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Reactions of ML_4Cl_2 (M = Mo, W; L = PMe_3, $PMePh_2$) with Epoxides, Episulfides, CO_2, Heterocumulenes, and Other Substrates: A Comparative Study of Oxidative Addition by Oxygen Atom, Sulfur Atom, or Nitrene Group Transfer

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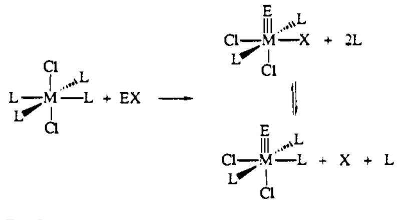
Abstract: A comparative survey of the reactivity of the divalent molybdenum and tungsten chloro–phosphine complexes ML_4Cl_2 (M = Mo, W; L = PMe_3, $PMePh_2$) toward oxidation by a variety of oxygen atom, sulfur atom, and nitrene donors is presented. In general, reactions result in net two-electron oxidation of the metal center, producing metal oxo, sulfido, and imido complexes. The reactions can also be described as oxidative addition reactions, in many cases oxidative addition of C═X double bonds. Reactions are apparently thermodynamically driven by the propensity of Mo and W to form strong multiple bonds with oxygen, sulfur, and nitrogen. ML_4Cl_2 compounds react with ethylene oxide and ethylene sulfide to produce oxo and sulfido tris(phosphine) species, $M(E)L_3Cl_2$ (E = O, S), in equilibrium with oxo and sulfido ethylene species $M(E)(CH_2{=}CH_2)L_2Cl_2$. Isocyanates (RN═C═O; R = ^{t}Bu, *p*-tolyl) and ^{t}BuN═C═N^{t}Bu react to form imido tris(phosphine) and imido carbonyl or imido isonitrile complexes, respectively. Phosphine sulfides are desulfurized forming sulfido complexes, but phosphine oxides are unreactive. The π-acids formed in these reactions—for instance, CO from cleavage of RNCO—bind more strongly to the tungsten(IV) versus the molybdenum(IV) oxo, sulfido, and imido products. Similarly, the equilibria for π-acid coordination are more favorable when the ligand is $PMePh_2$ than when L = PMe_3. For all of the complexes, reactions are slowed by free phosphine, consistent with a mechanism involving an initial dissociation of a phosphine ligand followed by trapping of the coordinatively unsaturated species by the oxidizing substrate. Ligand loss from ML_4Cl_2 is rapid for L = $PMePh_2$ at ambient temperatures but slower for L = PMe_3, with half-lives for PMe_3 loss of 18 min at 24 °C for $Mo(PMe_3)_4Cl_2$ and 6 min at 69 °C for $W(PMe_3)_4Cl_2$. For the molybdenum complexes MoL_4Cl_2 (L = PMe_3, $PMePh_2$), dimerization to the known Mo(II) quadruply bound species $Mo_2L_4Cl_4$ is competitive with oxidation at the metal center. In reactions involving stronger oxidants (SO_2, DMSO, and N_2O), the formation of trivalent species ML_3Cl_3 is often observed, indicating that chlorine atom transfer processes also occur.

Introduction

Oxidative addition is a fundamental reaction in organometallic chemistry, typically involving cleavage of single bonds such as H–H and H_3C–I.[3] Oxygen atom transfer and related reactions are receiving increased attention as key transformations in inorganic chemistry, because of their intrinsic interest as multielectron inner-sphere electron-transfer processes and because of their apparent involvement in a range of biochemical processes.[4] We have been studying novel reactions of $W(PMePh_2)_4Cl_2$ (**2b**) in which a double bond (e.g., in cyclopentanone or carbon dioxide) or two single bonds (e.g., in epoxides) are cleaved to give oxo, sulfido, or imido tungsten complexes (eq 1; M = W, L = $PMePh_2$).[5]



(1)

E = O, S, NR; X = CO, $CH_2{=}CH_2$, CNR (R = ^{t}Bu, *p*-tolyl)

These reactions can be viewed as oxidative addition reactions or be equally well described as oxygen atom, sulfur atom, or nitrene group transfer reactions, and they therefore provide an important bridge between these two classes of reactions. They are unusual oxidative addition reactions because two bonds in the substrate are broken, forming a divalent ligand (E = O, S, or NR) and a neutral ligand.[5c] Viewed as atom-transfer reactions, they are remarkable because of the strength of the bond being broken; for instance, removal of an oxygen atom from CO_2 requires 127 kcal/mol. The reactions are also of interest because they are fundamental transformations of (and important synthetic routes to) complexes with metal–ligand multiple bonds. This is an area of continuing growth and importance, as these species have been implicated as reactive intermediates in a range of industrial processes, enzymatic reactions, and reactions in organic synthesis.[4]

In this article we extend this chemistry to the tungsten trimethylphosphine complex, $W(PMe_3)_4Cl_2$ (**2a**), and the isoelectronic d^4 molybdenum complexes, $Mo(PMe_3)_4Cl_2$ (**1a**) and $Mo(PMePh_2)_4Cl_2$ (**1b**). [Throughout this paper, compounds labeled **a** contain PMe_3 ligands, and those labeled **b** have $PMePh_2$ groups.] Comparison of the behavior of these complexes illuminates the mechanisms of these interesting transformations and provides a more complete picture of the scope of the reactions. We begin with the stability and lability of the four divalent complexes ML_4Cl_2 (M = Mo, W; L = PMe_3, $PMePh_2$), followed by their reactions with each class of substrates in turn.

Results

Thermal Stability and Phosphine Exchange of ML_4Cl_2. Anaerobic benzene or toluene solutions of complexes **1–2** are stable for weeks at ambient temperatures. At 80 °C, however, the molybdenum complexes $Mo(PMe_3)_4Cl_2$ (**1a**) and $Mo(PMePh_2)_4Cl_2$ (**1b**) react to form the known[6] quadruply bonded

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(1) University of Washington David M. Ritter Fellow.

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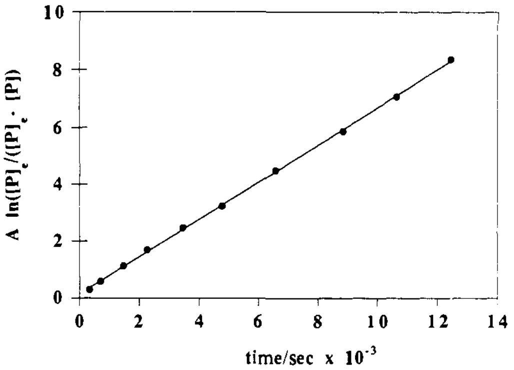
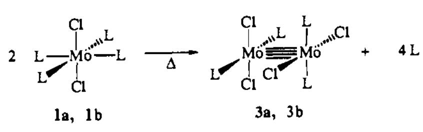


Figure 1. Plot showing first-order approach to equilibrium kinetics for the reaction of $Mo[P(CH_3)_3]_4Cl_2$ (0.064 M) plus 40 equiv of $P(CD_3)_3$. The ordinate is the function $4\{[P]_e/[P]_i\} \ln \{[P]_e/([P]_e - [P]_t)\}$ where $[P]_t$ is the concentration of $P(CH_3)_3$ at time *t*, $[P]_e$ is the final equilibrium concentration, and $[P]_i$ is the initial concentration of bound $P(CH_3)_3$.

Mo(II) dimers $Mo_2L_4Cl_4$ (L = PMe_3 (**3a**), $PMePh_2$ (**3b**)) along with free phosphine (eq 2). Complexes **3** were identified by



(2)

L = PMe_3, $PMePh_2$

comparison of their ^1H and ^{31}P NMR spectra with authentic samples. The reaction is essentially complete within 0.5 h at 80 °C when L is $PMePh_2$ (**1b**) but requires a week at this temperature for **1a**. $W(PMe_3)_4Cl_2$ has been previously reported to form $W_2(PMe_3)_4Cl_4$ in refluxing dibutyl ether,[7] although no reaction is observed upon heating in benzene for weeks at 80 °C. $W(PMePh_2)_4Cl_2$ decomposes rapidly (<0.5 h) when heated to 80 °C in benzene, but the known[7] tungsten quadruply bound dimer is not observed; the tungsten products have not been identified but appear to be paramagnetic as only free $PMePh_2$ is detected by ^1H NMR and no solids are observed. In all cases, decomposition is fastest during the early stages of reaction and proceeds more slowly as the concentration of phosphine increases, suggesting phosphine inhibition.

The rate of phosphine exchange in the PMe_3 complexes **1a** and **2a** has been determined by monitoring their reaction with PMe_3-d_9 by ^1H NMR (eq 3). Both reactions follow first-order approach

$$\underset{\mathbf{1a,\ 2a}}{M[P(CH_3)_3]_4Cl_2} + xP(CD_3)_3 \rightleftarrows M[P(CH_3)_3]_{4-x}[P(CD_3)_3]_xCl_2 + xP(CH_3)_3 \quad (3)$$

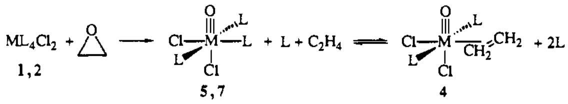
to equilibrium kinetics (e.g., Figure 1). This is consistent with a mechanism involving rate-limiting dissociation of PMe_3 (eqs 4 and 5; L = $P(CH_3)_3$, L* = $P(CD_3)_3$) and is also consistent with the observation of phosphine inhibition during dimerization of **1a**. The rate of approach to equilibrium of **1a** is the same for initial concentrations of $P(CD_3)_3$ of 0.7 and 2.5 M, which rules out an associative pathway.

$$ML_4Cl_2 \xrightarrow{k} [ML_3Cl_2] + L \quad (4)$$

$$[ML_3Cl_2] + L^* \rightarrow ML_3L^*Cl_2 \quad (5)$$

Dissociation of PMe_3 from the molybdenum complex **1a** occurs at ambient temperatures, with a half-life for exchange of the first phosphine of 18 min (k = 6.6 (1) × 10^{-4} s^{-1} at 24 °C). The tungsten analog **2a** is essentially inert at room temperature, but at 69 °C has a half-life for exchange of 7 min (k = 2.5 × 10^{-3} s^{-1}).[8] Loss of $PMePh_2$ from **1b** and **2b** is much more facile. Reaction of **1b** with ≥4 equiv of PMe_3 at ambient temperatures yields **1a** quantitatively within 15 min. **2b** is completely consumed within 5 min of reaction with PMe_3 forming mixed phosphine complexes, with complete substitution to produce **2a** requiring 24 h.

Reactions of ML_4Cl_2 with Ethylene Oxide and Ethylene Sulfide. Complexes **1** and **2** deoxygenate ethylene oxide to produce Mo(IV) or W(IV) terminal oxo complexes (eq 6; the reactions of **2b** have already been described in detail[5a,b,d]). The PMe_3 derivatives



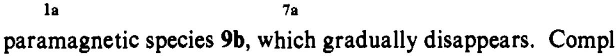
(6)

require heating to 80 °C while **1b** and **2b** react at ambient temperatures. The reactions are fastest in the early stages, slowing as the concentration of free phosphine increases, again indicating phosphine inhibition. These features are typical of essentially all of the reactions of **1** and **2**. Phosphine inhibition was confirmed for the reaction of **1a** with ethylene oxide (2:1) by the addition of 4 equiv of PMe_3, which slows the reaction by a factor of 5.

The oxo ethylene and oxo tris(phosphine) complexes were identified primarily by their NMR spectra (Table I), which show features characteristic of many of the compounds described here. The trans equivalent phosphine ligands appear as a triplet in ^1H NMR spectra (J_{PH} = 4 Hz) and a third phosphine, when present, appears as a doublet (J_{PH} = 8 Hz). The ^{31}P NMR spectra show a singlet for the bis(phosphine) species, and the tris(phosphine) compounds exhibit a triplet and a doublet, consistent with the trans and meridonal geometries shown.

Reactions of the tungsten complexes with ethylene oxide produce equilibrium mixtures of oxo ethylene species $W(O)(CH_2{=}CH_2)L_2Cl_2$ **4** and oxo tris(phosphine) complexes $W(O)L_3Cl_2$ **5**. With $PMePh_2$ as the ligand, the equilibrium lies toward coordination of ethylene (**4b**; K_{eq} = 2 × 10^2), but with PMe_3, **5a** is strongly favored over **4a** (K_{eq} = 9.6 × 10^{-4}). Complex **4a** can be generated by treatment of **5a** with ethylene, but it has not been isolated. The reaction of **2a** also forms a small amount of $W(PMe_3)_3Cl_3$ (**6a**),[9] the product of chlorine atom transfer to **2a**.

