Catalytic Oxidation

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Catalytic Degenerate and Nondegenerate Oxygen Atom Transfers Employing N_2O and CO_2 and a M^{II}/M^{IV} Cycle Mediated by Group 6 M^{IV} Terminal Oxo Complexes**

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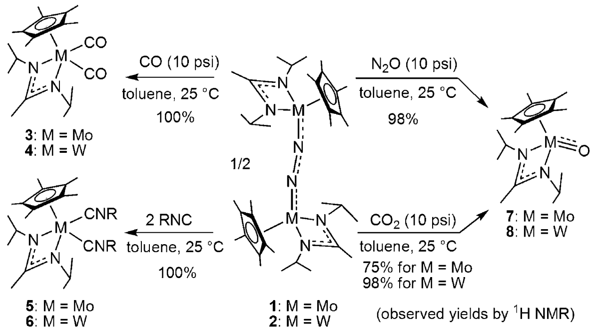
The development of transition-metal-catalyzed transformations that employ molecular oxygen (O_2), carbon dioxide (CO_2), and nitrous oxide (N_2O) as inexpensive and chemically benign "green" oxidants for the industrial-scale production of specialty and commodity chemicals is of significant scientific, commercial, and environmental interest.[1–3] To achieve this goal, a fine thermodynamic balance must be established for reaction pathways involving oxygen atom transfer (OAT) to, and from, a given metal center in a fashion that favors productive substrate oxidation.[4] Herein, we report a new class of low-valent Group 6 metal complex that, in the case of molybdenum, can mediate the direct oxidation of *tert*-butyl isocyanide, *t*BuNC, to the corresponding isocyanate, *t*BuNCO, through nondegenerate OAT utilizing N_2O as a chemical oxidant according to: $RN{\equiv}C + N_2O \rightarrow RN{=}C{=}O + N_2$.[5] We further detail the ability of this same class of metal complex to serve as a photocatalyst for the reversible degenerate OAT between CO and CO_2 in the case of molybdenum and tungsten. For both nondegenerate and degenerate OAT processes, which proceed at near ambient conditions, key intermediates have been isolated and structurally characterized, including midvalent terminal oxo metal complexes, the first unequivocal examples of η^2-(OCNR) metal complexes that are supported by a κ^2-*O*,*C* bonding motif, and finally, a rare example of a η^2-CO_2 tungsten complex that can engage in elimination of either CO or CO_2. Collectively, these results serve to establish catalytically competent OAT cycles that are based on a Group 6 metal M^{II}/M^{IV} formal oxidation state couple.[6] By way of contrast, all biological molybdenum- and tungsten-dependent oxotransferase enzymes investigated to date appear to favor thermal OAT mechanisms based on a M^{IV}/M^{VI} couple.[4]

We have previously reported that the Group 6 dinuclear "end-on-bridged" dinitrogen complexes, $[\{Cp^*M[N(i\text{Pr})C(Me)N(i\text{Pr})]\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)]$ ($Cp^* = \eta^5\text{-}C_5Me_5$), for M = Mo (**1**) and W (**2**), can function as convenient M^{II} synthons for $[Cp^*M\{N(i\text{Pr})C(Me)N(i\text{Pr})\}(L)_2]$, where L = CO for M = Mo (**3**) and W (**4**), and $L = CN(2,6\text{-}Me_2C_6H_3)$ for M = Mo (**5**) and W (**6**), according to Scheme 1.[7] In keeping with known literature precedent,[8] this M^{II} synthon analogy for **1** and **2** was extended further in the present work through demonstration that the corresponding terminal M^{IV} oxo compounds, $[Cp^*M(O)\{N(i\text{Pr})C(Me)N(i\text{Pr})\}]$ for M = Mo (**7**) and W (**8**), could be isolated in modest to excellent yields through oxidative OAT with N_2O under near ambient conditions (25 °C, 10 psi) (see Scheme 1).[9] As the results in Scheme 1 further reveal, it was determined that **7** and **8** could also be obtained from **1** and **2**, respectively, through facile OAT employing CO_2 (10 psi) at room temperature. Mayer and coworkers[10] have previously reported a similar $W^{II} \rightarrow W^{IV}$ oxygen atom abstraction of CO_2 by $[WCl_2(PMePh_2)_4]$ that yielded the tungsten oxo, carbonyl complex, $[W(O)(CO)Cl_2(PMePh_2)_2]$.



