Inorganic Chemistry

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Synthesis and Reactivity of a Transition Metal Complex Containing Exclusively TEMPO Ligands: Ni(η^2-TEMPO)$_2$

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Supporting Information

ABSTRACT: The reaction of Ni(COD)$_2$ with two equivalents of the TEMPO radical at 68 °C affords the 16 e$^-$ "bow-tie" complex Ni(η^2-TEMPO)$_2$, **1**, in 78% yield. Compound **1** reacts with *tert*-butyl isocyanide and phenylacetylene at room temperature to yield the 16 e$^-$ distorted square planar nickel complexes Ni(η^2-TEMPO)(η^1-TEMPO)(CN^{t}Bu), **2**, and Ni(η^2-TEMPO)(η^1-TEMPO*H*)(CCPh), **4**, respectively. The facile reactivity of **1** is aided by the transition of the TEMPO ligand from an η^2 to η^1 binding mode. Complex **4** is an unusual example of hydrogen atom transfer from phenylacetylene to a coordinated TEMPO ligand.

The TEMPO (2,2,6,6-tetramethylpiperidine-N-oxyl) radical has received much industrial interest in both the past and present day.[1] It plays a major role in polymerization initiation reactions,[2] as well as generating paramagnetic compounds possessing extremely high spins.[3] The free radical also shows high proficiency in oxidation reactions[1,4] and is used as spin-probes/labels in ESR studies to understand the environment in complex chemical systems.[5] However, the coordination chemistry of this TEMPO radical and its subsequent organometallic complexes have been much less thoroughly investigated. Several existing metal-TEMPO complexes exhibit interesting catalytic abilities, including alcohol oxidation, which is not surprising when the many mesomeric forms of TEMPO binding are considered.[6] It has been shown that the complex Cu(Cl)$_2$(TEMPO) quantitatively oxidizes benzyl alcohol to benzaldehyde,[6b] and it was later shown that the complex Cu(Bipy)(Br)$_2$ catalyzes the conversion of benzyl alcohol to benzaldehyde with use of cocatalytic TEMPO and KOH.[6c,d]

While there are a number of transition metal−TEMPO complexes, where the TEMPO ligand is bound to the metal center via an η^1-TEMPO coordination mode[7] as well as in an η^2-TEMPO fashion,[8] there is only one structural example of a metal−TEMPO complex that contains solely TEMPO as the ligand system. This was observed in the complex [(η^1-ONC$_5$H$_6$Me$_4$)$_2$Sm(μ-η^1:η^2-ONC$_5$H$_6$Me$_4$)]$_2$, which contains both η^1- and η^2-TEMPO ligands.[9] The versatility of the binding mode of the TEMPO ligand (η^1 versus η^2) was also very elegantly demonstrated in a series of titanium complexes.[10]

We now wish to report the first example of an unsaturated transition metal complex, Ni(η^2-TEMPO)$_2$, **1**, that is supported exclusively by η^2-TEMPO ligands and its subsequent reactions with *tert*-butyl isocyanide and phenylacetylene, which are assisted by the flexibility of the TEMPO ligand.

The new complex Ni(η^2-TEMPO)$_2$, **1**, was obtained in 78% yield from the reaction of Ni(COD)$_2$ with TEMPO in refluxing hexane (68 °C). The molecule was characterized crystallographically, see Figure 1. Compound **1** is a mononuclear nickel complex with two TEMPO ligands in the η^2-coordination mode. The molecule is crystallographically centrosymmetrical but overall has approximate C_{2h} symmetry. The N−Ni−O angle is 43.88(4)°. The nickel, nitrogen, and oxygen atoms all lie in the same plane to form a "bow-tie" type structure with the Ni atom in the center. The N−O bond distance of 1.4136(12) Å is longer than that found in free TEMPO [1.283(9) Å].[11] The geometry around the nitrogen atom is pyramidal [O1−N1−C5 = 110.83(9)°, O1−N1−C9 = 110.97(9)°, C5−N1−C9 = 116.59(9)°], and the Ni−N and Ni−O bond distances are short [Ni1−N1 = 1.9360(10) Å, Ni1−O1 = 1.8404(11) Å]. These structural parameters are consistent with the bidentate η^2-TEMPO coordination mode and formulation of a reduced TEMPO radical as a monoanionic TEMPO ligand. The oxidation state on the Ni can be considered to be formally Ni(II) with the Ni atom having a 16 electron configuration.