The corresponding molybdenum complexes also deoxygenate ethylene oxide. **1a** yields the oxo tris(phosphine) complex **7a** and ethylene (eq 7). With **1b**, the initial products are **7b** and a new



(7)

paramagnetic species **9b**, which gradually disappears. Complex **9b** is also formed immediately when **1b** is treated with ethylene (eq 8). Complex **9b** shows two broad peaks in the ^1H NMR spectrum at −11.5 and −15.5 ppm in a 1:2 ratio due to the PCH_3Ph_2 protons (the methyl protons of $Mo(PMePh_2)_4Cl_2$ resonate at −13 ppm), suggesting that **9b** is the Mo(II) monoethylene adduct $Mo(CH_2{=}CH_2)(PMePh_2)_3Cl_2$, analogous to the previously reported $W(CH_2{=}CH_2)(PMe_3)_3Cl_2$.[9] The disappearance of **9b** in the above reaction is due to its oxidation to **7b** by ethylene oxide.

$$\underset{\mathbf{1b}}{Mo(PMePh_2)_4Cl_2} + CH_2{=}CH_2 \rightleftarrows \underset{\mathbf{9b}}{Mo(PMePh_2)_3(CH_2{=}CH_2)Cl_2} + PMePh_2 \quad (8)$$

Molybdenum oxo ethylene complexes **8**, while not formed from epoxides, can be detected upon treatment of **7** with an excess of ethylene (eq 9). As in the tungsten compounds, the $PMePh_2$ derivative (**8b**) is more readily formed than the PMe_3 complex **8a**, although neither equilibrium is very favorable (K_{eq} ≅ 1 × 10^{-3} for **8a** and 9 × 10^{-2} for **8b** at 24 °C). This has prevented their isolation; they have been identified by the similarity of their ^1H and ^{31}P NMR spectra to those of **5** (Table I).

$$\underset{\mathbf{7a,b}}{Mo(O)L_3Cl_2} + CH_2{=}CH_2 \rightleftarrows \underset{\mathbf{8a,b}}{Mo(O)(CH_2{=}CH_2)L_2Cl_2} + L \quad (9)$$

Ethylene sulfide reacts rapidly with **1a**, **2a**, and **2b** at ambient temperatures to give rare examples of phosphine complexes with

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[7] Sharp, P. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 1430–1431.

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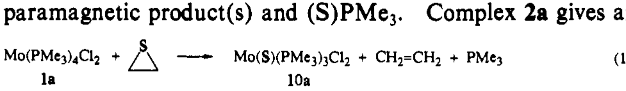
Table I. Selected NMR (^{1}H and ^{31}P) and IR Data

complex	^{1}H NMR^a δ (m, J_{PH} (Hz), no. H)	^{31}P{^{1}H} NMR^a δ (m, J_{PP} (Hz)) J_{WP} (Hz)	IR^b ν_{CO} or ν_{CN} (cm^{-1})	ref
$Mo(O)(PMe_3)_3Cl_2$ (**7a**)	1.37 (t, 4, 18 H), 1.26 (d, 8, 9 H)	−2.6 (t, 21), −9.2 (d, 21)		*c*
$Mo(O)(PMePh_2)_3Cl_2$ (**7b**)	2.24 (t, 4, 6 H), 1.54 (d, 8, 3 H)	8.2 (t, br), 16.0 (d, 13)		*d*
$Mo(O)(CO)(PMe_3)_2Cl_2$ (**18a**)	*e*	−9.1 (s)^e	2020 (C_6D_6)^e	this work
$Mo(O)(CO)(PMePh_2)_2Cl_2$ (**18b**)	2.21 (t, 4, 6 H)	13.2 (s)	2041 (C_6D_6)	*f*
$Mo(O)(CH_2{=}CH_2)(PMe_3)_2Cl_2$ (**8a**)	*g* 3.28 (d, 13, 2H), 3.07 (d, 13, 2 H)^h	5.25 (s)		this work
$Mo(O)(CH_2{=}CH_2)(PMePh_2)_2Cl_2$ (**8b**)	2.48 (t, 4, 6 H)^i 3.24 (d, 12, 2 H), 2.81 (d, 12, 2 H)^{h,i}	19.8 (s)		this work
$Mo(O)(CN\text{-}p\text{-}Tol)(PMe_3)_2Cl_2$ (**25a**)	1.47 (t, 4, 18 H), 1.92 (s, 3 H)^j	−7.1 (s)	2132 (Nujol)	this work
$Mo(O)(CN\text{-}p\text{-}Tol)(PMePh_2)_2Cl_2$ (**25b**)	2.39 (t, 4, 6 H), 1.89 (s, 3 H)^j	16.8 (s)	2127 (Nujol)	this work
$W(O)(PMe_3)_3Cl_2$ (**5a**)	1.44 (t, 4, 18 H), 1.44 (d, 4, 9 H)	−25.0 (d, 4) J_{WP} = 342 −30.9 (t, 4) J_{WP} = 446		*k*
$W(O)(PMePh_2)_3Cl_2$ (**5b**)	2.22 (t, 4, 6 H), 1.67 (d, 8, 3 H)	0.0 (s) J_{WP} = 340 −16.7 (s) J_{WP} = 413		*k*
$W(O)(CO)(PMe_3)_2Cl_2$ (**13a**)	1.33 (t, 4, 18 H)	−17.5 (s) J_{WP} = 330	1995 (C_6D_6)	*f*
$W(O)(CO)(PMePh_2)_2Cl_2$ (**13b**)	2.22 (t, 4, 6 H)	4.6 (s) J_{WP} = 331	2006 (Nujol)	*f*
$W(O)(CH_2{=}CH_2)(PMe_3)_2Cl_2$ (**4a**)	1.40 (t, 4, 18 H) 2.64 (m, br)^{h,l}	−14.9 (s) J_{WP} = 275		this work
$W(O)(CH_2{=}CH_2)(PMePh_2)_2Cl_2$ (**4b**)	2.43 (t, 4, 6 H) 2.77 (m, 2 H), 2.24 (m, 2 H)^h	8.5 (s) J_{WP} = 342		*f*
$W(O)(CN\text{-}p\text{-}Tol)(PMe_3)_2Cl_2$ (**27a**)	1.51 (t, 5, 18 H), 2.03 (s, 3 H)^j	−16.8 (s) J_{WP} = 338	2079 (C_6D_6)	this work
$Mo(S)(PMe_3)_3Cl_2$ (**10a**)	1.51 (t, 4, 18 H), 1.46 (d, 8, 9 H)	−6.08 (t, 20), −11.4 (d, 20)		this work
$W(S)(PMe_3)_3Cl_2$ (**11a**)	1.56 (t, 4, 18 H), 1.67 (d, 8, 9 H)	−41.7 (d, 4) J_{WP} = 271 −54.4 (t, 4) J_{WP} = 335		this work
$W(S)(PMePh_2)_3Cl_2$ (**11b**)	2.24 (t, 4, 6 H), 2.01 (d, 8, 3 H)	−22.3 (s, br) J_{WP} = 270 −37.6 (s, br) J_{WP} = 320		*f*
$W(S)(CO)(PMePh_2)_2Cl_2$	2.18 (t, 4, 6 H)	4.0 (s) J_{WP} = 266	1986 (C_6D_6)	*f*
$W(S)(CH_2{=}CH_2)(PMe_3)_2Cl_2$ (**12a**)	1.56 (t, 4, 18 H) 3.44 (m, 2 H), 2.71 (m, 2 H)^h	−13.9 (s) J_{WP} = 212		this work
$W(S)(CH_2{=}CH_2)(PMePh_2)_2Cl_2$ (**12b**)	2.32 (t, 4, 6 H) 3.17 (m, 2 H), 2.63 (m, 2 H)^h	8.1 (s) J_{WP} = 208		*f*
$Mo(N\text{-}p\text{-}Tol)(PMe_3)_3Cl_2$ (**25a**)	1.43 (t, 4, 18 H), 1.28 (d, 8, 9 H) 1.89 (s, 3 H)^j	4.9 (t, 18), −7.9 (d, 18)		*m*
$Mo(N\text{-}p\text{-}Tol)(CO)(PMe_3)_2Cl_2$ (**19a**)	1.32 (t, 4, 18 H), 1.85 (s, 3 H)^j	−10.3 (s)	1971 (C_6D_6)	this work
$Mo(N\text{-}p\text{-}Tol)(CO)(PMePh_2)_2Cl_2$ (**19b**)	2.31 (t, 4, 6 H), 1.74 (s, 3 H)^j	13.9 (s)	1986 (C_6D_6)	this work
$Mo(N^tBu)(PMe_3)_3Cl_2$ (**26a**)	1.42 (t, 4, 18 H), 1.24 (d, 8, 9 H) 1.01 (s, 9 H)^j	5.7 (t, 18), −7.3 (d, 18)		this work
$Mo(N^tBu)(CO)(PMe_3)_2Cl_2$ (**21a**)	1.35 (t, 4, 18 H), 0.83 (s, 9 H)^j	−10.3 (s)	1968 (C_6D_6)	this work
$Mo(N^tBu)(CO)(PMePh_2)_2Cl_2$ (**21b**)	2.32 (t, 4, 6 H), 0.79 (s, 9 H)^j	14.7 (s)	1985 (C_6D_6)	this work
$Mo(N^tBu)(CN^tBu)(PMePh_2)_2Cl_2$ (**23b**)	2.45 (t, 4, 6 H) 1.01 (s, 9 H), 0.72 (s, 9 H)^j	20.2 (s)	2095 (C_6D_6)	this work
$W(N\text{-}p\text{-}Tol)(CO)(PMe_3)_2Cl_2$ (**20a**)	1.39 (t, 4, 18 H), 1.89 (s, 3 H)^j	−20.3 (s) J_{WP} = 288	1947 (C_6D_6)	this work
$W(N\text{-}p\text{-}Tol)(CO)(PMePh_2)_2Cl_2$ (**20b**)	2.32 (t, 4, 6 H), 1.76 (s, 3 H)^j	3.5 (s) J_{WP} = 292	1964 (C_6D_6)	*f*
$W(N^tBu)(CO)(PMe_3)_2Cl_2$ (**22a**)	1.44 (t, 4, 18 H), 0.93 (s, 9 H)^j	−19.4 (s) J_{WP} = 295	1944 (C_6D_6)	this work
$W(N^tBu)(CO)(PMePh_2)_2Cl_2$ (**22b**)	2.34 (t, 4, 6 H), 0.74 (s, 9 H)^j	4.2 (s) J_{WP} = 288	1966 (Nujol)	*f*
$W(N^tBu)(CN^tBu)(PMe_3)_2Cl_2$ (**24a**)	1.57 (t, 4, 18 H) 1.28 (s, 9 H), 1.07 (s, 9 H)^j	−20.4 (s) J_{WP} = 299		this work
$W(N^tBu)(CN^tBu)(PMePh_2)_2Cl_2$ (**24b**)	2.48 (t, 4, 6 H) 0.99 (s, 9 H), 0.77 (s, 9 H)^j	6.0 (s) J_{WP} = 288	2090 (C_6D_6)	*f*

[a] NMR spectra taken in C_6D_6 solution at ambient temperatures unless otherwise indicated. Additional resonances for some of the compounds listed here are given in the Experimental Section. [b] IR spectra were taken as Nujol mulls or in C_6D_6 solution, as indicated. Complete spectra for some of the compounds listed here are given in the Experimental Section. [c] Carmona, E.; Galindo, A.; Sanchez, L.; Nielson, A. J.; Wilkinson, G. *Polyhedron* **1984**, *3*, 347–352. [d] Reference 34. [e] Addition of CO to a solution of $Mo(O)(PMe_3)_3Cl_2$ generates a small amount of a new species, tentatively assigned as **18a**. The ^{1}H NMR signals for the PMe_3 ligands were not observed, presumably because they are masked by those of $Mo(O)(PMe_3)_3Cl_2$. [f] Reference 5b. [g] Complex **8a** is detected in equilibrium with $Mo(O)(PMe_3)_3Cl_2$ upon addition of $CH_2{=}CH_2$; the ^{1}H NMR signals for the PMe_3 ligands of these compounds were not observed, presumably because they are masked by those of $Mo(O)(PMe_3)_3Cl_2$. [h] Ethylene resonances. [i] Spectrum was taken at 5 °C. [j] Methyl resonances of *p*-tolyl or *tert*-butyl group(s). [k] Reference 36. [l] Only one ethylene resonance is observed for **4a**. [m] Reference 14.