Scheme 1. Synthesis of M^{II} and M^{IV} complexes from a common precursor for M = Mo and W.

Compounds **7** and **8** are diamagnetic, crystalline solids for which spectroscopic and elemental analyses are fully consistent with the structures depicted. Single-crystal X-ray analyses provided the solid-state molecular structures of **7** and **8** which displayed a high degree of isostructural similarity between the two compounds, and as such, only that of **8** is presented in Figure 1.[9,11] In keeping with expected periodic trends,[12] however, the second-row molybdenum complex **7** exhibits a slightly shorter molybdenum–oxygen bond of 1.7033(19) Å as compared with the corresponding tungsten–oxygen bond of 1.7234(17) Å for **8**. While these bonds are significantly longer than the tungsten–oxygen bond of 1.684 Å determined for $[W(O)Cl_4]$[13] and of 1.689(6) Å for $[W(O)(CO)Cl_2(PMePh_2)_2]$,[10] both **7** and **8** possess metal–oxygen bonds that are shorter than the corresponding values reported for the bis(η^5-cyclopentadienyl) (also known as "metallocene") derivatives, $[(MeCp)_2M(O)]$ ($MeCp = \eta^5\text{-}C_5H_4Me$) [cf., Mo–O 1.721(2) Å and W–O 1.744(5) Å, respectively] for which a formal metal–oxygen bond order

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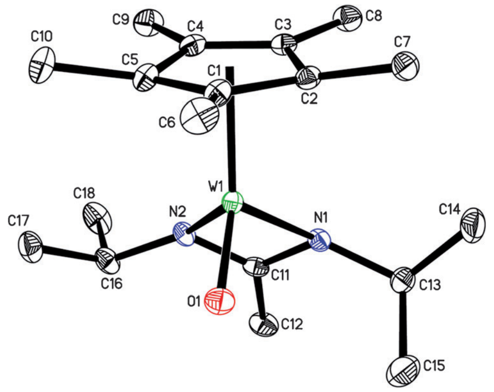
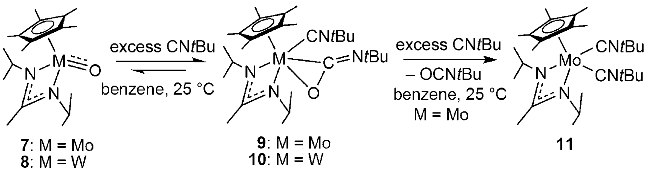


Figure 1. Molecular structure (30% thermal ellipsoids) of **8**. Hydrogen atoms have been removed for clarity.

of two has been proposed.[14–16] Accordingly, based on these simple bond-length comparisons, we currently favor the assignment of a M–O bond order for **7** and **8** that lies somewhere between two and three.[17] This bond order formalization for **7** and **8** further implies a lower nucleophilicity for the terminal oxo group, as compared to that experimentally determined for [$(MeCp)_2M(O)$] and related metallocene terminal oxo complexes, such as [$Cp_2M(O)$] (Cp = η^5-C_5H_5) and [$Cp^*{}_2M(O)$].[18,19]

As shown in Scheme 2, addition of a slight excess of *t*BuNC to a toluene solution of **7** and **8**, followed by removal of toluene in vacuo and crystallization from pentane at −30 °C for 18 h, provided modest to excellent yields of the corresponding diamagnetic, crystalline complexes, [Cp*M{η^2-OCN*t*Bu)}(CN*t*Bu){N(*i*Pr)C(Me)N(*i*Pr)}] where M = Mo (**9**) and W (**10**).[9] Importantly, single-crystal X-ray analyses of **9** and **10** served to establish a κ^2-(*O*,*C*) ligation of the *t*BuNCO group, which, to the best of our knowledge, is the first time that this coordination mode for a metal-complexed isocyanate has been unequivocally established.[20,21] In the solid state, **9** and **10** proved to be nearly isostructural, and accordingly only that of **9** is presented in Figure 2, along with selected geometric parameters. Finally, solid-state infrared spectra (KBr) displayed two sets of strong absorption bands at 2112 (w/sh) cm^{-1} and 1628 (w/sh) cm^{-1} for **9**, and at 2085, 2054 cm^{-1} and 1622, 1603 cm^{-1} for **10**.[9]



Scheme 2. Synthesis of κ^2-(*O*,*C*)-OCN*t*Bu metal complexes.