We have found that **1** reacts with *tert*-butyl isocyanide, CN^{t}Bu, at room temperature to afford the complex Ni(η^2-TEMPO)-(η^1-TEMPO)(CN^{t}Bu), **2**, in 90% yield. Compound **2** was also characterized by single crystal X-ray diffraction, see Figure 2. The overall molecular structure consists of the Ni atom bound to one η^2-TEMPO liagnd, an η^1-TEMPO ligand, and a CN^{t}Bu group in a distorted square-planar configuration.

The N−O bond distances [N1−O1 = 1.3850(10) Å and N2−O2 = 1.4354(10) Å] and the pyramidal geometry around the nitrogen atoms [O1−N1−C10 = 112.69(7)°, O2−N2−C19 = 108.66(7)°] suggests that both TEMPO ligands in this complex have been formally reduced to monoanionic TEMPO forms, with Ni formally in the +2 oxidation state with a 16 electron configuration. The ^{1}H NMR spectrum at room temperature consists of a series of broad overlapping resonances indicative of some dynamical processes occurring in solution. Raising the temperature continuously to 90 °C resulted in some sharpening of the peaks; however, as shown in Supporting Information Figure S1, some broadening remained even at that temperature. At temperatures above 90 °C, the complex decomposes. It is clear that some broadening and exchange occur at higher temperatures as well; however, the exact nature of the fluxional process remains unresolved and is beyond the scope of this report.

It can be anticipated that the addition of CN^{t}Bu to **1** would generate the 18 electron complex **3**, as shown in Figure 3, where

Received: April 9, 2011
Published: May 18, 2011

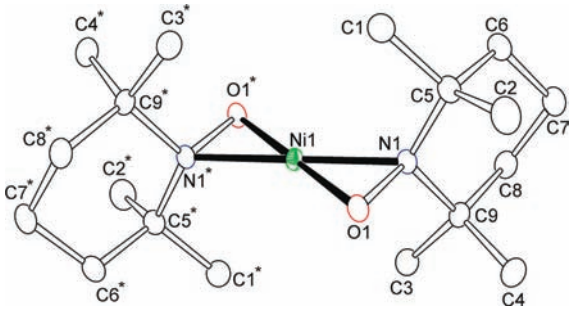


Figure 1. An ORTEP showing the molecular structure of Ni-(η^2-TEMPO)$_2$, **1**, with thermal ellipsoids set at 50% probability.

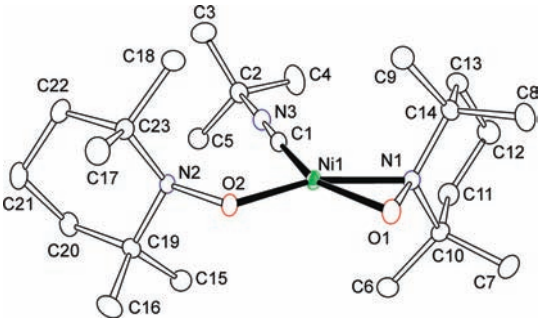


Figure 2. An ORTEP showing the molecular structure of Ni(η^2-TEMPO)-(η^1-TEMPO)(CN^{t}Bu), **2**, with thermal ellipsoids set at 50% probability.

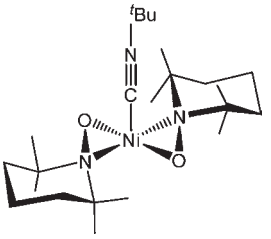


Figure 3. Proposed structure of **3**.

the TEMPO ligands remain η^2-coordinated to give a rectangular pyramidal type structure around Ni.