terminal sulfido ligands. These products are analogous to the oxo species formed from ethylene oxide. However, the reactions of ethylene sulfide are not as clean as those of ethylene oxide, and they are generally quite sensitive to the amount of oxidant present: in each instance, phosphine sulfide is formed as well as more free ethylene and phosphine than should be formed stoichiometrically. Complex **1a** reacts with ethylene sulfide to yield $Mo(S)(PMe_3)_3Cl_2$ (**10a**; eq 10), but this is unstable in the solution, decomposing to paramagnetic product(s) and $(S)PMe_3$. Complex **2a** gives an equilibrium mixture of $W(S)(PMe_3)_3Cl_2$ (**11a**) and $W(S)(CH_2{=}CH_2)(PMe_3)_2Cl_2$ (**12a**) ($K_{eq} \simeq 7 \times 10^{-2}$), while **2b** yields solely the sulfido ethylene species $W(S)(CH_2{=}CH_2)(PMePh_2)_2Cl_2$ (**12b**). In addition, significant amounts of $W(PMe_3)_3Cl_3$ are observed in the reaction of **2a**. Complex **1b** reacts readily with ethylene sulfide, but a sulfido derivative is not observed in the NMR, only $(S)PMePh_2$ and free $CH_2{=}CH_2$; the molybdenum product(s) has not been identified. When **1b** is reacted with less than 1 equiv of ethylene sulfide, **9b** is also detected in the reaction mixture (cf. eq 8).



(10)

Reactions with CO_2 and Heterocumulenes. Reactions of the tungsten complexes **2a** and **2b** with CO_2 at ambient temperatures produce equilibrium mixtures of the oxo carbonyl complexes $W(O)(CO)L_2Cl_2$ (**13**) and the oxo complexes **5** (eq 11). Again,

$$\underset{\mathbf{2}}{WL_4Cl_2} + CO_2 \rightarrow \underset{\mathbf{13}}{W(O)(CO)L_2Cl_2} + 2L \rightleftarrows \underset{\mathbf{5}}{W(O)L_3Cl_2} + CO + L \quad (11)$$

Table II. Products of the Reactions of ML_4Cl_2 (**1**,**2**) with *p*-TolN=C=O, ^{t}BuN=C=O, and ^{t}BuN=C=N^{t}Bu[a]

complex	substrate *p*-TolN=C=O	^{t}BuN=C=O	^{t}BuN=C=N^{t}Bu
$Mo(PMe_3)_4Cl_2$ (**1a**)	$Mo(N\text{-}p\text{-}Tol(CO)L_2Cl_2$ (1.0) $Mo(N\text{-}p\text{-}Tol)L_3Cl_2$ (0.6) $Mo(CO)_2L_3Cl_2$ (0.2)	$Mo(N^tBu)L_3Cl_2{}^b$ (1.0) $[Mo_2(CO)_xL_4Cl_y]^c$ (0.7) MoL_3Cl_3 (0.3)	$Mo_2L_4Cl_4$ (1.0)^b $Mo(N^tBu)L_3Cl_2$ (0.3)
$Mo(PMePh_2)_4Cl_2$ (**1b**)	$Mo(N\text{-}p\text{-}Tol)(CO)L_2Cl_2$	$Mo(N^tBu)(CO)L_2Cl_2$	$Mo(N^tBu)(CN^tBu)L_2Cl_2$
$W(PMe_3)_4Cl_2$ (**2a**)	$W(N\text{-}p\text{-}Tol)(CO)L_2Cl_2$ (1.0)^b $W(O)(CN\text{-}p\text{-}Tol)L_2Cl_2$ (0.7)	$W(N^tBu)(CO)L_2Cl_2{}^b$	$W(N^tBu)(CN^tBu)L_2Cl_2{}^b$
$W(PMePh_2)_4Cl_2$ (**2b**)	$W(N\text{-}p\text{-}Tol)(CO)L_2Cl_2$	$W(N^tBu)(CO)L_2Cl_2$	$W(N^tBu)(CN^tBu)L_2Cl_2$

[a] Products were identified by ^1H and $^{31}P\{^1H\}$ NMR. Ratios of products formed are given to the right of each species. [b] Reaction was heated at 80 °C. [c] The identity of this species has not been fully established; see text.

the equilibrium lies almost entirely toward the π-acid complex **13** with $PMePh_2$ as the ligand (the ratio of **13b** to **5b** is 9:1 when the reaction is carried out in a sealed NMR tube), while the opposite is observed for PMe_3 species (**13a**:**5a** = 1:9).

In contrast, the reaction of $Mo(PMe_3)_4Cl_2$ (**1a**) with 3 equiv of CO_2 is quite slow (60% reacted after 2 weeks at 80 °C) and gives a variety of products (eq 12): decomposition to the dimer **3a** (cf. eq 2) is the major product (48% of reacted **1a**), along with the oxo complex **7a** (20%), the known Mo(III) complex $Mo(PMe_3)_3Cl_3$ (**14**)[10] (13%), small amounts of a new μ-oxo dimer **15** (3%), and a new diamagnetic product (**16**) (15%). The μ-oxo species **15** is identified on the basis of its ^1H and ^{31}P spectra, which are identical in appearance to those of the recently reported analogous μ-sulfido species.[11] Complex **15** is also formed on heating a mixture of **1a** and **7a**; as these are present in reaction 12, the formation of **15** is not surprising. The new diamagnetic species (**16**) is believed to be a Mo carbonyl dimer on the basis of its NMR spectrum and CO stretching frequencies (C_6D_6) at 1846 and 1780 cm^{-1}. **16** is also formed in a 1:2 mole ratio with **14** on heating **1a** and $Mo(CO)_2(PMe_3)_3Cl_2$ (**17**),[12] in effect heating **1a** with a very limited amount of CO (**1a** + CO → **17**).[13]

$$\begin{aligned}\underset{\mathbf{1a}}{Mo(PMe_3)_4Cl_2} + CO_2 &\rightarrow Mo_2(PMe_3)_4Cl_4\ (\mathbf{3a})\ +\\ &Mo(O)(PMe_3)_3Cl_2\ (\mathbf{7a})\ +\\ Mo(PMe_3)_3Cl_3\ (\mathbf{14}) &+ Mo_2(\mu\text{-}O)(\mu\text{-}Cl)(PMe_3)_5Cl_3\ (\mathbf{15})\ +\\ &\text{“}Mo_2(CO)_x(PMe_3)_4Cl_y\text{”}\ (\mathbf{16}) \qquad (12)\end{aligned}$$

Complex **1b** is unreactive with 4 atm of CO_2 over weeks at ambient temperatures. Heating a benzene solution in a sealed NMR tube with 3 equiv of CO_2 results in clean, rapid production of the dimer **3b** without the formation of any oxo-containing species. The lack of reaction of **1b** with CO_2 is not due to any instability of the likely product, $Mo(O)(CO)(PMePh_2)_2Cl_2$ (**18b**), which is readily formed from **7b** and CO[5b] and is stable at 80 °C. Even under excess CO, no reduction of **18b** to Mo(II) compounds is observed. The potential equilibrium **1b** + $CO_2 \rightleftarrows$ **18b** + $2PMePh_2$ is not established because the barrier for the reaction of **1b** with CO_2 is apparently larger than that for decomposition of **1b** to **3b** (eq 2). While **18b** is readily formed from **7b** and CO, the analogous reaction of **7a** produces little if any oxo carbonyl (a weak stretcn, possibly due to a bound CO, is seen in the solution IR spectrum at 2020 cm^{-1}, and a singlet is observed in the ^{31}P NMR; Table I).

Carbonyl sulfide, SCO, reacts readily with **1a**, **1b**, and **2a** to form predominantly phosphine sulfide and the divalent carbonyl complexes $M(CO)_2(PMe_3)_3Cl_2$ (M = Mo, W) and $Mo(CO)_2(PMePh_2)_2Cl_2$. The dicarbonyl complexes can all be prepared independently by addition of small amounts of CO to the starting materials.[12] For **2a**, significant amounts of $W(PMe_3)_3Cl_3$ are also formed, and for **1b** other uncharacterized diamagnetic species are observed as well. Isolated $W(S)(PMe_3)_3Cl_2$ (see below) is reactive toward CO to give $W(CO)_2(PMe_3)_3Cl_2$ and $(S)PMe_3$. This suggests that terminal sulfido species may be formed as kinetic products in the reactions of **1** and **2a** with SCO, but that these sulfido complexes are inherently unstable with respect to formation of phosphine sulfide, divalent carbonyl species, and perhaps other unobserved product(s) (as the reaction does not balance). These results are in sharp contrast to the reaction of **2b** with SCO, which cleanly produces the stable sulfido carbonyl species $W(S)(CO)(PMePh_2)_2Cl_2$.[5b]

Complexes **1** and **2** react with isocyanates and di-*tert*-butylcarbodiimide to form imido, imido carbonyl, or imido isonitrile products, as summarized in Table II. The rates of reaction are, in each case, in the order *p*-tolylNCO > ^{t}BuNCO > ^{t}BuNCN^{t}Bu. For **1b**, for instance, the half-lives for reaction at 24 °C are ca. 2 min, 100 min, and 2 days, respectively. The reactivity of **1b** is essentially the same as that previously reported for **2b**, cleanly producing imido carbonyl and imido isonitrile complexes (eqs 13 and 14). The reactions of **1a**, however, result in mixtures of products. At ambient temperatures *p*-tolyl isocyanate yields both the imido carbonyl complex $Mo(NTol)(CO)(PMe_3)_2Cl_2$ (**19a**) and the known imido tris(phosphine) **25a**[14] (eq 15). The free CO from the formation of **25a** appears as trace amounts of $Mo(CO)_2(PMe_3)_3Cl_2$ (**17**). In the absence of **1**, an equilibrium is established between **25a**, **19a**, CO, and L. Reaction with *tert*-butyl isocyanate at 80 °C forms a rare example of a molybdenum *tert*-butyl imido complex, $Mo(N^tBu)(PMe_3)_3Cl_2$ (**26a**),[15] along with a significant amount of the carbonyl dimer **16** and

$$\begin{aligned}\underset{\mathbf{1b},\ \mathbf{2b}}{M(PMePh_2)_4Cl_2} + RNCO &\rightarrow\\ M(NR)(CO)(PMePh_2)_2Cl_2 &+ 2PMePh_2 \qquad (13)\\ R = p\text{-tolyl}&:\ \mathbf{19b},\ \mathbf{20b}\\ R = tert\text{-butyl}&:\ \mathbf{21b},\ \mathbf{22b}\end{aligned}$$

$$\begin{aligned}\underset{\mathbf{1b},\ \mathbf{2b}}{M(PMePh_2)_4Cl_2} + RNCNR &\rightarrow\\ M(NR)(CNR)(PMePh_2)_2Cl_2 &+ 2PMePh_2 \qquad (14)\\ R = tert\text{-butyl}&:\ \mathbf{23b},\ \mathbf{24b}\end{aligned}$$

$$\begin{aligned}\underset{\mathbf{1a}\ (L\,=\,PMe_3)}{MoL_4Cl_2} + TolNCO &\rightarrow \underset{\mathbf{19a}}{Mo(NTol)(CO)L_2Cl_2} +\\ &\underset{\mathbf{25a}}{Mo(NTol)L_3Cl_2} + L + CO \qquad (15)\end{aligned}$$

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(10) (a) Atwood, J. L.; Hunter, W. E.; Carmona-Guzman, E.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1980**, 467. (b) Gordon, J. C.; Poli, R. *Inorg. Chem.* **1991**, *30*, 4550–4554.

(11) Hall, K. A.; Critchlow, S. C.; Mayer, J. M. *Inorg. Chem.* **1991**, *30*, 3593. Hall, K. A. Manuscript in preparation.

