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Communications

Double Group Transfer Reactions of an Unsaturated Tantalum Methylidene Complex with Pyridine *N*-Oxides

Sarah M. Mullins, Robert G. Bergman,* and John Arnold*

Department of Chemistry, University of California, Berkeley, California 94720-1460

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*Summary: The electrophilic nature of the benzamidinate tantalum methylidene complex [TolC(NSiMe$_3$)$_2$]$_2$Ta(CH$_2$)CH$_3$ (**1**) allows for reactivity with pyridine N-oxides, which leads to the formation of the tantalum oxo complex [TolC(NSiMe$_3$)$_2$]$_2$Ta(O)CH$_3$ (**5**) and methylpyridines; treatment of **1** with the related nitrone species N-tert-butyl-α-phenylnitrone leads to overall different products. Mechanistic studies show the reactions proceed via regioselective methylene group transfer to the pyridine N-oxides.*

Metal−ligand multiply bonded species (M = X; X = CR$_2$, NR, O, S) are known to participate in a wide range of important atom and group transfer reactions. Cytochrome P450, for example, hydroxylates alkanes and epoxidizes olefins via an Fe═O intermediate.[1] Metal carbene metathesis reactions may be utilized to transfer a CR$_2$ group to unsaturated organic substrates (carbonyls, nitriles, alkenes, alkynes).[2,3] However, examples of CH$_2$ insertion into C−H bonds to yield saturated products are rare.[4−7] We now describe an unprecedented double group transfer reaction of [TolC(NSiMe$_3$)$_2$]$_2$Ta(CH$_2$)CH$_3$ (**1**)[8] in which pyridine *N*-oxides are simultaneously deoxygenated and regioselectively methylated with concomitant formation of a novel amidinate tantalum oxo complex. Reaction of **1** with nitrones, which are structurally similar to pyridine *N*-oxides, also occurs but yields different overall products. These results are markedly different from those obtained using the related, but electronically saturated, tantalum alkylidene complex Cp$_2$Ta(CH$_2$)CH$_3$.

No reaction was observed when the nucleophilic[9] tantalum methylidene complex **1** was treated with weak oxidants such as styrene oxide and triphenylphosphine oxide.[10] In contrast, **1** reacted with 1 equiv of pyridine *N*-oxide (**2a**) at room temperature to form the tantalum oxo complex [TolC(NSiMe$_3$)$_2$]$_2$Ta(O)CH$_3$ (**5**) and 2-methylpyridine[11] (**6a**) quantitatively by NMR integration vs trimethoxybenzene internal standard (eq 1). The methylidene complex also reacted quantitatively with 1 equiv of 2-methylpyridine *N*-oxide (**2b**) to form 2,6-dimethylpyridine[11] (**6b**) and oxo complex **5**. In these reactions, methylation occurs regioselectively at the unsubstituted ortho position in each pyridine *N*-oxide. The reaction with 2-methylpyridine *N*-oxide is significantly slower than that with the unsubstituted pyridine *N*-oxide

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[1] Masanori, S.; Roach, M. P.; Coulter, E. D.; Dawson, J. H. *Chem. Rev.* **1996**, *96*, 1.

[2] Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98.

[3] Schrock, R. R. *Science* **1983**, *219*, 13.

[4] Gunnoe, T. B.; White, P. S.; Templeton, J. L.; Casarrubios, L. *J. Am. Chem. Soc.* **1997**, *119*, 3171.

[5] Doyle, M. *Chem. Rev.* **1986**, *86*, 919.

[6] Doyle, M. P.; Forbes, D. C. *Chem. Rev.* **1998**, *98*, 911.

[7] Doyle, M. P.; Protopopova, M. N. *Tetrahedron* **1998**, *54*, 7919.

[8] The synthesis of **1** was originally reported in: Dawson, D. Y., Arnold, J. *Organometallics* **1997**, *16*, 1113.

[9] The methylidene complex **1** reacts at the CH$_2$ carbon with a variety of electrophiles, such as CH$_3$I and Me$_3$SiOTf.

[10] Monitoring the reactions of **1** with N$_2$O, trimethylamine *N*-oxide, morpholine *N*-oxide, or nitrosobenzene by ^{1}H NMR spectroscopy indicates the formation of multiple unidentified products.

[11] The identities of the methylpyridines were confirmed by comparison of the volatile materials (vacuum-transferred from the reaction mixture) to commercially available samples by ^{1}H, ^{13}C{^{1}H} NMR, and GC-MS.

