ with $ReCl_3L_3$. Surprisingly, in each reaction we observe at short times a small amount of the product of chlorine atom addition, $ReCl_4L_2$, WCl_3L_3, or $MoCl_3L_3$, even though the oxidant, $Mo(O)_2(dtc)_2$, does not contain any chlorine! Other oxidants must be present in the solutions.

In addition, the d^2 oxo products, $Re(O)Cl_3L_2$, $W(O)Cl_2L_3$, and $Mo(O)Cl_2L_3$, themselves react rapidly with $Mo(O)_2(dtc)_2$ to give mixtures of products. Product identification is difficult because of the number of materials present and the diamagnetic molybdenum–dtc complexes have overlapping NMR spectra. A reaction of $Mo(O)_2(dtc)_2$ and $Re(O)Cl_3L_2$ gave black crystals and a minor amount of yellow crystals. A yellow crystal was identified from its unit cell parameters[23] to be the known dimeric molybdenum(V) species $Mo_2(O)_4(dtc)_2$ (A).[16] The black crystal was identified by an X-ray crystal structure to be the oxo-bridged dimer $[Mo(O)Cl_2(dtc)(OPMePh_2)]_2(\mu\text{-}O)\cdot C_6D_6$ (B).[24]


A


B

Discussion

Complete oxygen atom transfer occurs from the d^2 oxo complexes $Re(O)Cl_3L_2$ and $Mo(O)Cl_2L_3$ to d^4 chloro–phosphine complexes of molybdenum and tungsten, MCl_2L_4 (eqs 1, 3, and 4). These reactions contrast with the more common observation of incomplete oxygen atom transfer;[2a] the stability of the d^2 terminal oxo products most likely encourages cleavage of any μ-oxo intermediates. We have not observed any reactions in the reverse direction, such as oxidation of rhenium(III) or reduction of tungsten(IV) (e.g., eq 2), indicating that thermodynamics dictate the direction of oxygen transfer: Re → Mo, Re → W, and Mo → W. The same trend of reactivity is observed in the chlorine atom transfer reactions between MCl_xL_{6-x} complexes: a chlorine atom is transferred from rhenium to molybdenum and tungsten and from molybdenum to tungsten. The rates of the oxygen atom transfer reactions (eqs 1–8) reflect the apparent driving force, and the same is true for the chlorine atom transfer processes (eqs 9–14). Thus transfer of an oxygen atom from $Re(O)Cl_3L_2$ to WCl_2L_4 or WCl_3L_3 is significantly faster than transfer to the analogous molybdenum compounds, and oxo transfer from $Mo(O)Cl_2L_3$ to WCl_2L_4 or WCl_3L_3 is slower still. The rates of reaction with $Mo(O)_2(dtc)_2$ are in the order $WCl_2L_4 > MoCl_2L_4 \gg ReCl_3L_3$.

The oxo transfer reactions involve exchange of an oxygen atom for a phosphine ligand; the thermodynamics are most likely dominated by the metal–oxygen bond strengths because they are so much greater than the metal–phosphine bond strengths.[30] This suggests that the Re–O bond is weaker than the Mo–O or W–O bonds and that Mo–O is weaker than W–O. The order of metal–oxygen multiple bond strengths, W > Mo > Re, is expected from the redox properties of the metals: tungsten is the most electropositive metal and the most difficult to reduce by removing an oxygen atom. For instance, $W(O)Cl_2L_3$ and $Mo(O)Cl_2L_3$ are not reduced by phosphines while $Re(O)Cl_3L_2$ is deoxygenated by $PMePh_2$ at ambient temperatures. Similarly, WCl_2L_4 is an extremely potent oxygen atom acceptor,[31] $MoCl_2L_4$ is less reactive,[17] and $ReCl_3L_3$ is almost inert.[32] On the other hand, the observed order contrasts with the common pattern that bond strengths increase on moving from second- to third-row transition metals.[33] The average gas-phase bond strengths for WO_3, MoO_3, and Re_2O_7 are 150, 141, and 150 kcal/mol (the rhenium value being an average of the bonds to six terminal oxo ligands and one μ-oxo ligand).[34]