In the presence of excess *t*BuNC, a benzene solution of **9** at 25 °C was observed to slowly produce *t*BuNCO with concomitant formation of a new product that was tentatively identified as being [Cp*Mo{N(*i*Pr)C(Me)N(*i*Pr)}{CN(*t*Bu)}$_2$] (**11**) on the basis of solution NMR characterization (see Scheme 2). Due to poor thermal stability displayed by **11** upon isolation, no further analytical or structural characterization of this compound was attempted.[9] On the other hand, even in the presence of a large excess of *t*BuNC, **10** does not engage in a similar reductive elimination of *t*BuNCO and a van't Hoff analysis conducted at 25 °C by ^{1}H NMR spectroscopy for the reversible equilibrium of **10** converting to **8** and two equivalents of *t*BuNC provided the thermodynamic parameters: $\Delta H^\circ = +19.9(7)$ kcal mol^{-1}; $\Delta S^\circ = +65.9(3)$ e.u; ΔG° (at 298 K) $= +0.6(7)$ kcal mol^{-1}.[9]

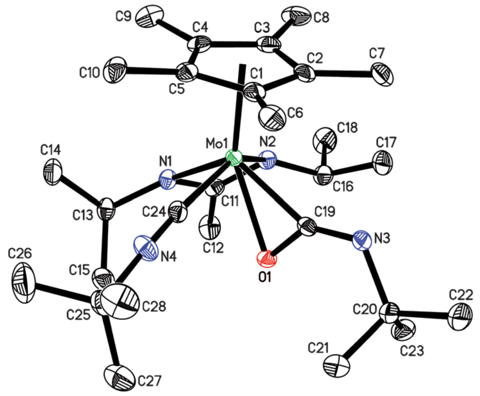
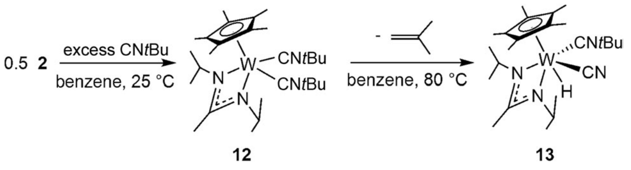


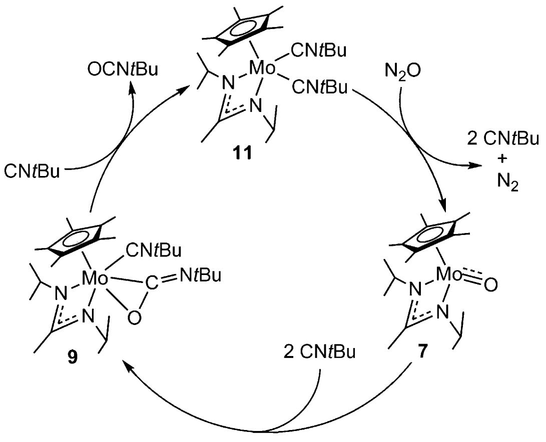
Figure 2. Molecular structure (30% thermal ellipsoids) of **9**. Hydrogen atoms have been removed for clarity. Selected bond lengths [Å] and bond angles [°]: Mo1–O1 2.1561(16), Mo1–C19 2.060(2), C19–O1 1.307(3), C19–N3 1.270(3); Mo1-C19-N3 147.81(18), Mo1-C19-O1 76.01(13), O1-C19-N3 136.1(2), Mo1-O1-C19 67.98(13), C19-N3-C20 118.6(2).