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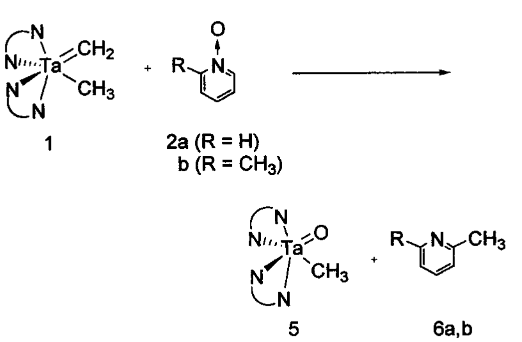


(1)

(minutes vs instantaneous). No reaction was observed under similar conditions with the disubstituted complexes 2,6-dimethylpyridine *N*-oxide and 2,6-dichloropyridine *N*-oxide. For comparison, no reaction was detected between $Cp_2Ta(CH_2)CH_3$ and pyridine *N*-oxide.

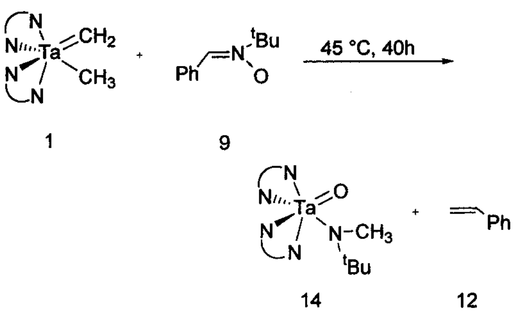
The tantalum oxo complex **5** was characterized by ^1H and $^{13}C\{^1H\}$ NMR and IR spectroscopy and X-ray crystallography. The IR spectrum of **5** revealed a strong stretch at 922 cm^{-1}, which is in the range reported for terminal Ta−O multiple bonds (850−1000 cm^{-1}).[12−15] The X-ray structure of **5**[16] shows a distorted-octahedral coordination geometry about tantalum and confirms the presence of a terminal oxo functionality (Figure 1). There is significant metal disorder (modeled as two tantalum atoms with partial occupancies of 77 and 23%, respectively; see Supporting Information). However, at 1.76 Å, the bond length for the major occupancy tantalum atom to the oxygen atom (Ta1−O1) is consistent with other data reported for Ta−O multiple bonds.[17]

The most reasonable mechanisms for these transformations are illustrated in Scheme 1. In mechanism **A**, prior coordination of the *N*-oxide oxygen atom to the tantalum center, leading to **3,** followed by proton transfer from the ortho C−H position of the pyridine *N*-oxide to the methylidene carbon forms dimethyl tantalum species **4**. Transfer of either Ta−methyl group affords the observed methylated pyridine **6**. Mechanism **B** also begins with *N*-oxide coordination, giving **3**, but is followed by formation of a five-membered metallacycle intermediate (**7**). A 1,2-hydride shift to the methylene moiety with concomitant cleavage of the N−O bond forms the methyl group of pyridine **6** and yields the observed tantalum product **5**. In a third possible mechanism **C**, methylidene attack upon the electrophilic[18] ortho carbon of the pyridine *N*-oxide (**8**), followed by oxygen coordination to the tantalum, forms the five-membered metallacycle **7** and the reaction continues as in mechanism **B**.

No intermediates are observed in the reaction, as followed by UV, IR, or ^1H NMR spectroscopy. Deuterium labeling studies were therefore undertaken to help distinguish these mechanistic alternatives. The reaction of methylidene complex **1** with ortho-deuterated pyridine-d_2 *N*-oxide yielded exclusively 2-(methyl-d_1)-6-d-pyridine (94% conversion by NMR integration vs trimethoxybenzene internal standard). Also, the reaction of **1** with 2-(methyl-d_3)-6-d-pyridine *N*-oxide yields exclusively 2-(methyl-d_3)-6-(methyl-d)pyridine (96%). Analysis of the vacuum-transferred volatile materials by GC-MS shows parent ions at m/z 95 and 111, corresponding to the expected methyl and dimethylpyridine products, respectively. A 1:1:1 triplet at 2.40 ppm, indicative of the CH_2D group, is present in both the ^1H and $^{13}C\{^1H\}$ NMR spectra for both partially deuterated methylpyridine products.