$Mo(O)_2(dtc)_2$ is the most reactive oxygen atom donor we have examined, even oxidizing $ReCl_3L_3$ (eq 15) and the d^2 oxo compounds $M(O)Cl_2L_3$ and $Re(O)Cl_3L_2$. This is likely due to the higher oxidation state of the molybdenum and to the presence

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(30) The metal–oxygen bond strengths are ≥100 kcal/mol (see below) while those of the M–$PMePh_2$ bonds are ca. 15–30 kcal/mol. The L_2Cl_3M–$PMePh_2$ bond is probably slightly stronger than the L_3Cl_2M–$PMePh_2$ bond because of lower steric crowding.

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of two oxo ligands, which reduces the Mo–O bond order[35] (the "spectator effect" of the second oxo[36]). The strength of the $(dtc)_2(O)Mo–O$ bond has been estimated on the basis of calorimetric data to be 96 kcal/mol,[37] and we have estimated the bond strength in $W(O)Cl_2L_3$ to be ≥ 138 kcal/mol on the basis of solution reactivity,[38] a remarkable difference of 40 kcal/mol.

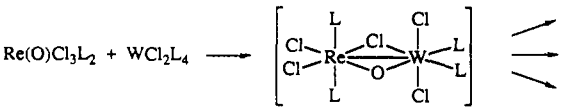
The variety of products in reactions 1–8 is remarkable—they are not simply two-electron oxygen atom transfer reactions. $Re(O)Cl_3L_2$ oxidizes WCl_3L_3 (eq 5) by net oxygen atom transfer (to $W(O)Cl_3L_2$), by chlorine atom transfer (to WCl_4L_2), and by O/Cl exchange (to $W(O)Cl_2L_3$). O/Cl exchange is oxygen addition with only one-electron redox change, supporting the suggestions of Woo and of Bottomley[3a–d] that oxygen (or nitrogen) transfer does not need to be a two-electron process. The transfer of a univalent atom such as chlorine in connection with oxygen or nitrogen atom transfer has been previously observed.[3] The reaction of $MoO_2(acac)_2$ and $MoCl_2(acac)_2$ to give 2 equiv of the molybdenum(V) complex $MoOCl(acac)_2$ has been suggested to proceed through a two-step mechanism of initial transfer of an oxygen atom and subsequent transfer of a chlorine.[3h] The reversible nitrogen atom transfer between $(OEP)Mn^{V}(N)$ and $(TTP)Mn^{III}Cl$ yielding $(OEP)Mn^{III}Cl$ and $(TTP)Mn^{V}(N)$ is thought to be initiated by the loss of chloride followed by nitrogen atom transfer through a μ-nitrido-bridged intermediate.[3a,b]

It is surprising that the d^2 oxo complexes $Re(O)Cl_3L_2$ and $Mo(O)Cl_2L_3$ can apparently act as $Cl^{\bullet}$ donors (eqs 1, 3, 4, 5, 7, and 8) because this would yield a d^3 oxo complex which should be unstable.[39] Oxo complexes are typically found only in d^0, d^1, or d^2 configurations,[39] and there are no isolated examples of d^3 rhenium- or molybdenum–oxo species.[40] Chlorine atom transfer, which does not generate two stable products, appears to be competitive with oxygen atom transfer, which does form two isolable species. This suggests that chlorine atom transfer is kinetically at least as facile as oxygen atom transfer. Consistent with this, d^2 $MoCl_4L_2$ transfers a chlorine atom significantly faster to d^3 WCl_3L_3 than d^2 $Mo(O)Cl_2L_3$ transfers an oxygen atom to WCl_3L_3 (half-lives ca. 180 vs <10 min, respectively). One might have expected that transfer of oxygen would be more facile because oxygen would appear to be the better bridging ligand (an important consideration in inner-sphere electron transfer processes[41]). However, recent work by Bullock, Creutz, and co-workers suggests that $Cl^{\bullet}$ is inherently more readily exchanged than Cl^{+}.[4]