The corresponding W^{II} bis(isocyanide) complex, [Cp*W{N(*i*Pr)C(Me)N(*i*Pr)}{CN(*t*Bu)}$_2$] (**12**), was prepared through treatment of the μ-N_2 complex **2** with an excess of *t*BuNC, but as Scheme 3 reveals, this compound also proved to be thermally unstable in solution by slowly converting to [Cp*W(H)(CN){N(*i*Pr)C(Me)N(*i*Pr)}{CN(*t*Bu)}] (**13**) [^{1}H NMR (400 MHz, [D$_6$]benzene, 25 °C): $\delta = 11.01$ ppm ($^1J(^{183}W$-$^1H) = 13.4$ Hz)]. Compound **13** was isolated in modest yield after heating a solution of **12** to 80 °C for an extended period of time and its solid-state structure was established by single-crystal X-ray analysis.[9] Based on literature precedent, it is reasonable to conclude that the **12**→**13** transformation involves δ-hydrogen atom transfer to metal that presumably proceeds with elimination of isobutene according to Scheme 3.[22]



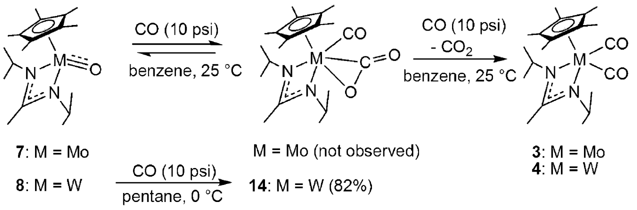
Scheme 3. Decomposition through δ-hydrogen atom transfer to metal.

Observation of OAT between a molecularly discrete metal oxo complex and an isocyanide leading to formation of an isocyanate product is quite rare, and, to the best of our knowledge, no catalytic equivalent of this process has ever been demonstrated for an early transition metal system.[5,23] Indeed, literature precedent would appear to argue against the probability of success in achieving such a goal for the Group 6 metals. More specifically, Mayer and co-workers[10c] have previously shown that the oxo, isocyanide complexes, $[M(O)\{CN\text{-}p\text{-}Tol\}Cl_2(PMe_3)_2]$ (M = Mo and W), show no propensity in solution for engaging in reversible formation and elimination of OCN-*p*-Tol. Furthermore, it is well known that the nucleophilic character of the oxo moiety in the Group 6 metallocene derivatives, $[Cp_2M(O)]$ (M = Mo and W), facilitates a variety of [2+2] cycloadditions with isocyanates and other electrophiles.[18] Thus, the key to establishing the catalytically competent OAT cycle for the oxidation of isocyanides to isocyanates that is presented in Scheme 4 was the discovery that, in solution, both **7** and **8** are unreactive towards an excess of *t*BuNCO; presumably due to a decreased nucleophilicity of the oxo group that is associated with a higher M–O bond order (see above). More specifically, starting with a 5:1 ratio of *t*BuNC to **11** (prepared in situ from **1**) in [D$_6$]benzene solution at 25 °C under an atmosphere of N_2O (10 psi) within a sealed NMR tube, ^{1}H NMR spectroscopy clearly showed the clean and steady production of multiple equivalents of *t*BuNCO.[9] Although the turnover frequency of this process is quite low under these conditions (ca. 1 equiv per week), the use of higher temperatures led to production of several as-of-yet-unidentified side-products. Notably, during catalysis, the only major species observed in solution by NMR spectroscopy is the η^2-OCN*t*Bu complex **9**; with only a trace of **11**, and none of **7**, being evident. Furthermore, no analogous catalytic OAT cycle occurs starting with the tungsten oxo complex **8** under identical conditions. Efforts to extend this catalytic OAT process to other classes of isocyanides and to optimize turnover frequencies under different reaction conditions are currently in progress.



Scheme 4. Catalytic oxidation of isocyanide to isocyanate with N_2O.