The deuterium labeling studies clearly suggest that the reaction proceeds by methylene rather than methyl transfer; i.e., mechanism **A** is not operative since methyl migration from **4** would be expected to transfer CH_3 and CH_2D at approximately the same rate. Given the highly electrophilic nature of the tantalum atom in **1**,[19] we believe formation of a tantalum/*N*-oxide adduct (mechanism **B**) is likely. This would also activate the ortho position of the pyridine *N*-oxide toward nucleophilic attack by the methylidene, as has been observed in the reactions of pyridine *N*-oxides with organic substrates.[20] The requirement of pyridine *N*-oxide coordination may help explain why pyridine *N*-oxide reacts with **1** but not with the electronically saturated analogue $Cp_2Ta(CH_2)CH_3$.

Nitrones (RR′C=N(O)R″) are structurally similar to pyridine *N*-oxides and are known to be useful intermediates in the synthesis of complex organic molecules.[21] Consequently, we were interested in whether the methylene transfer reaction described above would also occur with nitrones. Although no reaction was observed between **1** and *N*-*tert*-butyl-α-phenylnitrone (**9**) under ambient conditions, heating to 45 °C for 40 h afforded styrene[22] and a single new organometallic product (98% and 97% yields, respectively, by NMR integration vs trimethoxybenzene internal standard) (eq 2). Characterization of the organometallic product by ^1H, $^{13}C\{^1H\}$ NMR, IR, and mass spectroscopic techniques is consis-



(2)

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[12] Nugent, W. A.; Mayer, J. M. *Metal−Ligand Multiple Bonds*; Wiley: New York, 1988.

[13] LaPointe, R. E.; Wolczanski, P. T.; Mitchell, J. *J. Am. Chem. Soc.* **1986**, *108*, 6382.

[14] Deutscher, R. L.; Kepert, D. L. *Inorg. Chim. Acta* **1970**, *4*, 645.

[15] van Asselt, A.; Burger, B. J.; Gibson, V. C.; Bercaw, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 5347.

[16] Crystallographic data for **5**: colorless crystals, triclinic, $P\bar{1}$, $Z = 2$, $a = 10.6007(1)$ Å, $b = 11.1973(1)$ Å, $c = 16.8553(2)$ Å, $\alpha = 100.109(1)°$, $\beta = 94.627(1)°$, $\gamma = 106.974(1)°$, $R = 0.041$, GOF = 2.63.

[17] (a) Parkin, G.; van Asselt, A.; Leahy, D. J.; Whinnery, L.; Hua, N. G.; Quan, R. W.; Henling, L. M.; Schaefer, W. P.; Santarsiero, B. D.; Bercaw, J. E. *Inorg. Chem.* **1992**, *31*, 82. (b) For related Nb complexes see: Stewart, P. J.; Blake, A. J.; Mountford, P. *Inorg. Chem.* **1997**, *36*, 1982.

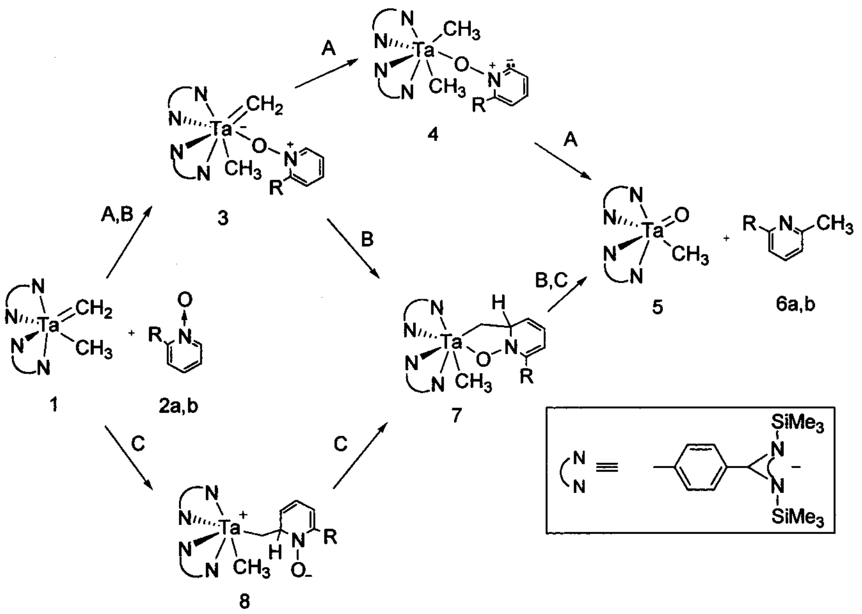
[18] Ochiai, E. *Aromatic Amine Oxides*; Elsevier: Amsterdam, 1967.

