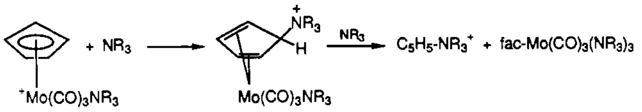
unexpected because neither NEt_3 nor aniline is as nucleophilic as pyridine. The nucleophilicity of the amine is the key property in this type of reaction because reaction 7 is proposed to proceed by nucleophilic attack on the Cp ring:[17]



Apparently neither aniline nor NEt_3 is nucleophilic enough for this step to occur. Control experiments are consistent with this suggestion; no reaction was observed between $Cp'Mo(CO)_3py^+$ and aniline in benzene solution.

In summary of the results with NEt_3 and aniline, $Cp'_2Mo_2(CO)_6$ does not give net disproportionation products when irradiated in the presence of these ligands. The unreactivity is probably the result of a facile back-reaction of the disproportionation products to re-form the $Cp'_2Mo_2(CO)_6$ dimer. That the back-reaction occurs is a consequence of the inability of the cationic product to react with these amines to form other products.

Conclusions. $Cp'_2Mo_2(CO)_6$ will disproportionate in a photochemical reaction with amines only when the cationic product of the reaction, $Cp'Mo(CO)_3(amine)^+$, can undergo further reaction. By reacting further, the cation is prevented from undergoing a back-reaction with the $Cp'Mo(CO)_3^-$ product. A net reaction occurs with pyridine because the $Cp'Mo(CO)_3py^+$ product reacts with pyridine according to eq 7. A net reaction occurs with ethylenediamine and cyclohexylamine because the cationic disproportionation products react to form carbamoyl complexes (eq 10). No net disproportionation reactions occur with NEt_3 or aniline because these amines are not nucleophilic enough to react according to eq 7 and they are incapable of forming carbamoyl complexes.

Acknowledgment. This work was supported by the National Science Foundation. D.R.T. acknowledges the Alfred P. Sloan Foundation for a Fellowship. Prof. R. J. Angelici is acknowledged for helpful discussions.

Registry No. $Cp'_2Mo_2(CO)_6$, 33056-03-0; py, 110-86-1; $Cp'Mo(CO)_3^-$, 64799-62-8; *fac*-$Mo(CO)_3(py)_3$, 66701-87-9; *cis*-$Mo(CO)_4(py)_2$, 16742-99-7; en, 107-15-3; NH_2(c-Hx), 108-91-8; $Cp'Mo(CO)_2(NH_2$(c-Hx))CONH(c-Hx), 123265-02-1; $Cp'Mo(CO)_2$(en-*N*)$CONHC_2H_4NH_2$, 123265-03-2; NH_2Ph, 62-53-3; NEt_3, 121-44-8; $Co'Mo(CO)_3py^+$, 123265-04-3.

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Isocyanide Complexes of Titanium(IV) and Vanadium(V): Concerning the Nonexistent Insertion of Isocyanides into a Metal-Chloride Bond

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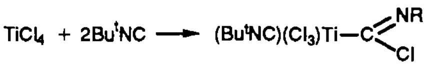
The addition of isocyanides to high-valent early-transition-metal halides is a known reaction reported in a number of papers[1] and reviewed recently.[2] In the specific case of titanium(IV) chloride, as in a few others, the reaction was often claimed to lead to the formation of a Ti-C functionality derived from the insertion of RNC into a Ti-Cl bond.[1] The role of $TiCl_4$ promoting the addition of isocyanides to a carbonylic function in a modified version of the Passerini reaction[3] was interpreted on the basis of the intermediate formation of the iminochloride functionality shown in complex A.[4,5]



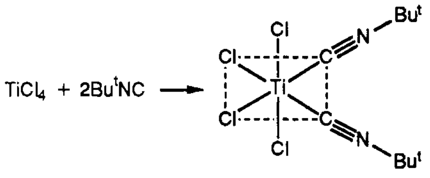
$$TiCl_4 + 2Bu^tNC \longrightarrow (Bu^tNC)(Cl_3)Ti{-}C{\overset{\displaystyle \nearrow NR}{\underset{\displaystyle \searrow Cl}{}}} \qquad (1)$$