Under an atmosphere of CO (10 psi) in benzene solution at 25 °C, both **7** and **8** are slowly converted to the corresponding bis(carbonyl) complexes **3** and **4**, respectively, over a period of several days according to Scheme 5. When ^{13}CO (99 %) was employed, following the course of these reactions by ^{13}C NMR spectroscopy showed co-production of $^{13}CO_2$. In the case of the molybdenum system, which undergoes quantitative conversion of **7** to **3**, no ^{1}H or ^{13}C resonances that could be assigned to intermediates were ever observed. In contrast, for the tungsten system, NMR spectroscopy revealed the presence of a dynamic reversible process that partially converts **8** into a single new complex under 10 psi pressure of CO. Although initial attempts to isolate this new compound were thwarted by the reversible nature of this transformation, pressurizing a pentane solution of **8** with CO in a sealed Schlenk tube, followed by slow crystallization of the resulting mixture at 25 °C, provided an 82 % yield of pentane-insoluble $[Cp^*W(\eta^2\text{-}CO_2)(CO)\{N(i\text{Pr})C(Me)N(i\text{Pr})\}]$ (**14**) according to Scheme 5. Fortunately, this selective crystallization from pentane provided single-crystals of **14** that were suitable for crystallographic analysis and Figure 3 presents the solid-state molecular structure of this complex, along with selected geometric parameters.[9] Structural information for η^2-CO_2 complexes of the early transition metals is sparse as examples for this class of compound remain very rare.[24] Finally, a solid-state (KBr) infrared spectrum for **14** displayed ν_{CO} at 1952 and 1686 cm^{-1}.



Scheme 5. Carbonylation of terminal metal oxo complexes.

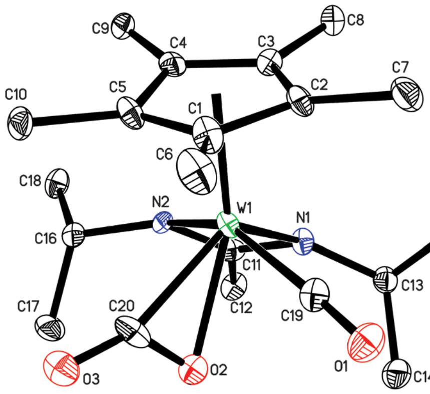
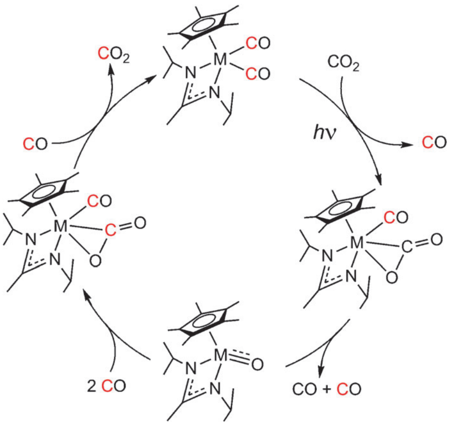


Figure 3. Molecular structure (30% thermal ellipsoids) of **14**. Hydrogen atoms have been removed for clarity. Selected bond lengths [Å] and bond angles [°]: W1–O2 2.165(9), W1–C20 2.079(12), C20–O2 1.335(17), C20–O3 1.185(16); W1-C20-O3 156.0(12), W1-C20-O2, 75.2(7), O3-C20-O2 128.7(12).

Although the bis(carbonyl) complexes **3** and **4** have formal M^{II} oxidation states, in solution, no thermal reaction occurs with either N_2O or CO_2.[25] It was reasoned, however, that photolytic elimination of a CO ligand might suffice to open a coordination site for complexation of CO_2, and subsequently, for generation of the corresponding terminal metal oxo complexes, **7** and **8**, through elimination of CO from the intermediate η^2-CO_2 species. Indeed, under an atmosphere of CO_2 (10 psi), photolysis of a [D$_6$]benzene solution of **3** within a Pyrex NMR tube using a Rayonet carousel of medium pressure Hg lamps did lead to conversion to **7** as followed by NMR spectroscopy.[9] Photoconversion of **4**→**8** occurred in similar fashion, but here, diagnostic NMR resonances for the intermediate η^2-CO_2 complex **14** were observed.[9]