Perhaps the reason the structure as shown in Figure 3 does not form is due to steric crowding of the methyl groups of the piperidine ring about the metal center, in addition to Ni(II) preferring a 16 electron configuration. Examination of a space-filling model of **1** reveals that there is probably not enough space between the methyl groups of TEMPO in the region above and below the N1−O1−N1*−O1* plane for a CN^{t}Bu molecule to penetrate the ligand environment and approach the Ni atom, see Figure 4a. However, as seen in Figure 4b, there probably is a sufficient opening along the plane for a CN^{t}Bu to approach the metal center.

Additionally, structure **3** may be compared to Ni(II) porphyrins where one axial site is bonded by a ligand. A recent study has shown that coordination of the axial sites in Ni(II) porphyrins results in the Ni center undergoing a spin transition from low spin (singlet) to high spin (triplet), and furthermore the entropy for the formation of a five coordinate Ni(II) porphyrin complex is exceptionally large and negative.[12] The porphyrin ligand system also is a rigid framework about the Ni center. Thus, preferring to remain as 16 electron Ni, as a CN^{t}Bu molecule approaches along

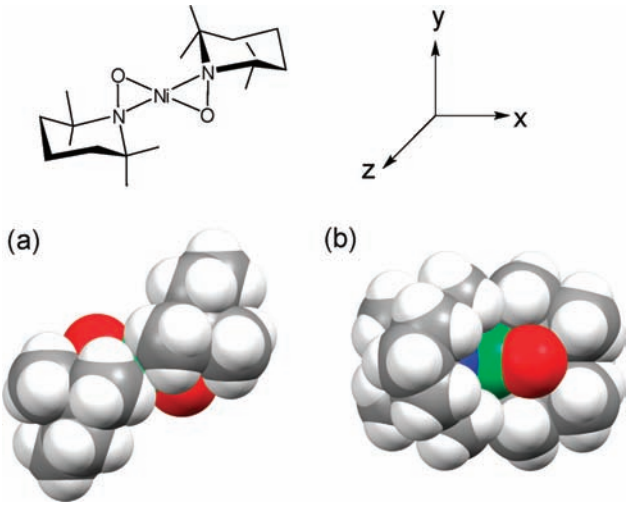


Figure 4. Space-filling model of the structure of **1**. (a) View down the C_2 (z) axis and (b) view down the xy plane. Atomic dimensions are the atomic van der Waals radii. The Ni atom is shown in green, O in red, N in blue, C in gray, and H in white.

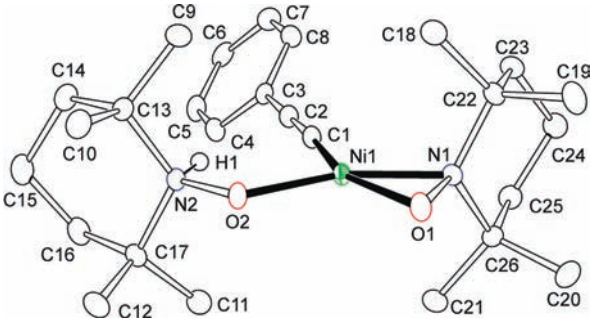


Figure 5. An ORTEP showing the molecular structure of Ni(η^2-TEMPO)(η^1-TEMPO*H*)(CCPh), **4**, with thermal ellipsoids set at 50% probability. Selected bond distances (Å) and angles (deg) are Ni1−O1 = 1.8868(7), Ni1−N1 = 1.8608(8), Ni1−O2 = 1.8927(7), Ni1−C1 = 1.8648(10), N1−O1 = 1.3869(10), N2−O2 = 1.4048(10), C1−C2 = 1.2205(14), N1−Ni1−O1 = 43.43(3), O1−N1−C22 = 112.57(7), O1−N1−C26 = 112.92(7), C22−N1−C26 = 118.21(7), O2−N2−C13 = 110.87(7), O2−N2−C17 = 110.52(7), C13−N2−C17 = 118.06(7).