A

This assumption was maintained in spite of Lippard's results[6] showing that the reaction of Bu^tNC with VCl_3 simply leads to the $[VCl_3(Bu^tNC)_3]$ adduct, instead of forming an inserted product. In the search for a structural confirmation of the unusual genesis of the organometallic functionality in reaction 1, we reconsidered the reaction of $TiCl_4$ with isocyanides. Since the isocyanides add to less acidic titanium chlorides derivatives without any insertion occurring,[7] we believed that the metal acidity might be, as suggested,[2] a major factor determining the insertion of RNC into a metal-chloride bond. Therefore, in addition to $TiCl_4$, we considered the vanadium(V) derivative $[PhNVCl_3(THF)_2]$.

Results and Discussion

The reaction of $TiCl_4$ with Bu^tNC, carried out in toluene, gave, independent of the Ti:RNC ratio, the *cis*-diisocyanide adduct $[TiCl_4(Bu_tNC)_2]$ (**1**) (85%).[8] When reaction 2 is carried out with a 1:1 Ti:RNC molar ratio, the excess of $TiCl_4$ remains unreacted in solution. The role of $TiCl_4$ left in solution should be eventually considered in the modified Passerini reaction, in case it is carried out by using a 1:1 Ti:RNC ratio.[4] The nature of R, however, is crucial in determining the RNC:$TiCl_4$ ratio, due either to steric factors or to the presence of donor atoms in its skeleton. We found, in fact, that $[TiCl_4(2,6\text{-}Me_2C_6H_3NC)]_2$[8] and $[TiCl_4(C{\equiv}NCH_2P(O)(OEt)_2)]_2$[8] are dimers containing one isocyanide ligand per titanium. In none of them, however, the insertion of the $-N{\equiv}C$ functionality in the Ti—Cl bond was found.[8] The IR spectrum of **1** both in the solid state and in solution showed a single sharp band at 2226 cm^{-1} in Nujol and at 2210 cm^{-1} in CH_2Cl_2. A sharp singlet for the Bu^t groups is found in the ^1H NMR at δ 1.59 (CD_2Cl_2). There are no additional bands appearing in the 1600-1700-cm^{-1} region, unless the IR spectrum is taken in the air or the solid exposed briefly to the air. Figure 1 shows the Nujol



(2)

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[†] Université de Lausanne.

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(8) The synthesis of $[TiCl_4(2,6\text{-}Me_2C_6H_3NC)]_2$ [ν(C≡N) (Nujol), 2210 cm^{-1}] and $[TiCl_4(C{\equiv}NCH_2P(O)(OEt)_2)]_2$ [ν(C≡N) (Nujol), 2245 cm^{-1}] have been carried out from a CH_2Cl_2 solution of $TiCl_4$. The isolated compounds have analytical and spectroscopic data in agreement with the proposed formula. The X-ray analysis is currently being carried out on both compounds.

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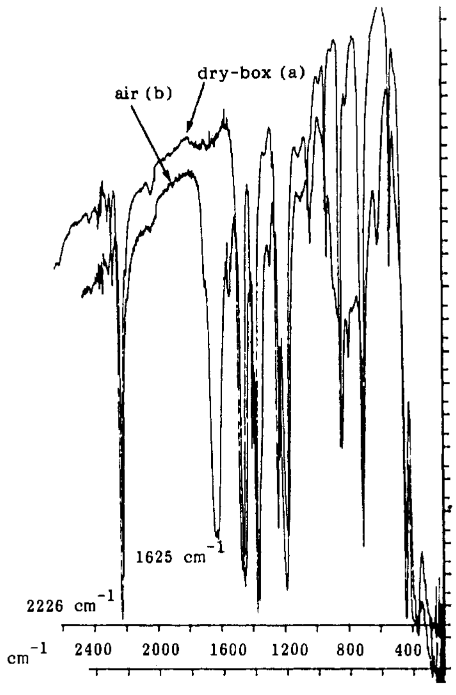


Figure 1. Infrared spectrum (Nujol) of [TiCl$_4$(Bu^{t}NC)$_2$], taken in the drybox (a) and in the air (b).