(12) (a) $Mo(CO)_2(PMe_3)_3Cl_2$ and $W(CO)_2(PMe_3)_3Cl_3$: Carmona, E.; Doppert, K.; Marin, J. M.; Poveda, M. L.; Sanchez, L.; Sanchez-Delgado, R. *Inorg. Chem.* **1984**, *23*, 530–534. (b) $Mo(CO)_2(PMePh_2)_2Cl_2$ (which has not been previously reported): ^1H NMR δ 1.65 (s, $P(CH_3)Ph_2$); ^{31}P NMR δ 11.5 (s, $P(CH_3)Ph_2$); IR $\nu_{CO}(C_6D_6)$ = 1942 (s), 1847 (s) cm^{-1}. The CO stretches are consistent with two carbonyls and fall roughly between those of $Mo(CO)_2(PMe_3)_3Cl_3$ [1920 (s), 1820 (s) cm^{-1} (C_6D_6)] and $Mo(CO)_2(PPh_3)_2Cl_2$ [1960 (s), 1890 (s) cm^{-1}) (Nujol)]: Colton, R.; Tomkins, I. B. *Aust. J. Chem.* **1966**, *19*, 1143–1146.

(13) The ^1H NMR of the complex shows two virtual triplets which are not coupled to each other and two triplets in the ^{31}P NMR which are coupled to each other, suggesting that the species contains two inequivalent pairs of trans-equivalent phosphines—a situation which is difficult to explain by invoking a single metal center. That this species (assuming that it is a dimer) is formed in a 1:2 ratio with $Mo(PMe_3)_3Cl_3$ suggests that it may be a Mo(I) dimer, the result of disproportionation of **1a** and $Mo(CO)_2(PMe_3)_3Cl_2$.

(14) Chou, C. Y.; Huffman, J. C.; Maatta, E. A. *Inorg. Chem.* **1986**, *25*, 822–826.

(15) $Mo(N^tBu)(PMe_3)_3Cl_2$ (**26a**) has been very recently reported, prepared by a quite different route: Green, M. L. H.; Konidaris, P. C.; Mountford, P.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1992**, 256–9.

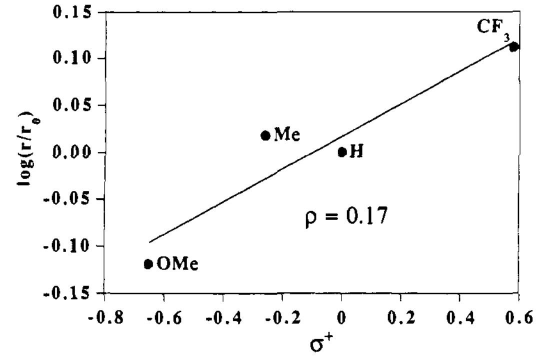


Figure 2. Hammett plot of log (r/r_0) versus σ^+. r_0 is the ratio of imido to oxo products formed in the reaction with phenyl isocyanate, and r is the analogous ratio for the other isocyanates. Plotting versus σ_p gave a poorer fit and a ρ value of 0.23.

$Mo(PMe_3)_3Cl_3$. Although the imido carbonyl complex $Mo(N^tBu)(CO)(PMe_3)_2Cl_2$ (**21a**) is not observed, it can be produced in equilibrium with complex **26a** on treatment with CO. Heating **1a** in the presence of $^tBuN{=}C{=}N^tBu$ gives mostly decomposition to the dimer **3a** with low yields of **26a**.

$W(PMe_3)_4Cl_2$ (**2a**) reacts at 80 °C with *tert*-butyl isocyanate and 1,3-di-*tert*-butylcarbodiimide cleanly (as is observed with **1b** and **2b**) to produce only imido carbonyl $W(N^tBu)(CO)(PMe_3)_2Cl_2$ (**22a**) and imido isonitrile species $W(N^tBu)(CN^tBu)(PMe_3)_2Cl_2$ (**24a**). With *p*-tolyl isocyanate, however, cleavage of both the C=N and C=O bonds is observed, producing imido carbonyl and oxo isonitrile species (eq 16). Complexes **20a** and **27a** are formed

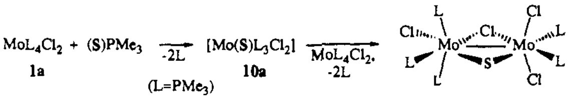
$$\underset{\textbf{2a}\ (L\,=\,PMe_3)}{WL_4Cl_2} + TolNCO \rightarrow \underset{\textbf{20a}}{W(NTol)(CO)L_2Cl_2} + \underset{\textbf{27a}}{W(O)(CNTol)L_2Cl_2} + 2L \quad (16)$$

in a 1:1 ratio at ambient temperatures, suggesting that there is little preference for cleavage of the isocyanate at the C=N vs the C=O bond, although performing the reaction at elevated temperatures (80 °C) favors the imido product (**20a**:**27a** = 2.5:1). The absence of $W(O)(CO)(PMe_3)_2Cl_2$ (**13a**) and $W(NTol)(CNTol)(PMe_3)_2Cl_2$ in the reaction indicates that the π-acid ligands in **20a** and **27a** are not labile. Complex **27a** can be formed independently by addition of *p*-tolyl isonitrile to $W(O)(PMe_3)_3Cl_2$ (**5a**) (and the analogous molybdenum oxo isonitrile complexes **25a** and **25b** are readily formed from CNTol plus **7a** and **7b**, respectively). None of the oxo isonitrile species has been observed to undergo isomerization to imido carbonyl species or vice versa.

It is remarkable that of all the reactions of **1** and **2** with isocyanates, only **2a** + TolNCO gives both C=N and C=O cleavage. To probe the origin of this lack of chemoselectivity, we have examined various para-substituted isocyanates and found that the substituent has only a slight effect. Phenyl isocyanate, 4-methoxyphenyl isocyanate, and 4-(trifluoromethyl)phenyl isocyanate all react to give mixtures of imido carbonyl and oxo isonitrile species, with the ratio varying only slightly from 1:0.76 to 1:1.29. A Hammett plot of this ratio versus σ^+ (Figure 2) yields a very small ρ value of 0.17.[16] Thus, while imido formation is slightly enhanced by electron-withdrawing groups on the isocyanate, the magnitude of the effect is remarkably small. For comparison, the dissociation of 3-arylpropanoic acids, where the aryl group is insulated from the acid by two methylene groups, is more sensitive to substituent effects on the aryl group (ρ = 0.24).[16]

Reactions with Phosphine Oxides and Phosphine Sulfides. The tungsten complexes **2a** and **2b** react with $(S)PMe_3$ or $(S)PMePh_2$, respectively, to form terminal sulfido complexes (eq 17). Trace amounts of $W(PMe_3)_3Cl_3$ (≤5%) are also observed for the reaction of **2a**. This is the best synthetic route to compounds **11**, as their high reactivity precludes the use of better sulfur atom donors. The reaction of **1a** with $(S)PMe_3$, however, proceeds at 80 °C to yield Mo(III) dimers with a bridging sulfido ligand (eq 18).[11] This reaction apparently occurs by initial sulfur atom transfer to form the terminal sulfido complex **10a**, similar to eq 17, but **10a** then conproportionates with **1a** to give the observed product (eq 18).[11]

$$\underset{\textbf{2a,b}}{WL_4Cl_2} + (S)PR_3 \rightarrow \underset{\textbf{11a,b}}{W(S)L_3Cl_2} + 2L \quad (17)$$



(18)

This scheme is supported by the reaction of **1a** with 0.5 equiv of ethylene sulfide, in which formation of **10a** occurs at ambient temperatures and conproportionation is observed upon heating to 60 °C. Complex **1b** also reacts with $(S)PMePh_2$, but the metal-containing product(s) of this reaction is apparently paramagnetic and NMR silent; only free $PMePh_2$ is observed.

None of the complexes **1**–**2** deoxygenate phosphine oxides to produce the terminal oxo complexes **5** and **7**, nor are these oxo complexes reduced by free phosphine (eq 19). The lack of reaction is thus due to a kinetic barrier. The tungsten complexes **2** have been shown to deoxygenate a phosphine oxide tethered to a phosphine, suggesting that part of the kinetic barrier for phosphine deoxygenation lies in the difficulty of initial coordination to W(II).[17]

$$\underset{\textbf{1, 2}}{ML_4Cl_2} + (O)PR_3 \;\cancel{\rightleftharpoons}\; \underset{\textbf{5, 7}}{M(O)L_3Cl_2} + 2\,L \quad (19)$$

Reactivity of 1 and 2 toward Miscellaneous Oxygen Atom Donors. Compounds **1** and **2** also react with O_2, SO_2, N_2O, and DMSO to produce the terminal oxo complexes **5** and **7** in variable yields (6–84%). The reactions are typically quite sensitive to the amount of oxidant present: with excess oxidant, oxo formation is often accompanied by production of phosphine oxide, phosphine sulfide (observed in the reaction with SO_2), and uncharacterized paramagnetic and/or diamagnetic species. These reactive oxidants can further oxidize **5** and **7** to higher valent species, which likely decompose to phosphine oxides and other products. Reactions of the PMe_3 complexes **1a** and **2a** with N_2O, DMSO, and SO_2 also result in formation of the trivalent species $M(PMe_3)_3Cl_3$ in yields ranging from 9 to 60%. The $PMePh_2$ complexes **1b** and **2b** generally do not produce significant amounts of such products, except that small amounts of $Mo(PMePh_2)_3Cl_3$ (~10%) are formed in the reaction of **1b** with DMSO. Traces of $W(PMe_3)_2Cl_4$ are also observed in reactions of **2a** with SO_2 and N_2O.

Complexes **1** and **2** all react with dioxygen very rapidly at ambient temperatures, immediately forming the oxo complexes **5** or **7** and NMR-silent species. These reactions with dioxygen are the only reactions we have found that proceed faster than phosphine loss, suggesting either an associative path or outer-sphere electron transfer.

Water and simple alcohols react with the molybdenum complexes **1** quite differently from their reported reactions with **2**, which form oxo and alkoxide complexes (e.g., eq 20[18]). For **2a**,

$$\underset{\textbf{2b}\ (L\,=\,PMePh_2)}{WL_4Cl_2} + MeOH \rightarrow \underset{\textbf{5b}}{W(O)L_3Cl_2} + CH_4 + W(OMe)_2L_2Cl_2 + H_2 \quad (20)$$

reaction with water produces the oxo complex **5a** and $W(H)_2(PMe_3)_4Cl_2$.[19] In contrast, **1a** is unreactive toward methanol and *p*-cresol and only slightly reactive toward water, producing, on heating, predominantly the dimer **3a** and only trace amounts (<10%) of the oxo complex **7a**. $Mo(PMePh_2)_4Cl_2$ (**1b**) is not

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[16] Sundberg, R. J.; Carey, F. A. *Advanced Organic Chemistry, Part A*; Plenum Press: New York, 1977; Tables 4.1 and 4.2, p 145.

[17] Brock, S. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1991**, *30*, 2138–2143. Brock and Mayer describe the deoxygenation of the monooxide of diphos, $Ph_2PCH_2CH_2P(O)Ph_2$, by **2b**.

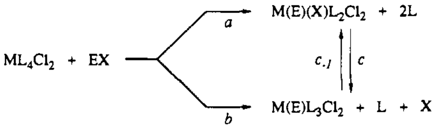
[18] Jang, S.; Atagi, L. M.; Mayer, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 6413–6414.

[19] Chiu, K. W.; Lyons, D.; Wilkinson, G.; Thornton-Pett, M.; Hursthouse, M. B. *Polyhedron* **1983**, *2*, 803–810.

oxidized by water, methanol, or *p*-cresol; remarkably, water and methanol catalyze its dimerization to **3b**. Addition of water to benzene solution of **1b** results in high-yield conversion to **3b** within days, while solutions of **1b** in dry benzene are stable for weeks at 25 °C. The nature of this unprecedented catalysis is not yet understood.

Discussion

The reactions described here typically involve two-electron oxidation of the molybdenum or tungsten center from the +2 to the +4 oxidation state with the formation of metal–oxygen, –sulfur, or –nitrogen multiple bonds (eq 21). Transfer of an oxygen atom,



(21)

a sulfur atom, or an NR group (E) from the oxidant to the metal typically leaves a good ligand X (such as CO or ethylene) for the metal center to bind. When this ligand binds to the metal (path a), eq 21 looks like an oxidative addition reaction, either oxidative addition of two single bonds (epoxides, episulfides) or oxidative addition of a double bond (CO_2, isocyanates). On the other hand, path b of eq 21 is commonly described as an atom-transfer reaction[4a] because it involves "simple" transfer of O, S, or NR from the substrate to the metal.