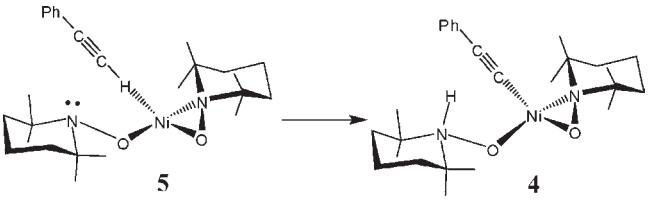
the N1−O1−N1*−O1* plane in **1**, one of the TEMPO ligands transforms to an η^1-TEMPO coordination mode serving as a two electron donor (−1 charge) ligand rather than a four electron donor (−1 charge) ligand in the η^2-TEMPO coordination mode.

While further exploring the reactivity of **1** with other donors, we were quite surprised to find that the reaction of **1** with phenylacetylene at room temperature yielded the complex Ni-(η^2-TEMPO)(η^1-TEMPO*H*)(CCPh), **4**, in 73% yield. The solid state structure of **4** is shown in Figure 5. Just like in **2**, complex **4** also adopts a distorted square-planar configuration around the Ni atom, but in place of the CN^{t}Bu group in **2**, there is a phenylacetylide group (η^1-C≡CPh) in **4**.

A ^{1}H NMR spectrum of **4** was recorded to establish the fate of the H atom from the phenylacetylene molecule. There was no evidence of a resonance in the hydride region; however, there was a resonance at 7.62 ppm with an appropriate integration of 1H. On the basis of the crystal structure data collected at 100 K, the H atom was located and refined satisfactorily on the atom N2, as

dx.doi.org/10.1021/ic2007342 |*Inorg. Chem.* 2011, 50, 5864–5866

Scheme 1. Proposed Formation for 4



shown in Figure 5. To confirm that the peak at 7.62 ppm in the ^{1}H NMR spectrum was indeed the H atom from phenylacetylene, we carried out the reaction of **1** with phenylacetylene-d_1 (99%). The proton NMR spectrum of **4**-d_1 showed all of the expected resonances for **4**, with the exception of the peak at 7.62 ppm, which was almost completely absent.

Compound **4** remains a 16 electron Ni(II) complex, with the η^1-TEMPO*H* ligand acting as a two electron donor neutral ligand. The η^1-TEMPO*H* ligand can be viewed as a monoanionic TEMPO that is now protonated at nitrogen, as in the tautomeric form of free TEMPO*H* (where H is bonded to O). This type of bonding mode for η^1-TEMPO*H* is quite rare in transition metal complexes, and there are only two other crystallographically characterized examples.[13] A recent theoretical study provides evidence for a similar transfer of hydrogen to TEMPO, where H atom abstraction by the nitrogen atom of TEMPO was possible for a copper−bipyridine−TEMPO catalyzed oxidation of alcohols.[14]

For the formation of **4** (see Scheme 1), a similar pathway involving a concerted mechanism may be proposed whereupon insertion of HCCPh results in one of the η^2-TEMPO ligands transitioning to an η^1-TEMPO mode, as shown in **5**. The η^1-TEMPO ligand now has a lone pair on the nitrogen that can act as a base abstracting the H atom of phenylacetylene to yield **4**.[15]

Here, we have shown that TEMPO can be used as the only ligand system in a transition metal complex. The facile addition of substrates to **1** is assisted by the synergistic effects between the Ni center and the facile ability of the TEMPO ligand to interconvert between η^2 and η^1 binding modes. Further studies are ongoing to understand this bifunctional cooperativity effect between the ligand and metal, which should be useful for ensuing catalytic reactions with these complexes.

■ ASSOCIATED CONTENT

Supporting Information. Characterization and crystallographic data of **1**, **2**, and **4** (CIF) and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org

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■ ACKNOWLEDGMENT

We thank the University of Miami for financial support.

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(15) Alternatively, a mechanism based on the oxidative addition of HCCPh could also occur, followed by H atom migration to the nitrogen of TEMPO. This mechanism is not preferred, because oxidative addition would entail that the H and CCPh groups add on to give an octahedral complex as an intermediate which would be highly strained, as the methyl groups of TEMPO shield the Ni atom (axial sites), as seen in Figure 4.