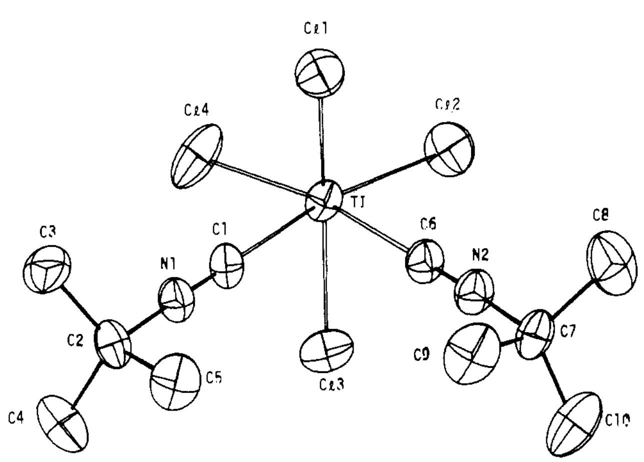


Figure 2. ORTEP drawing of compound **1**. Selected bond distances (Å) and angles (deg): Ti-Cl1 = 2.287 (3), Ti-Cl3 = 2.286 (3), Ti-Cl2 = 2.244 (3), Ti-Cl4 = 2.218 (2), Ti-C1 = 2.240 (8), Ti-C6 = 2.256 (6), N1-C1 = 1.145 (10), N2-C6 = 1.137 (8); C1-Ti- C6 = 76.7 (3), Cl4-Ti-C6 = 165.6 (2), Cl2-Ti-C1 = 165.5 (2), Cl1-Ti-Cl3 = 163.2 (1), Cl4-Ti-C1 = 89.0 (2), Cl4-Ti-Cl2 = 105.5 (1), Cl2-Ti-C6 = 88.9 (2), Ti-C1-N1 = 178.6 (6), Ti-C6-N2 = 178.7 (6).

spectra of **1** under nitrogen (a) and of **1** exposed to the air (b). The band centered at 1625 cm^{-1} has nothing to do with an imino group derived from the insertion of RNC into the Ti-Cl bond, but it is related to the hydrolysis of the isocyanide enhanced by the acidity of the metal, as shown by Lippard in case of [VCl$_3$(Bu^{t}NC)$_3$].[6] An ORTEP view of **1** is given in Figure 2 with the most relevant structural parameters, showing the cis arrangement of the isocyanide ligands. The titanium atom is in a pseudooctahedral environment. The Ti–C distances are significantly longer [Ti–C1, 2.240 (8) Å; Ti–C6, 2.256(6) Å] than those reported for the few bis(cyclopentadienyl)titanium isocyanide complexes so far structurally studied, i.e. [(η^5-C$_5$Me$_5$)$_2$Ti(Bu^t—NC)-η^2-Bu^{t}N=C—CH$_2$CH$_2$—CORe$_2$(CO)$_9$] [2.17 (2) Å],[9a] [(cp)$_2$Ti{η^2-C(Me)NBu^t}(CNBu^t)]BPh$_4$·MeCN [2.192 (6) Å],[9b] and [(cp)$_2$Ti(CO)(CNBu^t)] [2.112 (9) Å].[9c] On the basis of the results obtained from the reaction of TiCl$_4$ with isocyanides, the role of the TiCl$_4$ in the modified Passerini reaction[4,5] must be reconsidered. With this in mind, isocyanide and ketone adducts to TiCl$_4$ have been structurally characterized and their reactivity is under investigation.[10]

