

A Polyoxometalate Transfer Reagent: Synthesis, Structure, and Reactivity of Zirconocene Polyoxometalate [(PNbW₁₁O₄₀)₂ZrCp₂]⁶⁻

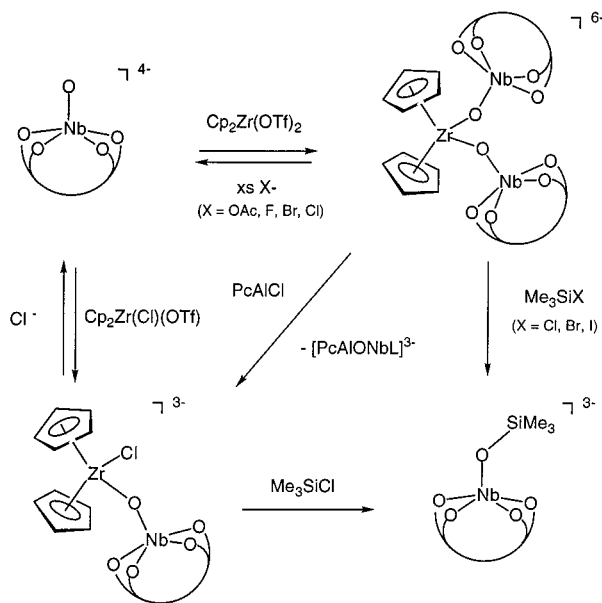
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The rising popularity of polyoxometalates¹ in catalysis, materials, and biological studies has increased efforts to both modify their properties and prepare new compounds.^{1,2} To date, synthetic methods that functionalize complete, intact polyoxometalates³ have relied largely on the use of electrophilic organic⁴ or organometallic species^{5–7} to bind to polyoxometalate surface oxygen atoms. Although studies have investigated many aspects of their reactivity, functionalized complete polyoxometalates have not themselves been used generally as reagents to prepare new derivatives.⁸ Polyoxometalate supported cyclopentadienyl complexes^{5,6} are potential candidates for such a reagent. Among this derivative class, the monocyclopentadienyl organometallic adducts of complete polyoxometalates have been prepared and thoroughly studied.⁶ Far less, however, is known about the biscyclopentadienyl adducts.⁹ In this communication, we describe the synthesis of the first polyoxometalate supported biscyclopentadienyl complex of Group 4, [(PW₁₁O₃₉NbO)₂ZrCp₂]⁶⁻, and use this complex

Scheme 1. The Formation and Chemistry of [(LNbO)₂ZrCp₂]⁶⁻ ^a



^a The lacunary Keggin ion, L = { α -PW₁₁O₃₉}⁷⁻, is represented by a curvilinear shape.

to demonstrate the transfer of the complete polyoxometalate [(PW₁₁O₃₉NbO)₂ZrCp₂]⁶⁻ to several molecular species.

Previous syntheses of polyoxometalate supported organometallic complexes have taken advantage of the enhanced Lewis basicity of oxygen atoms bound to Group 5 metals in mixed-metal polyoxometalates to coordinate to cationic organometallic fragments.² Using this synthetic strategy, the reaction of Cp₂Zr(OTf)₂·THF (Cp = C₅H₅⁻, OTf = O₃SCF₃⁻) with 2 equiv of the niobium-substituted polytungstate (*n*-Bu₄N)₄[(LNbO)₂ZrCp₂]⁶⁻ (where L = α -{PW₁₁O₃₉}⁷⁻) in acetonitrile forms (*n*-Bu₄N)₆[(LNbO)₂ZrCp₂]⁶⁻ in 91% yield (eq 1, Scheme 1).^{11,12} When the reaction is carried out with [(LNb*O)₂ZrCp₂]⁶⁻ in which the terminal ONb oxygen atom is enriched selectively with H₂*O (*O = ¹⁷O, 10% enriched),¹³ quantitative retention of the isotopic label in (*n*-Bu₄N)₆[(LNb*O)₂ZrCp₂]⁶⁻ is observed by ¹⁷O NMR spectroscopy as shown in eq 1. The ¹⁷O NMR chemical shift of [(LNb*O)₂ZrCp₂]⁶⁻ displays an upfield chemical shift to 554 ppm compared to 831 ppm for [(LNbO)₂ZrCp₂]⁶⁻,¹³ consistent with the presence of a Nb–O–Zr oxygen bridge.^{2a,12b,14} This resonance is in the range of the ¹⁷O NMR chemical shifts reported for related oxo-bridged niobium

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(11) Synthesis and characterization details are given in Supporting Information.