The mechanism of complete oxygen atom transfer reactions is typically thought to involve μ-oxo intermediates, M–O–M′, by analogy with incomplete atom transfer (eq 18).[2a] We suggest

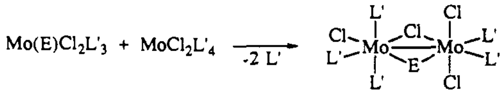
$$M{=}O + M' \rightleftarrows M{-}O{-}M' \rightleftarrows M + O{=}M' \qquad (18)$$

that our reactions proceed through an intermediate with both bridging oxide and chloride ligands (e.g. eq 19); cleavage of such



(19)

a dimer in various ways would lead to oxygen atom transfer, chlorine atom transfer, and O/Cl exchange (compare eq 1). Dimers of this kind are the stable products in the closely related reactions of molybdenum–trimethylphosphine complexes, formed on heating d^2 oxo and sulfido compounds with d^4 $MoCl_2L'_4$ (eq 20, $L' = PMe_3$); the sulfido derivative has been structurally



(20)

E = O, S; L' = PMe_3

C

characterized.[42] The formation of the dimers likely proceeds via initial phosphine loss from MCl_2L_4 or MCl_3L_3.[43] An outer-sphere electron transfer pathway is unlikely because the solvent polarity (benzene) is low and because reactions of the substitution-inert $WCl_2(diphos)_2$ with $Re(O)Cl_3L_2$ are much slower than those of labile WCl_2L_4. Added phosphine inhibits the reactions of WCl_3L_3, consistent with a phosphine loss pathway, as we have observed in many reactions of MCl_2L_4 species.[43]

The variety of pathways observed in these reactions show why transfer of an oxygen between metal centers is much more complex than oxygen atom transfer involving main group substrates. Oxygen atom transfer between molybdenum–dtc compounds and main group substrates is typically clean and straightforward, while we observe that $Mo(O)_2(dtc)_2$ reacts with all of the chloro–phosphine and oxo–chloro–phosphine complexes we have examined to give complex mixtures of products. Oxygen transfer and Cl and dtc exchange are both observed.

Conclusions

Both oxygen and chlorine atom transfer reactions are facile between tungsten, molybdenum, and rhenium chloro–phosphine complexes, for instance on reaction of $Re(O)Cl_3L_2$ and WCl_3L_3. Exchange of oxo and chloro ligands, a one-electron process, has also been observed. These reactions are rare examples of complete oxygen transfer, probably driven by the strength of the d^2 and d^1 metal–terminal oxo bonds. The observed direction of the oxygen transfer reactions (Re → Mo, Re → W, and Mo → W) indicates that the metal–oxygen bond strengths are in the order W > Mo > Re. The reactions typically yield mixtures of products, with O and Cl atom transfers and O/Cl exchange occurring at competitive rates. It is surprising that d^2 oxo complexes can act as chlorine atom donors because of the instability of the presumed resultant d^3 oxo compounds. $Mo(O)_2(dtc)_2$, which cleanly transfers an oxygen to main group substrates, yields a wide range of products on reduction by rhenium, molybdenum, and tungsten chloro–phosphine complexes, because oxygen, chlorine, and dtc exchange reactions are all competitive.

Acknowledgment. We thank K. A. Hall, L. M. Atagi, and S. N. Brown for helpful suggestions and K. A. Hall for preparing $MoCl_2L_4$ and $MoCl_4L_2$. We also thank D. A. Haas and B. H. Robinson for assistance with the EPR spectroscopy and T. Pratum for help with the 2-dimensional NMR. We are grateful to the National Science Foundation for financial support.

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(38) Reference 31a. The Re–O bond strength in $[Re(O)Cl_2(Me_3tacn)]^+$ has also been estimated to be 141 ± 9 kcal/mol (tacn = 1,4,7-triazacyclononane): Conry, R. R.; Mayer, J. M. *Inorg. Chem.* **1990**, *29*, 4862–7.

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(43) Essentially all reactions of these species are initiated by phosphine loss. See refs 17, 20, and 31 and: Atagi, L. M.; Critchlow, S. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1992**, *114*, 1483–4.