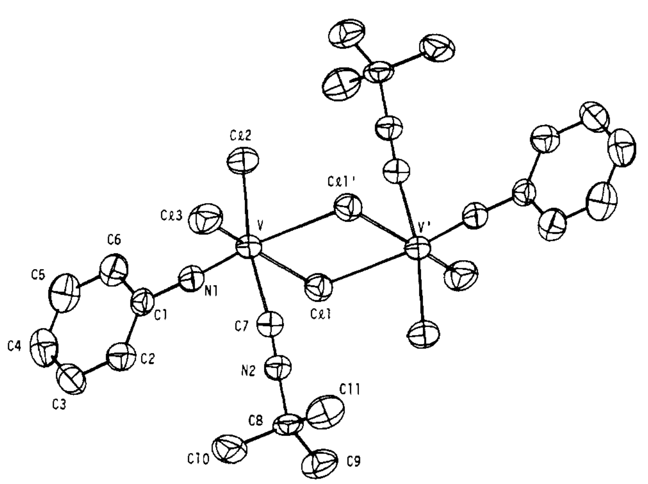
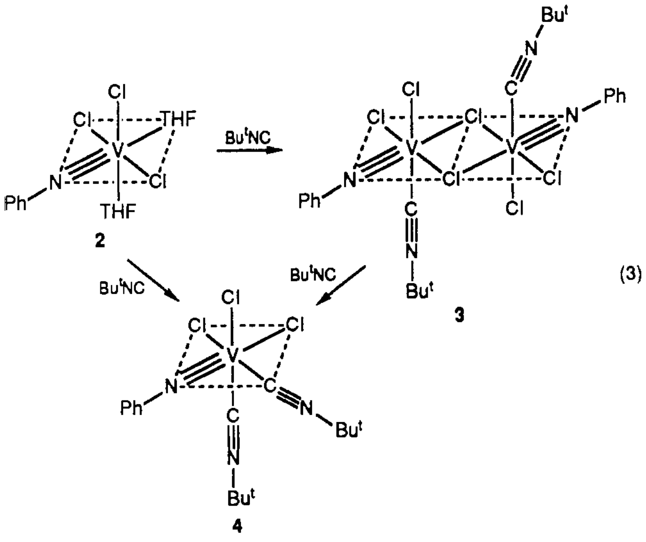


Figure 3. ORTEP drawing of compound **3**. Selected bond distances (Å) and angles (deg): V-Cl1 = 2.351 (1), V-Cl1' = 2.681 (1), V-Cl2 = 2.253 (1), V-Cl3 = 2.255 (2), V-N1 = 1.646 (4), V-C7 = 2.138 (4), N1-C1 = 1.368 (5), N2-C7 = 1.137 (5); N1-V-C7 = 91.9 (2), Cl1-V-Cl3 = 159.5 (1), Cl'-V-N1 = 173.3 (1), Cl2-V-C7 = 169.7 (1), Cl1'-V-Cl2 = 87.8 (1), Cl'-V-C7 = 82.2 (1), Cl2-V-N1 = 98.0 (1), V-N1-C1 = 176.5 (3); V-C7-N2 = 174.3 (4); V-Cl1-V' = 100.9 (1). A prime denotes a transformation of $-x$, $-y$, $-z$.

Complex **2**[11] has been chosen as representative of the very acidic vanadium(V). It reacts with Bu^{t}NC in a 1:1 or 1:2 molar ratio. The stoichiometry was established by following the reaction by IR means in solution.



(3)

Complexes **3** [ν(CN) (Nujol), 2239 cm^{-1}] and **4** [ν(CN) (Nujol), 2206 and 2232 cm^{-1}] were both isolated in a crystalline form. The acidity of the metal center is revealed by the C≡N stretchings moving above 2200 cm^{-1} from 2138 cm^{-1} in the free isocyanide. Secondary products forming from the insertion of the RNC into V–Cl bonds might be not detected, as supported by the absence of any band in the solid state or in solution in the 1600–1700-cm^{-1} region. The structure proposed for **4** represents

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[10] Carofiglio, T.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. Unpublished results.

[11] The synthesis of [PhNVCl$_3$(THF)$_2$] was performed as reported for the analogous *p*-tolyl derivative: Devor, D. D.; Lichtenham, J. D.; Takusagawa, F.; Maatta, E. A. *J. Am. Chem. Soc.* **1987**, *109*, 7408. The complex was fully characterized, including an X-ray structure determination.