Paths a and b are mechanistically distinct but closely related in the sense that they result in similar products. The data indicate that whether the ligand "X" is bound or free depends on the affinity of the oxidized metal center for the ligand and not necessarily on the nature of the oxidation pathway. For example, epoxides have been shown to oxidize **2b** by an atom-transfer pathway (b) (without the formation of an intermediate with W–C bonds), yet the dominant product from $\overline{CH_2CH_2O}$ is the oxo ethylene complex,[5d] the net pathway for these reactions being "b + c_{-1}". The likely mechanism for CO_2 and isocyanate cleavage resembles an oxidative addition, with an η^2-complex opening to the oxo carbonyl or imido carbonyl product via pathway a,[5c] yet in reactions of **1a** much of the CO is found free in the solution, the net pathway for these reactions being "a + c". Thus, the simple paradigm of the oxidative addition of double bonds E=X to give M(E)(X), derived from the chemsitry of $W(PMePh_2)_4Cl_2$ (**2b**),[5] is a special case of a range of possible pathways: a, a + c, b, or b + c_{-1}.

In addition to reaction pathways involving two-electron redox chemistry resulting in oxo, sulfido, or imido complexes, a number of reactions we have explored give small amounts of the one-electron oxidation products, ML_3Cl_3 (**6**, **14**). Complexes **6** and **14** are formally the result of chlorine atom addition to **1** and **2**, yet none of the reacting substrates contain chlorine. They occur more frequently in reactions involving the stronger oxidants, such as DMSO, although traces of **6a** are observed on reacting **2a** with TolNCO and $(S)PMe_3$. This suggests that oxidation beyond Mo(IV) or W(IV) may yield a species that can oxidize **1** or **2** by chlorine atom transfer. Such one-electron transfer (Cl addition) has been found to be a very common side reaction in our studies of intermetal oxygen atom transfer.[20] Thus while the reactivity of **1** and **2** is dominated by two-electron oxidation, this alone does not provide a complete picture of the redox chemistry occurring.

Binding of π-Acid Ligands to Mo(IV) and W(IV). π-Acid ligands such as CO and ethylene normally bind poorly to high oxidation state species, but d^2 complexes with strong π-donor ligands such as an oxo have a pair of electrons available for back-bonding.[5b] The position of the equilibrium for binding of the ligand X (eq 22) depends on both the M–X bond strength and the nature of the phosphine ligand with which X competes.

$$M(E)L_3Cl_2 + X \rightleftarrows M(E)(X)L_2Cl_2 + L \qquad (22)$$

PMe_3 binds much more strongly than $PMePh_2$ because of its higher basicity and smaller size, as evidenced by the lower lability of the phosphines in **1a** and **2a** compared to the $PMePh_2$ complexes **1b** and **2b**. Steric effects are particularly pronounced in the tris- or tetrakis(phosphine) complexes, with the central ligand in meridonal tris($PMePh_2$) complexes being quite labile. Thus, retaining the formed π-acid ligand is more favorable for the $PMePh_2$ complexes than for the PMe_3 complexes. For example, *tert*-butyl isocyanate reacts with complex **1b** to give an imido carbonyl complex **21b**, while it reacts with **1a** to yield the imido tris(phosphine) complex **26a**. In some instances, particularly in the reactions of **1a**, the π-acid ligand is found bound to a divalent metal center, a result of the high affinity of the electron-rich starting materials, ML_4Cl_2, for the π-acid.

Tungsten complexes have a higher affinity for binding a π-acid ligand relative to phosphine than analogous molybdenum complexes. Reactions of **1a** and **2a** with *tert*-butyl isocyanate, for instance, give tungsten imido carbonyl complexes but molybdenum imido tris(phosphine) species. Since the size difference of molybdenum and tungsten is very small, this is undoubtedly an electronic effect: tungsten is more electron rich than molybdenum (more easily oxidized), so that it binds π-acid ligands better than molybdenum (typical of second vs third row metals). This trend is evident in the increased back-bonding for W vs Mo, as revealed by a ca. 20 cm^{-1} difference in CO stretching frequencies (Table I): for $M(NTol)(CO)(PMePh_2)_2Cl_2$, for example, ν_{CO} = 1964 (W) and 1986 cm^{-1} (Mo). By this criterion, the PMe_3 complexes are more electron rich than the $PMePh_2$ analogs (11–22 cm^{-1}). While this suggests stronger binding of π-acids to the PMe_3 complexes, this is a minor factor in the equilibria summarized in eq 22 because it is overwhelmed by the metal's preference for PMe_3 over $PMePh_2$.

The multiply bonded ligand also affects the binding of π-acid ligands,[5b] with the imido complexes having the highest preference for a π-acid and the oxo species the lowest. This is due to greater back-bonding in the imido complexes, as revealed in the CO stretching frequencies. For instance, ν_{CO} in $Mo(E)(CO)(PMe_3)_2Cl_2$ compounds varies from 1968 cm^{-1} for E = N^tBu to 2020 cm^{-1} for E = O. In general, the order of ν_{CO} as a function of the multiply bonded group E is $N^tBu \cong NTol < S < O$. This trend suggests that the oxo ligands are the poorest π-donors, which is consistent with the high electronegativity of oxygen versus nitrogen or sulfur: O (3.5) > N (3.0) > S (2.5).[21] However, that the imido ligands are the best π-donors does not correlate with electronegativity but rather with basicity of the free ligands, as RN^{2-} is substantially more basic than either free O^{2-} or S^{2-} (cf., the pK_a's of the conjugate acids are RNH_2 ($\sim$38) $\gg$ H_2O (16) > H_2S (7)).[22] The lack of correlation with electronegativity may be due to sulfur being a third period element, which are thought to form weaker π-bonds because of their more diffuse p orbitals.

The preference for ligand binding to the same metal center appears to be CNR $\gg$ CO $\geq$ $CH_2=CH_2$. Isonitriles are always found bound to the metal center, while CO is readily lost from many of the complexes. Isonitriles are known to bind better to high-valent metal centers than CO or ethylene,[23] but it is unusual that in some instances ethylene and CO share roughly equal preference by the metal (e.g., **2a** + ethylene oxide versus **2a** + CO_2). This may be because ethylene, like an isonitrile, is expected to be an intrinsically better σ-donor than CO, a feature which would be unusually important in these high-valent complexes. In addition, the M(IV) compounds have only one pair of electrons available for back-bonding, perfect for ethylene but only utilizing one of the two π^*-orbitals of CO.

The metal–ligand multiple bond appears to be the primary determinant of the tungsten–phosphorus coupling constants for the *trans*-phosphine ligands, as the coupling constants fall in

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Table III. Substrate Bond Dissociation Energies[a] and Summary of Observed Reactions[b]

substrate (EX)	E	X	ΔH (kcal/mol)[a]	complex[b] 1a	1b	2a	2b	formation of $(E)PR_3$ ($E = O, S$)
N_2O	O	N_2	39	×	×	×	×	$OPMe_3$
$^1/_2O_2$	O		59[c]	×	×	×	×	$OPMe_3$
$\overline{CH_2CH_2O}$	O	$CH_2{=}CH_2$	84	×, Δ	×	×, Δ	×	
Me_2SO	O	Me_2S	86[d]	×	×	×	×	OPR_3
CH_3OH	O	CH_4	89[d]	–	–	×, Δ[e]	×[e]	
H_2O	O	H_2	117	(×, Δ)[f]	–	×, Δ[e]	×	
$OPPh_3$	O	PPh_3	126[d]	–	–	–	–	
CO_2	O	CO	127	×, Δ	–	×, Δ	×	
SO_2	O	SO	132	×	×	×	×	OPR_3, SPR_3
$OPMe_3$	O	PMe_3	139[g]	–	–	–	–	
$\overline{CH_2CH_2S}$	S	$CH_2{=}CH_2$	59	×	–	×	×	SPR_3
SCO	S	CO	74	–	–	–	×	SPR_3
$SPMePh_2$	S	$PMePh_2$	*h*	*j*	–	*j*	×	
$SPMe_3$	S	PMe_3	92[h]	×, Δ	*j*	×, Δ	*j*	
OC=NTol	NTol	CO	~88[i]	×	×	×, Δ	×	
O=CNTol	O	CNTol	~130[i]	–	–	×, Δ	–	
OC=N^{t}Bu	N^{t}Bu	CO	~88[i]	×, Δ	×	×, Δ	×	
^{t}BuN=CN^{t}Bu	N^{t}Bu	CN^{t}Bu	*k*	×, Δ	×	×, Δ	×	

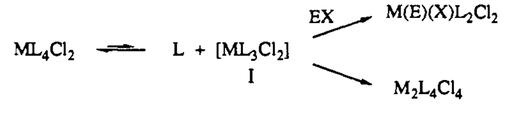
[a] ΔH for the reactions $XE \rightarrow X + E$ in the gas phase, compiled from the data in ref 25a unless otherwise indicated. [b] **1a** = $Mo(PMe_3)_4Cl_2$; **1b** = $Mo(PMePh_2)_4Cl_2$; **2a** = $W(PMe_3)_4Cl_2$; **2b** = $W(PMePh_2)_4Cl_2$; × = reaction proceeds to an oxo, sulfido, or imido product; Δ = slow or unreactive at 25 °C, heated to ca. 80 °C; – = did not react to form an observable oxo, sulfido, or imido complex. [c] $^1/_2\Delta H°$ for $O_2(g) \rightarrow 2O(g)$. [d] Reference 4a. [e] Other complexes, such as alkoxide or hydride species, also formed. [f] Trace amount (<10%). [g] Reference 25b,c. [h] Reference 26. The P=S bond dissociation energy in $SPMePh_2$ is likely to be less than the 92 kcal/mol of $SPMe_3$, perhaps by >10 kcal/mol, by analogy between $O{=}PPh_3$ and $O{=}PMe_3$. [i] The OC=NH bond strength is 88 kcal/mol and the O=CNH bond strength has been estimated as 130 kcal/mol in ref 5c. [j] Reaction not attempted. [k] Bond strength not known.

narrow ranges for each type of multiple bond, almost irrespective of the nature of the phosphine or the X ligand (PR_3, CO, CNR, $=CR_2$).[24] $J_{WP_{trans}}$ values are in the range 330–342 Hz for the oxo complexes $W(O)(X)L_2Cl_2$, 288–308 Hz for the imido compounds, and between 266 and 276 Hz for the sulfido derivatives, a pattern which parallels the electronegativity of the multiply bonded ligand (see above). The more electronegative the multiply bonded ligand, the more polar the multiple bond, which implies less metal s character in the bond. Thus, the tungsten s orbital is more available for bonding to other ligands, such as the phosphines, resulting in increased scalar coupling, $J_{WP_{trans}}$. The only exceptions to the observed ranges are the $J_{WP_{trans}}$ values for the ethylene complexes, which are, in each case, roughly 63 Hz lower: oxo, 263–275 Hz; imido, 232–245 Hz; sulfido, 208–212 Hz.

Thermodynamics of Atom Transfer. The transfer of an oxygen atom, sulfur atom, or nitrene group depends both on the strength of the bond(s) being broken in the substrate and on the strength of the metal–ligand multiple bond, which depends on the metal's ease of oxidation and its affinity for a multiple bond. (The binding of the π-acid ligand does not contribute appreciably to the driving force for these reactions, being at most a few kilocalories per mole more favorable than binding of a phosphine.) Table III shows the enthalpy required to remove an oxygen atom, a sulfur atom, or a nitrene from each of the substrates discussed and provides a summary of the reactions: whether an oxo, sulfido, or imido complex is formed, whether heating is required, and whether phosphine oxide and/or phosphine sulfide are observed.