Extension of the results presented above suggested the possibility of achieving a photocatalytic degenerate OAT cycle that proceeds according to Scheme 6. In practice, within a Teflon-valve-equipped Pyrex NMR tube, a premixed 1:1 ratio of ^{13}CO (99 %) and CO_2 was introduced at 10 psi to a [D$_6$]benzene solution of **3** (or **4**) containing a known amount of 1,2,5,6-tetramethylbenzene (durene) as an internal standard for ^{1}H NMR spectra. Photolysis of the reaction mixture using the Rayonet apparatus was then conducted with ^{13}C NMR spectra of the reaction mixture being taken periodically. Figure 4 presents selected partial ^{13}C NMR spectra showing the results of separate experiments starting with **3** and **4**. Gratifyingly, as is apparent, equilibration of the initial ^{13}CO and CO_2 occurs with time to produce a new gas mixture now containing both ^{13}CO and $^{13}CO_2$. It is also intriguing to note that, qualitatively, the tungsten system has a higher relative turnover frequency than the molybdenum system under identical conditions; potentially due to the higher rate of formation of **8** in the case of tungsten.



Scheme 6. Photocatalytic degenerate OAT between CO and CO_2. The red color represents ^{13}C (99 %)-labeled substrate.

In summary, the results presented here document the ability of a Group 6 M^{II}/M^{IV} couple to mediate thermal and photolytic OAT catalysis based on N_2O and CO_2 as chemical oxidants. Importantly, the supporting monocyclopentadienyl, monoamidinate (CpAm) ligand metal environment is key for modulating the nucleophilicity of the M^{IV} terminal oxo group that permits compatibility with products that are electrophilic in nature. The CpAm ligand set is also capable of establishing the required fine thermodynamic balance for OAT to, and from, a Group 6 metal center—which is critical for the success of catalytic nondegenerate and degenerate OAT-based transformations. In this regard, the small bite angle of the amidinate group might be a key structural element that provides steric access to the metal center for coordination of multiple equivalents of π-acceptor ligands that can contribute to the breaking of strong M^{IV} oxo bonds (cf, compounds **9**, **10** and **14**).[26] We are now presently investigating the full scope and limitations of catalytic and stoichiometric OAT processes employing N_2O and CO_2 as supported by CpAm Group 6 metal complexes.

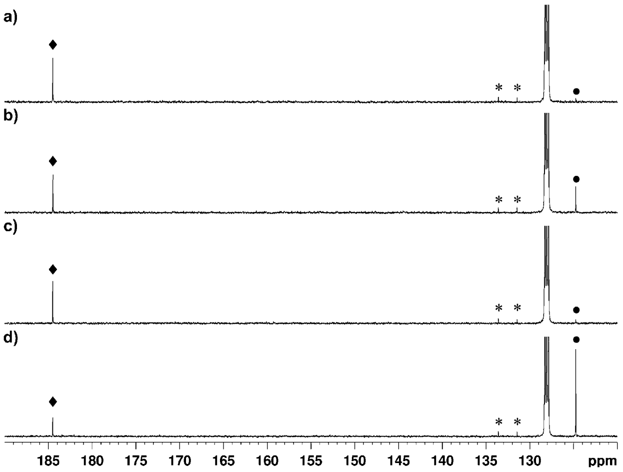


Figure 4. Partial ^{13}C NMR spectra for the photocatalytic equilibration of ^{13}CO and CO_2 using **3** after a) 0 h and b) 18 h, and for **4** after c) 0 h and d) 18 h. ^{13}C resonances are labeled as CO (◆), CO_2 (●) and durene (*) (internal standard). The large unlabeled ^{13}C resonances are for the [D$_6$]benzene solvent.

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[1] G. Henrici-Olivé, S. Olivé, *Angew. Chem.* **1974**, *86*, 1–12; *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 29–38.

[2] a) W. B. Tolman, *Angew. Chem.* **2010**, *122*, 1034–1041; *Angew. Chem. Int. Ed.* **2010**, *49*, 1018–1024; b) K. H. Theopold, O. M. Reinaud, S. Blanchard, S. Leelasubcharoen, A. Hess, S. Thyagarajan, *ACS Symp. Ser.* **2002**, *823*, 75–85; c) X. Yin, J. R. Moss, *Coord. Chem. Rev.* **1999**, *181*, 27–59.