Table I. Crystal Data for Complexes **1** and **3**

	1	**3**
formula	$C_{10}H_{18}Cl_4N_2Ti$	$C_{22}H_{28}Cl_6N_4V_2\cdot C_7H_8$
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a, Å	9.124 (1)	12.846 (1)
b, Å	17.360 (2)	12.525 (1)
c, Å	11.942 (1)	11.238 (1)
α, deg	90	90
β, deg	108.25 (1)	91.52 (1)
γ, deg	90	90
V, Å^3	1796.4 (3)	1807.5 (3)
Z	4	2
intens meas method	three points, individual profiles	
refinement method	full-matrix least squares	
$R = \sum\|\Delta F\|/\sum\|F_o\|$	0.042	0.044
$R_w = \sum w^{1/2}\|\Delta F\|/\sum w^{1/2}\|F_o\|$	0.046	0.050

Table II. Fractional Atomic Coordinates (×10^4) for Complex **1**

atom	*x*/*a*	*y*/*b*	*z*/*c*
Ti	2815 (1)	3916 (1)	2724 (1)
Cl1	3415 (2)	3119 (1)	1406 (2)
Cl2	1302 (2)	3069 (1)	3261 (2)
Cl3	2984 (2)	4753 (1)	4237 (2)
Cl4	1223 (2)	4651 (1)	1357 (2)
N1	5798 (7)	4969 (3)	2437 (5)
N2	5948 (7)	3093 (3)	4687 (5)
C1	4799 (8)	4604 (4)	2532 (6)
C2	7102 (8)	5431 (4)	2327 (7)
C3	7061 (9)	5398 (5)	1065 (7)
C4	6849 (10)	6229 (5)	2733 (8)
C5	8562 (9)	5061 (5)	3131 (8)
C6	4887 (8)	3365 (4)	4037 (6)
C7	7377 (8)	2773 (4)	5532 (6)
C8	7248 (10)	1906 (5)	5429 (9)
C9	8702 (9)	3078 (6)	5171 (7)
C10	7408 (10)	3046 (6)	6725 (8)

one of the three possible geometric isomers, two of them having a cis arrangement of the isocyanide ligands. The proposed cis isomer is in agreement with the two C≡N stretchings observed in the IR spectrum and the singlet for the Bu^t substituent at the isocyanide ligand. An X-ray analysis was carried out to clarify the structure of **3**. An ORTEP view of **3** is reported in Figure 3, with some relevant structural parameters. Each vanadium atom in the centrosymmetric dimer is six-coordinate in a distorted octahedral arrangement. The bridging chlorine atoms in the equatorial plane are in an unsymmetrical arrangement, the V–Cl distance trans to the multiple V–N bond being 0.33 Å longer than the other one. This bond is in its turn 0.1 Å longer than the vanadium distances to the terminal chlorines, values which are close to that in $[V((Ntol)Cl(O\text{-}2,6\text{-}C_6H_3(CH_3)_2)_2]_2$,[11] [2.240 (1) Å]. The V–C distance is slightly longer than those found in $[VCl_3(Bu^tNC)_3]$.[6] The absence of any insertion of isocyanide into the M–Cl bond of highly acidic early-transition-metal halides prompts us to reexamine the role of Lewis acids, MX_n, in the modified version of the Passerini reaction.[4,5] A fundamental question should be: does $TiCl_4$ assist the Passerini reaction via the interaction with the isocyanide or the carbonylic function?

Experimental Section

Synthesis of Complex 1. Bu^{t}NC (1.62 g, 19.5 mmol) was added to a toluene solution (100 mL) of $TiCl_4$ (1.73 g, 9.1 mmol). A light yellow solid crystallized in a few minutes from the solution. It was filtered and washed with *n*-hexane (ca. 85%). The same synthesis can be carried out equally well in CH_2Cl_2.[1] Longer reaction times and different Ti:RNC molar ratios in either toluene or CH_2Cl_2[1,4] always gave red solutions from which the isolated solid, washed carefully, was the same yellow diisocyanide derivative. Anal. Calcd for $C_{10}H_{18}N_2Cl_4Ti$: C, 33.74; H, 5.10; N, 7.87. Found: C, 34.01; H, 5.25; N, 7.76. Recrystallization from hot toluene gave crystals suitable for the X-ray analysis.