Strong bonds are cleaved in these reactions, including the C=O double bond in CO_2 (127 kcal/mol)[25] and the $S{=}PR_3$ bond of ca. 92 kcal/mol,[26] suggesting that the metal–ligand multiple bonds are quite strong as well. Concurrent oxidation of a phosphine, when observed, provides a large additional driving force. An estimate of the $L_3Cl_2W{\equiv}O$ bond strength in **5b** of ≳138 kcal/mol has been obtained from the reactions of **2** with CO_2.[27] (The metal–oxygen multiple bond is written as a triple bond because that is the best molecular orbital description.[28]) The tungsten–sulfur and tungsten–nitrogen bond strengths in $L_3Cl_2W{\equiv}S$ and $L_3Cl_2W{\equiv}N^tBu$ can also be crudely estimated to be ≳100 kcal/mol on the basis of the desulfurization of $(S)PMe_3$ ($D[R_3P{=}S] \cong 92$ kcal/mol and cleavage of RNCO (assuming $D[RN{=}CO] \cong D[HN{=}CO] = 88$ kcal/mol[5c]). A similar rough estimate can be obtained for the molybdenum–nitrogen bond because **1a** and **1b** also cleave isocyanates.

Scheme I



$$ML_4Cl_2 \rightleftharpoons L + \underset{\textbf{I}}{[ML_3Cl_2]} \begin{array}{l} \xrightarrow{EX} M(E)(X)L_2Cl_2 \\ \longrightarrow M_2L_4Cl_4 \end{array}$$

The strengths of the $L_3Cl_2Mo{\equiv}O$ and $L_3Cl_2Mo{\equiv}S$ bonds are not amenable to the same kind of estimates because they are not cleanly formed in reactions with CO_2 and $(S)PR_3$, but these bonds are still likely to be quite strong. Oxygen atom transfer is observed from CO_2 to **1a**, and molybdenum oxo complexes such as $Mo(O)(CO)(PMePh_2)_2Cl_2$ (**18b**) are resistant to reduction by CO or phosphines. (In contrast, isoelectronic d^2 rhenium oxo complexes are typically reduced readily by phosphines.[29]) The lack of clean reactions of **1a** or **1b** with CO_2 is most likely a kinetic effect (see below) rather than being due to insufficient driving force. The multiple bonds formed by molybdenum are expected to be somewhat weaker than the tungsten analogs because molybdenum compounds are in general not as easily oxidized and because bonds are typically weaker to second row than to third row transition elements.[30] While there is little direct evidence for this trend from these reactions reported here, it is supported by our recent studies of intermetal oxygen atom transfer.[20]

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(25) (a) Bond strengths are calculated using $\Delta H_f°$ values from *The NBS Tables of Thermodynamic Properties*; Wagman, D. D., Ed.; American Chemical Society and the American Institute of Physics for the National Bureau of Standards: Washington, D.C., 1982; Vol. 1. (b) Long, L. H.; Sackman, J. F. *Trans. Faraday Soc.* **1957**, *53*, 1606. (c) Claydon, A. P.; Fowell, P. A.; Mortimer, C. T. *J. Chem. Soc.* **1960**, 3284.

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(27) More complete discussions of the assumptions inherent in this type of estimate can be found in ref 5c and Conry, R. R.; Mayer, J. M. *Inorg. Chem.* **1990**, *29*, 4862–4867.

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Mechanistic Considerations. The reactions of compounds **1** and **2** are significantly slower than the rate of phosphine loss (except for reactions of O_2) and are inhibited by the presence or buildup of free phosphine. Substrates such as SO_2, which oxidize the liberated phosphine to phosphine oxide or phosphine sulfide, react unusually rapidly, because phosphine inhibition is reduced. These observations indicate that the reactions proceed through a coordinatively unsaturated ML_3Cl_2 intermediate (**I**) via preequilibrium loss of phosphine (Scheme I). **I** can be trapped by the substrate EX to form oxo, sulfido, or imido complexes, or it can dimerize to the quadruply bonded compounds $M_2L_4Cl_4$ (**1a**, **1b**, and **2a**; **2b** decomposes to unidentified paramagnetic materials). For the molybdenum complexes **1**, dimerization is competitive with oxidation, while the tungsten complexes **2** only undergo oxidation (except for entirely unreactive substrates such as phsophine oxides). This reflects the preferences of these elements: tungsten compounds are typically more easily oxidized, while metal–metal bonds are more easily formed for molybdenum. In one sense, this can be viewed as competition between metal–ligand and metal–metal multiple bonds, although it is not clear whether the competition is kinetically or thermodynamically controlled.

The selectivity for oxidation vs dimerization is determined by the affinity of the intermediate for the substrate. Epoxides and episulfides (and aziridines) oxidize **2b** by direct oxygen or sulfur atom abstraction through a σ-bound adduct,[5d] while CO_2 and heterocumulenes likely form η^2-bound adducts.[5c] Coordination of the substrate in the former case relies on the Lewis acidity of the metal center (the substrate acting as a simple σ-donor), while in the latter case the π-basicity of the metal is also important, as the ligand acts as a π-acid. The molybdenum species, being less electron rich, have lower affinities for π-acid substrates, so that dimer formation is often competitive with oxidation.

The intermediate **I** most likely behaves as a soft Lewis acid (low-valent and coordinated to phosphines), which may account for the apparent preference for oxidation by softer substrates over harder ones. For instance, reactions with ethylene sulfide are much more rapid than those with ethylene oxide, and phosphine sulfides oxidize **1** and **2** while phosphine oxides do not. Similar observations have been made in reactions of **2b** with alcohols and thiols[18] and with a chelating phosphine/phosphine oxide.[17]

Isocyanate oxidative addition generally occurs by cleavage of the sterically more hindered but thermodynamically weaker C=N bond (the C=O bond is about 40 kcal/mol stronger than C=N[5c]). This is consistent with the formation of an η^2-(C,N) adduct, the typical mode of η^2-isocyanate binding. That $W(PMe_3)_4Cl_2$ alone of the ML_4Cl_2 species cleaves both the C=N and C=O bonds of aryl isocyanates—but not *tert*-butyl isocyanate—is difficult to explain. The imido and oxo products do not interconvert, so that this is not an equilibrium effect. $W(PMe_3)_4Cl_2$ is the most electron rich of the ML_4Cl_2 species, but the Hammett analysis shows that only a slight electronic influence is exerted by the isocyanate on the preference for imido versus oxo formation. In addition, sterics do not seem to play a crucial role, as the larger *tert*-butyl isocyanate is cleaved by **2a** exclusively at the more hindered C=N bond rather than at the C=O bond.

Conclusions

The molybdenum(II) and tungsten(II) complexes MCl_2L_4 (L = PMe_3, $PMePh_2$) abstract an oxygen atom, a sulfur atom, or a nitrene (NR) group from a wide range of substrates, including epoxides and episulfides, CO_2 and isocyanates, phosphine sulfides, and DMSO (Table III). A major driving force is the formation of a strong metal–oxygen, metal–sulfur, or metal–nitrogen multiple bond. These reactions can be viewed as atom-transfer or oxidative addition reactions. The $PMePh_2$ complexes are much more reactive than PMe_3 derivatives because of their much faster rate of phosphine loss. For the molybdenum(II) complexes, oxidation is competitive with decomposition to quadruply bonded dimers $Mo_2Cl_4L_4$, while dimers are not observed for tungsten. Reduction of the substrate typically generates a π-acid ligand, ethylene from epoxides or episulfides and CO or CNR from CO_2 and isocyanates, which often binds to the metal oxo, sulfido, or imido product. The equilibria of formation of these d^2 π-acid complexes are more favorable in the more electron-rich tungsten compounds and for the more sterically crowded $PMePh_2$ complexes. Isocyanates react specifically by cleavage of the C=N bond to give imido carbonyl complexes, except for the reactions of $W(PMe_3)_4Cl_2$ with aryl isocyanates, which yield roughly equal amounts of oxo isonitrile and imido carbonyl products.

Experimental Section

General Considerations. All experiments were performed under a nitrogen or an argon atmosphere or under vacuum employing high-vacuum line, Schlenk, and standard glove box techniques. Solvents were dried according to standard procedures.[31] All reagents were degassed on the vacuum line, checked for purity by NMR, and if necessary dried by standard means, except gases which were used directly from the cylinder without further purification. Deuterated solvents were purchased from Cambridge Isotope Laboratories. All gases were purchased from Matheson except carbonyl sulfide (K & K Laboratories, Inc.) and ethylene (MG Industries). Isocyanates and 1,3-di-*tert*-butylcarbodiimide were purchased from Aldrich. PMe_3, $PMePh_2$, $(O)PMe_3$, $(O)PMePh_2$, and $(O)PPh_3$ were purchased from Aldrich and Strem, degassed (where applicable), and used without further purification. The following compounds have been previously reported: $Mo(PMe_3)_4Cl_2$ (**1a**),[32] $Mo(PMePh_2)_2Cl_4$,[33] $Mo(O)(PMePh_2)_3Cl_2$ (**7b**),[34] $W(PMe_3)_4Cl_2$ (**2a**) and $W(PMePh_2)_4Cl_2$ (**2b**),[35] and $W(O)(PMe_3)_3Cl_2$ (**5a**) and $W(O)(PMePh_2)_3Cl_2$ (**5b**).[36] The $W(E)(X)(PMePh_2)_2Cl_2$ compounds, $Mo(O)(CO)(PMePh_2)_2Cl_2$ and $W(O)(CO)(PMe_3)_2Cl_2$, have been reported in ref 5b. $W(PMe_3)_4Cl_2$ (**2a**), $W(PMePh_2)_4Cl_2$ (**2b**),[35] *p*-tolyl isonitrile,[37] $(S)PMePh_2$,[38] and PMe_3-d_9[39] were prepared following published procedures.

NMR spectra were acquired at ambient temperatures (24 ± 2 °C) using Bruker WM-500, AF-300, and AC-200 and Varian VXR-300 Fourier transform spectrometers. The ^1H NMR spectra were referenced relative to TMS, ferrocene, or the residual protons in the solvent. The $^{31}P\{^1H\}$ NMR spectra were recorded at 202.5, 121.4, or 81.0 MHz and were referenced to external 85% H_3PO_4. The $^{13}C\{^1H\}$ NMR spectra were recorded at 75.43 MHz and referenced relative to benzene-d_6 (δ 128 ppm). Only nonaromatic resonances have been reported for the complexes. Spectra are reported as δ (ppm) (number of hydrogens, multiplicity, coupling constants (in hertz), assignment). Infrared spectra were recorded on a Perkin-Elmer 1600 FTIR as Nujol mulls or in benzene solutions using NaCl cells, and they are reported in cm^{-1}. Intensities of IR bands are reported as (s) = strong, (w) = weak, or (sh) = shoulder.

Many reactions studied were performed in sealed NMR tubes. The reaction between $Mo(PMe_3)_4Cl_2$ (**1a**) and an excess of SO_2 is a representative example: In the dry-box, an NMR tube sealed to a ground glass joint is charged with 15 mg (3.2×10^{-5} mol) of $Mo(PMe_3)_4Cl_2$ (**1a**) and 3 mg of ferrocene. Benzene-d_6 (0.5 mL) is added and the tube is fitted to a 25.7-mL gas addition bulb. The apparatus is attached to the vacuum line and cooled slowly with liquid nitrogen to −196 °C, and the head space is degassed. The frozen tube is isolated from the gas addition bulb, and 69 Torr of SO_2 is admitted into the line and the bulb. A 25.7-mL aliquot of gas (9.6×10^{-5} mol at 298 K) is isolated from the rest of the line and condensed into the NMR tube which is then sealed with a torch. The frozen tube is slowly thawed to ambient temperature, and the ensuing reaction is followed by NMR. NMR yields of products are reported as the % of metal reactant (**1** or **2**) observed initially which is required to produce a given product, referenced to TMS or ferrocene as an internal standard.