[3] *Ullmann's Encyclopedia of Industrial Chemistry*, 7th ed. (Ed.: B. Elvers), Wiley-VCH, Weinheim, **2011**.

[4] a) R. H. Holm, E. I. Solomon, A. Majumdar, A. Tenderholt, *Coord. Chem. Rev.* **2011**, *255*, 993–1015; b) C. Lorber, J. P. Donahue, C. A. Goddard, E. Nordlander, R. H. Holm, *J. Am. Chem. Soc.* **1998**, *120*, 8102–8112; c) J. P. Donahue, C. R. Goldsmith, U. Nadiminti, R. H. Holm, *J. Am. Chem. Soc.* **1998**, *120*, 12869–12881.

[5] For late transition metal and noble metal catalyzed oxidation of RNC to RNCO employing O_2 or CO_2 as the oxidants, see: a) S. Otsuka, A. Nakamura, Y. Tatsuno, *J. Chem. Soc. Chem. Commun.* **1967**, 836; b) S. Németh, L. I. Simandi, *Inorg. Chim. Acta* **1982**, *64*, L21–L22; c) D. L. DeLaet, R. Del Rosario, P. E. Fanwick, C. P. Kubiak, *J. Am. Chem. Soc.* **1987**, *109*, 754–758; d) J. Wu, P. E. Fanwick, C. P. Kubiak, *Organometallics* **1987**, *6*,

1805 – 1807; e) T. J. Deming, B. M. Novak, *J. Am. Chem. Soc.* **1993**, *115*, 9101 – 9011; f) R. J. Angelici, *J. Organomet. Chem.* **2008**, *693*, 847 – 856, and references therein.

[6] For chemical turnover of a W^{II}/W^{IV} OAT cycle, see: U. Jayarathne, P. Chandrasekaran, H. Jacobsen, J. T. Mague, J. P. Donahue, *Dalton Trans.* **2010**, *39*, 9662 – 9671, and ref. [10].

[7] P. P. Fontaine, B. L. Yonke, P. Y. Zavalij, L. R. Sita, *J. Am. Chem. Soc.* **2010**, *132*, 12273 – 12285.

[8] a) M. R. Smith III, P. T. Matsunaga, R. A. Andersen, *J. Am. Chem. Soc.* **1993**, *115*, 7049 – 7050; b) W. A. Howard, M. Waters, G. Parkin, *J. Am. Chem. Soc.* **1993**, *115*, 4917 – 4918.

[9] Experimental details are provided in the Supporting Information.

[10] a) F. M. Su, C. Cooper, S. J. Geib, A. L. Rheingold, J. M. Mayer, *J. Am. Chem. Soc.* **1986**, *108*, 3545 – 3547; b) J. C. Bryan, S. J. Geib, A. L. Rheingold, J. M. Mayer, *J. Am. Chem. Soc.* **1987**, *109*, 2826 – 2828; c) K. A. Hall, J. M. Mayer, *J. Am. Chem. Soc.* **1992**, *114*, 10402 – 10411.

[11] We wish to acknowledge the contribution of Wesley Farrell who prepared and isolated an analytically pure and crystalline sample of **7** suitable for single-crystal X-ray analysis.

[12] B. Cordero, V. Gomez, A. E. Platero-Prats, M. Reves, J. Escheverria, E. Cremades, F. Barragan, S. Alvarez, *Dalton Trans.* **2008**, 2832 – 2838.

[13] K. Iijima, S. Shibata, *Chem. Lett.* **1972**, 1033 – 1036.

[14] a) N. D. Silavwe, M. Y. Chiang, D. R. Tyler, *Inorg. Chem.* **1985**, *24*, 4219 – 4221; b) N. D. Silavwe, M. R. M. Bruce, C. E. Philbin, D. R. Tyler, *Inorg. Chem.* **1988**, *27*, 4669 – 4676; c) G. T. Baxley, A. A. Avey, T. M. Aukett, D. R. Tyler, *Inorg. Chim. Acta* **2000**, *300*, 102 – 112.