Synthesis of Complexes 3 and 4. Bu^{t}NC (0.39 g, 4.69 mmol) was added to a toluene solution (100 mL) of $[PhNVCl_3(THF)_2]$ (0.92 g, 2.35 mmol). The solution color changed from green to deep green. Partial evaporation of the solvent and allowing the solution to stand gave yellow crystals of **3** containing a molecule of toluene per dimer (80%). Anal. Calcd for $C_{29}H_{36}N_4Cl_6N_4V_2$: C, 46.09; H, 4.76; Cl, 9.40; N, 7.41. Found: C, 46.61; H, 4.90; Cl, 9.27; N, 7.36. ^1H NMR (δ, CD_2Cl_2): 7.33 (m, 5 H, Ph), 1.55 (s, 9 H, Bu^t). When the reaction was carried out with a 2:1 Bu^{t}NC:V molar ratio, a yellow-green crystalline solid formed (70%). Anal. Calcd for $C_{16}H_{23}Cl_3N_3V$: C, 46.34; H, 5.59; Cl, 25.65; N, 10.13. Found: C, 46.14; H, 5.50; Cl, 25.67; N, 10.06. ^1H NMR (δ, CD_2Cl_2): 7.49 (m, 5 H, Ph), 1.53 (s, 18 H, Bu^t).

Table III. Fractional Atomic Coordinates (×10^4) for Complex **3**[a]

atom	*x*/*a*	*y*/*b*	*z*/*c*
V	622 (1)	383 (1)	1536 (1)
Cl1	−609 (1)	1106 (1)	177 (1)
Cl2	2014 (1)	1112 (1)	668 (1)
Cl3	1477 (1)	−838 (1)	2667 (1)
N1	481 (3)	1281 (3)	2589 (3)
N2	−1456 (3)	−863 (3)	2425 (3)
C1	426 (3)	2039 (3)	3461 (3)
C2	−285 (3)	1940 (4)	4365 (4)
C3	−318 (4)	2728 (4)	5233 (4)
C4	335 (4)	3586 (4)	5187 (4)
C5	1047 (4)	3674 (4)	4303 (5)
C6	1099 (4)	2915 (4)	3427 (4)
C7	−725 (3)	−475 (3)	2074 (4)
C8	−2414 (3)	−1349 (4)	2871 (4)
C9	−3323 (4)	−742 (4)	2319 (5)
C10	−2370 (4)	−1234 (5)	4203 (4)
C11	−2414 (4)	−2506 (4)	2483 (5)
C1S	5632 (5)	622 (6)	5410 (7)
C2S	4539 (9)	1137 (10)	3655 (11)
C3S	4129 (12)	118 (12)	3784 (13)
C4S	5385 (10)	1216 (10)	4678 (11)
C5S	4725 (11)	460 (11)	4397 (12)

[a] The site occupation factors for the disordered toluene molecule are 1.0 for C1S and C2S and 0.5 for C2S, C3S, and C4S.

X-ray Crystallography. Crystal data are given in Table I. A total of 1272 (corrected for absorption) and 2300 unique reflections for complexes **1** and **3**, respectively, were collected at room temperature on a Philips PW 1100 single-crystal diffractometer (Mo Kα radiation, λ = 0.71069 Å). The structures were solved by Patterson and Fourier methods. Final atomic coordinates are listed in Tables II and III.

Acknowledgment. We thank the Fonds National Suisse de la Recherche Scientifique (Grant No. 2000-5.031) for financial support.

Registry No. **1**, 123148-55-0; **2**, 123168-66-1; **3**, 123148-57-2; **4**, 123148-58-3; $[TiCl_4(2,6\text{-}Me_2C_6H_3NC)]_2$, 123148-59-4; $[TiCl_4(C{\equiv}NCH_2P(O)(OEt)_2)]_2$, 123148-60-7.

Supplementary Material Available: Listings of experimental details associated with the X-ray studies, hydrogen coordinates, anisotropic thermal parameters, and bond distance and angles for **1** and **3** (8 pages); tables of observed and calculated structure factors for complexes **1** and **3** (21 pages). Ordering information is given on any current masthead page.

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Kinetic Study of the Formation of the Oxo Diperoxo Complex of Tungsten(VI) in Aqueous Perchloric Acid Solution

M. Ashraf Islam and Richard C. Thompson*

Received April 25, 1989

We have shown that the peroxo ligands in the oxo diperoxo complexes of molybdenum(VI) and tungsten(VI) are impressively activated toward both oxygen atom transfer and inner-sphere, one-electron-reduction reactions in aqueous solution.[1-3] This

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(1) Ghiron, A. F.; Thompson, R. C. *Inorg. Chem.* **1988**, *27*, 4766.
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