$Mo(PMePh_2)_4Cl_2$ (1b). A 200-mL three-neck flask was charged with 5.0 g of $Mo(PMePh_2)_2Cl_4$ (5.2×10^{-3} mol) and 0.23 g (6.2 mmol) of activated magnesium turnings. A rubber septum was attached to one of the necks and the other was stoppered. THF (100 mL) was condensed

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into the flask on the vacuum line, the reddish suspension was warmed to room temperature, and 3.2 mL (1.1×10^{-2} mol) of $\mathrm{PMePh_2}$ was added via syringe. The mixture was stirred for about 3 h (until the magnesium disappeared), and a clear dark ruby red solution developed. The solution was filtered under vacuum and stripped of volatiles, resulting in dark reddish-yellow residues which were then taken up in 90 mL of fresh toluene and filtered away from the magnesium salts. The filtrate was evaporated to dryness, the residues were redissolved in 25 mL of toluene, and the solution was concentrated and cooled slowly to −15 °C in an ice–acetone bath. Addition of 35 mL of pentane caused precipitation of a bright yellow solid, which was filtered, washed with 4 × 5 mL of diethyl ether, dried, stirred in 30 mL of pentane for a few hours to remove sequestered toluene and ether, filtered, and dried in vacuo overnight: yield, 4.15 g (55%); ^{1}H NMR 9.4 (broad, $\mathrm{PCH_3}\mathit{Ph}_2$), 8.5 (broad, $\mathrm{PCH_3}\mathit{Ph}_2$), 6.5 (broad, $\mathrm{PCH_3}\mathit{Ph}_2$), −13 (3 H, very broad, $\mathrm{PC}\mathit{H}_3\mathrm{Ph_2}$); IR (Nujol) 3054 (w), 1960 (w), 1890 (w), 1812 (w), 1665 (w), 1586 (w), 1483 (sh), 1435 (sh), 1336 (w), 1310 (w), 1287 (w), 1271 (w), 1193 (w), 1095 (w), 1072 (w), 1028 (w), 968 (w), 896 (s), 885 (s), 842 (w), 736 (s), 695 (s), 678 (sh). Anal. Calcd for $\mathrm{MoCl_2P_4C_{52}H_{52}}$: C, 64.54; H, 5.42. Found: C, 63.64; H, 5.35.

Mo(PMe$_3$)$_4$Cl$_2$ (1a). The preparation of $\mathrm{Mo(PMe_3)_4Cl_2}$ (**1a**) has been previously reported,[32] but the complex is more easily isolated using a procedure analogous to that described for $\mathrm{Mo(PMePh_2)_4Cl_2}$ (**1b**) above. The crude product obtained after filtering away the magnesium salts may be purified by simply stirring the solids in a minimum amount of THF, followed by filtering, washing them with pentane, and drying in vacuo. **1a**: yield, 65% (based on the reduction of 5.0 g of $\mathrm{Mo(PMe_3)_3Cl_4}$); ^{1}H NMR −8.7 (36 H, broad s, $\mathrm{P(C}\mathit{H}_3)_3$).

Mo(N^{t}Bu)(PMe$_3$)$_3$Cl$_2$ (26a). To a 500-mL round-bottom flask equipped with a magnetic stir bar was added 0.50 g of $\mathrm{Mo(PMe_3)_4Cl_2}$ (**1a**) (1.1 mmol) followed by 200 mL of toluene and 0.36 mL of *tert*-butyl isocyanate (3.0 mmol). The flask was fitted with a water-cooled condenser, and the yellow reaction mixture was allowed to reflux for 9 h while the apparatus was vented through a nitrogen bubbler on the vacuum line. During the first few hours of reflux, the solution became a burgundy red color which remained throughout the duration of the reaction. Use of a large vessel helps prevent formation of a byproduct (formed from the reaction between the carbon monoxide produced and the starting material) by allowing the CO generated to partition into a larger head space. After refluxing, the volatiles were stripped away under vacuum to give a reddish colored solid. NMR ($\mathrm{C_6D_6}$) of the solid indicated that the imido product had formed along with some of the byproduct. Separation of the two products by recrystallization of the solids from toluene and diethyl ether afforded the imido complex as a purple solid, which was then washed several times with ether and dried in vacuo: yield, 0.10 g (20%); ^{1}H NMR 1.42 (18 H, t, *J* = 4, *trans*-$\mathrm{P(C}\mathit{H}_3)_3$), 1.24 (9 H, d, *J* = 8, *cis*-$\mathrm{P(C}\mathit{H}_3)_3$), 1.01 (9 H, s, $\mathrm{C(C}\mathit{H}_3)_3$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR 5.7 (t, *J* = 18, *cis*-$\mathit{P}\mathrm{Me_3}$), −7.3 (d, *J* = 18, *trans*-$\mathit{P}\mathrm{Me_3}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR 31.6 (s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 24.4 (d, *J* = 24, *cis*-$\mathrm{P(}\mathit{C}\mathrm{H_3)_3}$), 18.8 (t, *J* = 11, *trans*-$\mathrm{P(}\mathit{C}\mathrm{H_3)_3}$) (the tertiary carbon of the ^{t}Bu group was not observed); IR (Nujol) 1413 (sh), 1357 (sh), 1295 (w), 1274 (w), 1236 (s), 1213 (w), 942 (s), 843 (w), 805 (w), 736 (w), 668 (w). Anal. Calcd for $\mathrm{MoCl_2P_3NC_{13}H_{36}}$: C, 33.49; H, 7.78; N, 3.00. Found: C, 33.08; H, 7.73; N, 2.96.

Mo(N^{t}Bu)(CO)(PMePh$_2$)$_2$Cl$_2$ (21b). In a 25-mL glass reaction bomb was placed 0.20 mg of $\mathrm{Mo(PMePh_2)_4Cl_2}$ (**2b**) (2.1×10^{-4} mol). The flask and its contents were degassed on the vacuum line, and 8 mL of dry toluene was condensed into the vessel. The resulting amber yellow solution was brought to ambient temperature, and 28 μL (3.6×10^{-4} mol) of *tert*-butyl isocyanate was added. The reaction mixture was then stirred for 2.5 days, whereupon the solution became a dark amber color. The solution was transferred to a 25-mL Kjeldahl flask fitted to a frit, and the volatiles were removed under vacuum. The resulting greenish colored oil was triturated with 1 mL of diethyl ether, and an orange solid separated. Addition of 8 mL of pentane and filtration of the mixture gave an olive-orange colored solid, which was washed with pentane three times and dried in vacuo; yield, 0.067 g (67%). The solids were recrystallized from toluene–$\mathrm{Et_2O}$, affording the imido complex **21b** as a light orange solid: ^{1}H NMR 2.32 (6 H, t, *J* = 4. *trans*-$\mathrm{PC}\mathit{H}_3\mathrm{Ph_2}$), 0.79 (9 H, s, $\mathrm{C(C}\mathit{H}_3)_3$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR 14.7 (s, *trans*-$\mathit{P}\mathrm{CH_3Ph_2}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR 70.9 (s, $\mathit{C}\mathrm{(CH_3)_3}$), 30.0 (s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$). 15.1 (s, *trans*-$\mathrm{P}\mathit{C}\mathrm{H_3Ph_2}$) (the carbonyl carbon was not observed); IR (Nujol) 1983 (s) (ν_{CO}), 1939 (sh). 1438 (sh), 1318 (w), 1280 (w), 1227 (m), 1099 (m), 1073 (w), 1030 (w). 999 (w), 895 (s), 804 (w), 754 (sh), 742 (m), 693 (m). Anal. Calcd for $\mathrm{MoCl_2P_2NOC_{31}H_{35}}$: C, 55.87; H, 5.29; N, 2.10. Found: C, 55.89: H. 5.34; N, 2.08.

Mo(N-*p*-Tol)(CO)(PMePh$_2$)$_2$Cl$_2$ (19b). In a 25-mL glass reaction bomb was placed 0.20 g (2.1×10^{-4} mol) of $\mathrm{Mo(PMePh_2)_4Cl_2}$ (**1b**). The contents of the flask were degassed. and 8 mL of toluene was added followed by 31 μL (2.5×10^{-4} mol) of *p*-tolyl isocyanate, producing an immediate purple colored solution. This solution was stirred for 3.5 h and was then transferred to a 25-mL flask attached to a frit. The volatiles were removed by vacuum to give a purple oil, which upon trituration with 1 mL of diethyl ether resulted in the separation of a purple solid. Addition of 8 mL of pentane caused the precipitation of solids, which were filtered, washed with 3 × 1 mL of pentane, and dried; yield, 0.12 g (81%). The complex was recrystallized from toluene–$\mathrm{Et_2O}$ to obtain an analytically pure sample of **19b**: ^{1}H NMR 6.65 (2 H, d, *J* = 8, $\mathrm{CH_3C_6}\mathit{H}_4\mathrm{N}$), 6.36 (2 H, d, *J* = 8, $\mathrm{CH_3C_6}\mathit{H}_4\mathrm{N}$), 2.31 (6 H, t, *J* = 4, *trans*-$\mathrm{PC}\mathit{H}_3\mathrm{Ph_2}$), 1.74 (3 H, s, $\mathrm{C}\mathit{H}_3\mathrm{C_6H_4N}$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR 13.9 (s, *trans*-$\mathit{P}\mathrm{CH_3Ph_2}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR 21.4 (s, $\mathit{C}\mathrm{H_3C_6H_4N}$), 14.1 (t, *J* = 13, *trans*-$\mathrm{P}\mathit{C}\mathrm{H_3Ph_2}$) (the carbonyl carbon was not observed); IR (Nujol) 3062 (sh), 2360 (w), 2005 (s), 1960.5 (s) (ν_{CO}), 1588 (w), 1484 (sh), 1435 (sh), 1407 (w), 1317 (w), 1281 (w), 1188 (w), 1170 (w), 1100 (m), 1030 (w), 1011 (w), 999 (w), 922 (w), 892 (s), 884 (s), 848 (w), 820 (m), 740 (m), 730 (s), 693 (s), 652 (w). Anal. Calcd for $\mathrm{MoCl_2P_2NOC_{34}H_{33}}$: C, 58.30; H, 4.75; N, 2.00. Found: C, 57.91; H, 4.72; N, 2.02.

Mo(N^{t}Bu)(CN^{t}Bu)(PMePh$_2$)Cl$_2$ (23b). In a 25-mL glass reaction bomb was placed 0.25 g (2.6×10^{-4} mol) of $\mathrm{Mo(PMePh_2)_4Cl_2}$ (**1b**). The contents were degassed on the vacuum line, and 9 mL of dry benzene was condensed over the solid followed by the addition of 149 μL (7.8×10^{-4} mol) of di-*tert*-butylcarbodiimide. The contents were stirred at ambient temperature for 1 month, whereupon the solution became dark amber in color. The volatiles were removed under vacuum, giving a red gum which was taken up in pentane and triturated until a light purple solid precipitated. The solids were filtered over a frit, redissolved in toluene, and filtered, and the dark red-olive solution was concentrated until a purple-red solid precipitated. The solids were filtered, washed with 5 × 1 mL of diethyl ether, and dried in vacuo. **23b**: yield, 49 mg (27%); ^{1}H NMR 2.45 (6 H, d, *J* = 4, *trans*-$\mathrm{PC}\mathit{H}_3\mathrm{Ph_2}$), 1.01 (9 H, s, $\mathrm{C(C}\mathit{H}_3)_3$), 0.72 (9 H, s, $\mathrm{C(C}\mathit{H}_3)_3$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR 20.2 (s, *trans*-$\mathit{P}\mathrm{CH_3Ph_2}$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR 69.9 (s, $\mathit{C}\mathrm{(CH_3)_3}$), 56.8 (s, $\mathit{C}\mathrm{(CH_3)_3}$), 30.8 (s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 30.2 (s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 16.5 (t, *J* = 14, *trans*-$\mathrm{P}\mathit{C}\mathrm{H_3Ph_2}$) (the isonitrile carbon was not observed); IR (Nujol) 2128 (s) (ν_{CN}), 1588 (w), 1574 (w), 1318 (w), 1305 (w), 1278 (w), 1228 (m), 1210 (w), 1156 (w), 1126 (w), 1099 (m), 1072 (w), 1029 (w), 999 (w), 898 (s), 855 (w), 839 (w), 800 (w), 753 (sh), 745 (m), 695 (s), 683 (sh).