[15] L. Luo, G. Lanza, I. L. Fragala, C. L. Stern, T. J Marks, *J. Am. Chem. Soc.* **1998**, *120*, 3111 – 3122.

[16] a) A. J. Bridgeman, L. Davis, S. J. Dixon, J. C. Green, I. N. Wright, *J. Chem. Soc. Dalton Trans.* **1995**, 1023 – 1027; b) J. R. Galsworthy, J. C. Green, M. L. H. Green, M. Müller, *J. Chem. Soc. Dalton Trans.* **1998**, 15 – 20.

[17] a) W. A. Nugent, B. L. Haymore, *Coord. Chem. Rev.* **1980**, *31*, 123 – 175; b) W. A. Nugent, J. M. Mayer, *Metal-Ligand Multiple Bonds*, Wiley-Interscience, New York, **1988**.

[18] a) M. L. H. Green, A. H. Lynch, M. G. Swanwick, *J. Chem. Soc. Dalton Trans.* **1972**, 1445 – 1447; b) P. Jernakoff, G. L. Geoffroy, A. L. Rheingold, S. J. Geib, *J. Chem. Soc. Chem. Commun.* **1987**, 1610 – 1611; c) R. S. Pilato, G. L. Geoffroy, A. L. Rheingold, *J. Chem. Soc. Chem. Commun.* **1989**, 1287 – 1288; d) R. S. Pilato, D. Rubin, G. L. Geoffroy, A. L. Rheingold, *Inorg. Chem.* **1990**, *29*, 1986 – 1990; e) R. S. Pilato, C. E. Housmekerides, P. Jernakoff, D. Rubin, G. L. Geoffroy, A. L. Rheingold, *Organometallics* **1990**, *9*, 2333 – 2341.

[19] a) G. Parkin, J. E. Bercaw, *Polyhedron* **1988**, *7*, 2053 – 2082; b) G. Parkin, R. E. Marsh, W. P. Schaefer, J. E. Bercaw, *Inorg. Chem.* **1988**, *27*, 3262 – 3264; c) G. Parkin, J. E. Bercaw, *J. Am. Chem. Soc.* **1989**, *111*, 391 – 393; d) G. Parkin, *Prog. Inorg. Chem.* **1998**, *47*, 1 – 165; e) J. H. Shin, D. G. Churchill, B. M. Bridgewater, K. Pang, G. Parkin, *Inorg. Chim. Acta* **2006**, *359*, 2942 – 2955.

[20] P. Braunstein, D. Nobel, *Chem. Rev.* **1989**, *89*, 1927 – 1945.

[21] F. Minzoni, C. Pelizzi, G. Predieri, *J. Organomet. Chem.* **1982**, *231*, C6-C8.

[22] a) C. M. Giamdomenico, L. H. Hanau, S. J. Lippard, *Organometallics.* **1982**, *1*, 142 – 148; b) W. D. Jones, W. P. Kosar, *Organometallics* **1986**, *5*, 1823 – 1829; c) W. A. Herrmann, B. Menjón, E. Herdtweck, *Organometallics* **1991**, *10*, 2134 – 2141.

[23] Y. Kim, J. Gallucci, A. Wojcicki, *J. Am. Chem. Soc.* **1990**, *112*, 8600 – 8602.

[24] a) P.-F. Fu, M. A. Khan, K. M. Nicholas, *J. Am. Chem. Soc.* **1992**, *114*, 6579 – 6580; b) P.-F. Fu, M. A. Khan, K. M. Nicholas, *J. Organomet. Chem.* **1996**, *506*, 49 – 59; c) T.-F. Wang, C.-C. Hwu, C.-W. Tsai, K.-J. Lin, *Organometallics* **1997**, *16*, 3089 – 3090.

[25] G. Fachinetti, C. Floriani, A. Chiesi-Villa, C. Guastini, *J. Am. Chem. Soc.* **1979**, *101*, 1767 – 1775.

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