[19] The anionic bis(trimethylsilyl)benzamidinate ligand is generally considered to be a four-electron donor for early transition metals. Consequently, the electronic unsaturation of **1** (14e) allows formation of the adduct, while its saturated analogue $Cp_2Ta(CH_2)CH_3$ (18e) does not. This is consistent with the reactivity of many Schrock carbenes, in which formation of an adduct prior to reaction occurred only for carbene complexes with formal electron counts lower than 18e.

[20] Katritzky, A. R.; Lagowski, J. M. *Chemistry of the Heterocyclic N-Oxides*; Academic Press: New York, 1971; p 258.

[21] Breuer, E. *Nitrones, Nitronates and Nitroxides*; Wiley: Chichester, U.K., 1989; pp 139−311.

Scheme 1



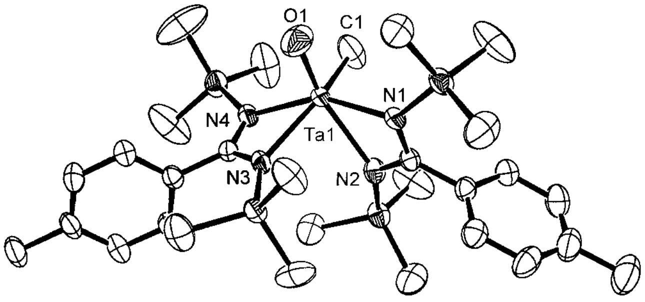
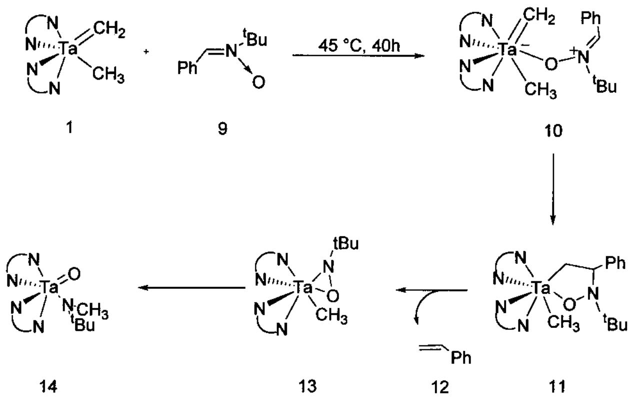


Figure 1. ORTEP diagram of **5** with H atoms and Ta2 omitted for clarity.

tent with its formulation as [TolC(NSiMe$_3$)$_2$]$_2$Ta(O)(N^{t}BuMe) (**14**). In addition, methanolysis of the isolated organometallic product yields *tert*-butylmethylamine (>99% yield), as determined by ^{1}H NMR and GC-MS, consistent with the postulated structure.

We propose that the nitrone reaction is initiated in a manner analogous to the pyridine *N*-oxide reaction, with the oxide moiety first forming a Lewis acid–base adduct at the Ta center (**10**, Scheme 2). The carbene may then attack the carbon–nitrogen double bond to form a cycloadduct (**11**, analogous to **7** in Scheme 1). Alkene elimination affords the tantalum η^2-nitrosobutane complex **13**, which rearranges via methyl group migration from tantalum to nitrogen to give the isolated complex **14**.[23]

Scheme 2



In conclusion, we have observed novel atom transfer reactions between **1** and pyridine *N*-oxides or nitrones, in which Ta–oxo and organic products with new C–C bonds are formed. The enhanced electrophilicity of the bis(trimethylsilyl)benzamidinate system **1** leads to new reaction pathways that are unavailable in the analogous Cp-containing complexes. Further investigation of the mechanisms of these reactions is ongoing.

Acknowledgment. We acknowledge the assistance of Dr. Ryan Powers in the solution of the X-ray crystal structure of [TolC(NSiMe$_3$)$_2$]$_2$Ta(O)CH$_3$. We are grateful to NSF Grant No. CHE-9633374 (to R.G.B.) and the donors of the Petroleum Research Fund, administered by the American Chemical Society (to J.A.), for financial support.

Supporting Information Available: Text giving analytical data for all compounds and tables of crystal data and structure solution and refinement details, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[22] The identity of the styrene was confirmed by comparison of the volatile materials (vacuum-transferred from the reaction mixture) to a commercially available sample by ^{1}H and ^{13}C{^{1}H} NMR and GC-MS.

[23] The imine, tBuNCPh(Me), and **5** do not react at 45 °C, ruling out a mechanism directly analogous to the pyridine *N*-oxide example, where **5** and tBuNCPh(Me) are initially formed but react further to eventually yield **14** and styrene.