W(N^{t}Bu)(CO)(PMe$_3$)$_2$Cl$_2$ (22a). In a 25-mL glass reaction bomb was placed 0.25 g (4.5×10^{-4} mol) of $\mathrm{W(PMe_3)_4Cl_2}$ (**2a**). The contents of the flask were degassed on the vacuum line, and 8.5 mL of toluene was condensed over the solid followed by the addition of 102 μL (9.0×10^{-4} mol) of *tert*-butyl isocyanate. The reaction mixture was heated to 70 °C for 6.75 h, producing a red-orange colored solution. The volatiles were then removed under vacuum, yielding a red-orange solid which was redissolved in 4.0 mL of fresh toluene and heated for an additional 2.75 h. The volatiles were removed again, and the red-orange solids were scraped from the walls of the bomb, recrystallized from toluene–diethyl ether, and dried in vacuo. **22a**: yield, 200 mg (88%); ^{1}H NMR 1.44 (18 H, t, *J* = 4, *trans*-$\mathrm{PC}\mathit{H}_3$), 0.93 (9 H, s, $\mathrm{C(C}\mathit{H}_3)_3$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR −19.4 (s, *trans*-$\mathit{P}\mathrm{(CH_3)_3}$, $J_{\mathrm{PW}} = 295$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR 68.1 (s, $\mathit{C}\mathrm{(CH_3)_3}$), 30.8 (s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_3}$), 16.5 (t, *J* = 15, *trans*-$\mathrm{P(}\mathit{C}\mathrm{H_3)_3}$) (the carbonyl carbon was not observed); IR (Nujol) 1947 (s) (ν_{CO}), 1900 (sh), 1418 (sh), 1358 (w), 1302 (w), 1282 (w), 1258 (s), 1218 (w), 947 (s), 861 (w), 851 (w), 808 (w), 741 (w), 673 (w), 604 (w). Anal. Calcd for $\mathrm{WCl_2P_2NOC_{11}H_{27}}$: C, 26.11; H, 5.38; N, 2.77. Found: C, 26.15; H, 5.25; N, 2.76.

W(S)(PMe$_3$)$_3$Cl$_2$ (11a). In a 25-mL reaction bomb were placed 0.25 g (4.5×10^{-4} mol) of $\mathrm{W(PMe_3)_4Cl_2}$ (**2a**) and 58 mg (5.4×10^{-4} mol) of $\mathrm{(S)PMe_3}$ (Aldrich). The contents of the vessel were degassed on the vacuum line, 8 mL of toluene was added, and the resulting solution was stirred for 5.5 h at 80 °C. During this time the color of the reaction mixture became reddish-purple. The volatiles were removed under vacuum, and the greenish residue was redissolved in 4 mL of fresh toluene giving a dark burnt peach solution, which was heated at 80 °C for an additional 1.5 h. The resultant purple solution was transferred to a 25-mL Kjeldahl flask fitted to a frit and stripped again of volatiles to give a greenish residue. The residue was recrystallized at −15 °C from toluene–pentane, washed with pentane, and dried in vacuo to give complex **11a** as a dark green solid. The complex **11a** cocrystallizes with trace amounts (~5%) of a byproduct in the reaction, $\mathrm{W(PMe_3)_3Cl_3}$ (**6a**), which cannot be separated:[40] yield, 0.15 g (65%); ^{1}H NMR 1.67 (9 H, d, *J* = 8, *cis*-$\mathrm{P(C}\mathit{H}_3)_3$), 1.56 (18 H, t, *J* = 4, *trans*-$\mathrm{P(C}\mathit{H}_3)_3$); $^{31}\mathrm{P}\{^1\mathrm{H}\}$ NMR −54.4 (t, *J* = 4, *cis*-$\mathit{P}\mathrm{(CH_3)_3}$, $J_{\mathrm{PW}} = 335$), −41.7 (d, *J* = 4. *trans*-$\mathit{P}\mathrm{(CH_3)_3}$), $J_{\mathrm{PW}} = 271$); $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR 33.8 (d. *J* = 31, *cis*-$\mathrm{P(}\mathit{C}\mathrm{H_3)_3}$,

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[40] The difficulty of separating trivalent species $\mathrm{ML_3Cl_3}$ from tetravalent $\mathrm{M(O)L_3Cl_2}$ (M = Mo. W; L = phosphine) has been recently discussed: (a) Yoon. K.; Parkin. G.; Rheingold, A. L. *J. Am. Chem. Soc.* **1991**, *113*. 1437–1438; **1992**, *114*. 2210–2218. (b) Desrochers. P. J.; Nebesny. K. W.; LaBarre. M. J.; Lincoln. S. E.; Loehr. T. M.; Enemark, J. *J. Am. Chem. Soc.* **1991**, *113*, 9193.

22.7 (t, $J = 14$, *trans*-P(CH_3)$_3$); IR (Nujol) 1418 (sh), 1343 (sh), 1299 (w), 1280 (m), 1158 (w), 1086 (w), 950 (s), 857 (m), 772 (w), 727 (m), 669 (m).

W(N^{t}Bu)(CN^{t}Bu)(PMe$_3$)$_2$Cl$_2$ (24a). In a 25-mL reaction bomb was placed 0.25 g (4.5×10^{-4} mol) of $W(PMe_3)_4Cl_2$ (**2a**). The contents of the vessel were degassed on the vacuum line, and 9 mL of dry benzene was added followed by the addition of 259 μL (1.3×10^{-3} mol) of di-*tert*-butylcarbodiimide. The reaction mixture was then stirred at 80 °C for 34 h, during which time the solution became a reddish-orange color. The volatiles were removed under vacuum giving an red-orange solid, a few milligrams of which was analyzed by ^{1}H NMR to determine the extent of reaction. The solids were taken up in 4 mL of fresh benzene, treated with 5.4 μL of additional di-*tert*-butylcarbodiimide (a 3-fold excess to react with the 5% of **2a** which remained unreacted by NMR), and heated further for 2 h. The reaction mixture was again stripped of volatiles, and the red-orange solids were scraped from the bomb. Recrystallization from toluene–diethyl ether gave ruby red crystals of **24a**: yield, 202 mg (80%); ^{1}H NMR 1.57 (18 H, t, $J = 4$, *trans*-P(CH_3)$_3$), 1.28 (9 H, C(CH_3)$_3$), 1.07 (9 H, C(CH_3)$_3$); ^{31}P{^{1}H} NMR −20.4 (s, *trans-P*(CH_3)$_3$, $J_{PW} = 299$); ^{13}C{^{1}H} NMR 67.6 (s, *C*(CH_3)$_3$), 61.6 (s, *C*(CH_3)$_3$), 31.7 (s, C(*C*H$_3$)$_3$), 31.4 (s, C(*C*H$_3$)$_3$), 17.0 (t, $J = 14$, *trans*-P(*C*H$_3$)$_3$) (the isonitrile carbon was not observed); IR (Nujol) 2012 (sh), 1916 (s), 1457 (s), 1414 (sh), 1363 (sh), 1302 (w), 1286 (w), 1280 (w), 1262 (s), 1236 (w), 1199 (s), 1039 (w), 957 (s), 855 (w), 806 (w), 739 (s), 675 (w). Anal. Calcd for $WCl_2P_2N_2C_{15}H_{36}$: C, 32.11; H, 6.47; N, 4.99. Found: C, 32.19; H, 6.31; N, 4.95.

Kinetics of Phosphine Exchange. Two solutions of $Mo(PMe_3)_4Cl_2$ (**1a**) in C_6D_6 (27 and 30 mg/mL) were prepared in NMR tubes which were attached to Teflon needle valves. The solutions were frozen (−196 °C) and degassed on the vacuum line and then treated with 12 and 40 equiv of PMe$_3$-d_9 (0.7 and 2.5 M, respectively). Upon thawing of the tubes to ambient temperature (24 ± 2 °C), the equilibration of the free deuterio and bound protio phosphine was monitored by ^{1}H NMR and found to follow the integrated rate expression $kt = 4\{[P]_e/[P]_i\} \ln \{[P]_e/([P]_e - [P]_t)\}$, where $[P]_e$ is the $[PMe_3]_{free}$ at equilibrium, $[P]_i$ is the initial amount of $[PMe_3]$ bound to $M(PMe_3)_4Cl_2$, and $[P]_t$ is the $[PMe_3]_{free}$ at time t. In this expression, k is the rate constant for loss of a single phosphine from $Mo(PMe_3)_4Cl_2$; isotope effects have been neglected. The derived first-order rate constants were 6.6×10^{-4} and 6.5×10^{-4} s^{-1}, respectively, for the two runs at different concentrations of PMe$_3$-d_9.

Hammett Study of Para-Substituted Phenyl Isocyanates with 2a. A stock solution of $W(PMe_3)_4Cl_2$ (**2a**) in C_6D_6 (60.0 mg/mL) was prepared and then dispensed in 250-μL aliquots into each of the four NMR tubes followed by a 3-fold molar excess of the following isocyanates: *p*-tolyl isocyanate (10.1 μL), phenyl isocyanate (8.7 μL), 4-(trifluoromethyl)phenyl isocyanate (11.5 μL), and 4-methoxyphenyl isocyanate (10.4 μL). An additional 250-μL aliquot of C_6D_6 was added to each tube, the tubes were degassed and sealed, and the ambient temperature reactions were monitored by ^{1}H NMR. After approximately 3 weeks, most of the **2a** in the tubes had reacted to form mixtures of tungsten oxo and imido products, identified by the similarity of their spectra to related compounds and distinguished by their respective J_{WP} values. Assignments for the ^{1}H spectra were made by ^{1}H{^{31}P} decoupling experiments.

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Gated Electron-Transfer Behavior in Copper(II/I) Systems. Comparison of the Kinetics for Homogeneous Cross Reactions, NMR Self-Exchange Relaxation, and Electrochemical Data for a Copper Macrocyclic Tetrathioether Complex in Aqueous Solution

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Abstract: The kinetics of electron-transfer reactions involving $Cu^{II/I}$([14]aneS$_4$) reacting with a series of selected counterreagents have been measured in aqueous solution at 25 °C, $\mu = 0.10$ M (ClO_4^-). The reagents utilized include four oxidants [$Ru(NH_3)_4bpy^{3+}$, $Ni([14]aneN_4)^{3+}$, $Ru(NH_3)_2(bpy)_2^{3+}$, and $Fe(4,7\text{-}Me_2phen)_3^{3+}$] and four reductants [$Co(Me_4[14]tetraeneN_4)^{2+}$, $Ru(NH_3)_4bpy^{2+}$, $Ru(NH_3)_5isn^{2+}$, and $Ru(NH_3)_5py^{2+}$], which were selected to provide a variety of reagent self-exchange rate constants and overall reaction potentials, thereby yielding a range of cross reaction rate constant values. Application of the Marcus equation to the cross reaction rate constants for the four *reduction* studies yielded consistent self-exchange rate constant values of $\log k_{11(red)} = 3.78$ (±0.26) for $Cu^{II/I}$([14]aneS$_4$). By contrast, the two *oxidation* kinetic studies having the largest reaction potentials [i.e., using $Ru(NH_3)_2(bpy)_2^{3+}$ and $Fe(4,7\text{-}Me_2phen)_3^{3+}$ as oxidants] yielded $\log k_{11(ox)} \approx 0$ (±0.26), while the *oxidation* reactions with smaller reaction potentials [i.e., using $Ru(NH_3)_4bpy^{3+}$ and $Ni([14]aneN_4)^{3+}$ as oxidants] yielded an apparent value of $\log k_{11(ox)} \approx 2.5$ for $Cu^{II/I}$([14]aneS$_4$) when *relatively small concentrations* of the counteroxidant were used. Upon an increase in the $Ni([14]aneN_4)^{3+}$ concentration, however, $k_{11(ox)}$ appeared to decrease until, at relatively high concentrations of the Ni(III) reagent, limiting first-order kinetic behavior was observed. In an independent study, NMR line-broadening measurements were made on Cu^I([14]aneS$_4$) solutions containing variable amounts of Cu^{II}([14]aneS$_4$) to obtain a direct measurement of $\log k_{11(ex)} \approx 3.88 \pm 0.09$ at 25 °C ($\Delta H^{\ddagger} = 20.7 \pm 4.5$ kJ mol^{-1}; $\Delta S^{\ddagger} = -101 \pm 13$ J K^{-1} mol^{-1}). This is in direct agreement with the values calculated from the reduction reactions. The patterns in the kinetic behavior of $Cu^{II/I}$([14]aneS$_4$) are shown to be consistent with a dual-pathway square scheme, as characterized by rapid-scan cyclic voltammetry. For Cu^IL oxidation reactions, the conformational change to form a metastable Cu^IL species becomes rate-limiting under specific conditions, resulting in the appearance of "gated" electron-transfer kinetics; ultimately, the oxidation reaction switches to the alternate reaction pathway.

Introduction

In previous work we have reported the results of homogeneous electron-transfer kinetic studies on both the oxidation and reduction of Cu(II)/(I) complexes involving an entire series of macrocyclic and acyclic polythioethers (L).[2] In that investigation,

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