(12) Related Group 4 metallocene–metal oxoanion conjugates have been prepared by halide displacement reactions: (a) Cp₂TiCl₂ with [WO₄]²⁻ or [Mo₂O₇]²⁻; Carofiglioti, T.; Floriani, C.; Rosi, M.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* 1997, 30, 33245. (b) Cp₂M'Cl₂ (M' = Ti, Zr) with Cp*M(O)₃⁻ (M = Mo, W; Cp* = C₅Me₅); Rau, M. S.; Kretz, C. M.; Geoffroy, G. L. *Organometallics* 1994, 13, 1624.

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(16) Colorless needles grown from CH₃CN solution by vapor diffusion of Et₂O in a vial under N₂: crystal system, space group: triclinic, P1, Z = 2. Cell constants: *a* = 14.3725(2) Å, α = 73.468(1)°, *b* = 26.2888(1) Å, β = 76.193(1)°, *c* = 26.5749(4) Å, γ = 84.178(1)°. *V* = 9341.7(3) Å³. *Z* = 2. *R* (*I* > 2 σ (*I*)): *R*₁ = 0.0818, *wR*₂ = 0.1622. GOF(*F*²) = 1.132. The presence of disordered solvent molecules is likely. X-ray crystallographic details are provided in the Supporting Information.

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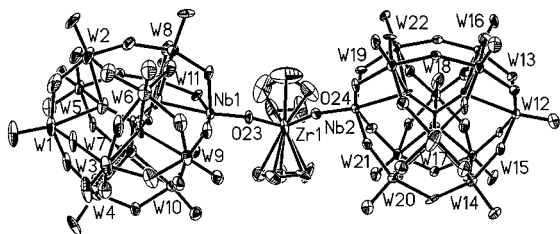
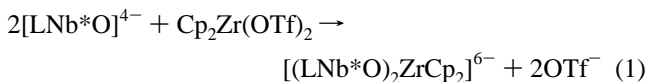


Figure 1. ORTEP Representation of $[(\text{LNbO})_2\text{ZrCp}_2]^{6-}$ with selected atom labels omitted for clarity.

polyoxometalates^{4c,7,15} and heterobimetallic complexes $[\text{Cp}_2\text{Zr}(\mu\text{-O})_2[\text{Cp}^*\text{M}(\text{O})_2]_2]$ ($\text{M} = \text{Mo}, \text{W}$).^{12b}



A crystal structure of $(n\text{-Bu}_4\text{N})_6[(\text{LNbO})_2\text{ZrCp}_2]$ reveals that the anion contains two complete $[\text{LNbO}]^{4-}$ ions acting as ligands coordinated to the $\{\text{Cp}_2\text{Zr}\}^{2+}$ center by the formerly terminal ONb oxygen atom in $[\text{LNbO}]^{4-}$ as shown in Figure 1.¹⁶ The two bent Nb–O–Zr bond angles of $159(1)^\circ$ and $148(1)^\circ$ fall within the range ($142.5\text{--}161.5^\circ$) reported for two related complexes $[(\text{MeCp})_2\text{Ti}(\mu_2\text{-MoO}_4)]_2$ and $[\{\text{Cp}_2\text{Zr}\}(\mu\text{-O})_2\{\text{Cp}^*\text{W}(\text{O})_2\}]_2$.¹² The Nb–O–Zr bond angle is likely to be influenced largely by steric interactions due to the lack of π bonding by the $\{\text{Cp}_2\text{Zr}\}^{2+}$ fragment.¹⁷ The Zr–O bond lengths in $[(\text{LNbO})_2\text{ZrCp}_2]^{6-}$ of 2.04(2) and 2.07(2) Å are consistent with single bond lengths.^{12,17,18} A short Nb–O bond distance of 1.80(1) Å in both $\{\text{NbOZr}\}$ fragments is observed, indicative of considerable multiple bond character.¹⁹ A similar Nb–O bond distance of 1.78 Å was reported in a polyoxometalate with a Nb–O–U bridge, $[\text{Cp}_3\text{U}(\text{NbW}_5\text{O}_{19})_2]^{3-}$.⁷ The structural data suggest that the multiply bonded terminal ONb oxygen atom of each $[\text{LNbO}]^{4-}$ anion acts as a two-electron donor, i.e., $\text{Zr} \leftarrow \text{:ONbL}$, to yield an 18-electron zirconocene complex.²⁰ Aside from the NbO and NbOZr metrical data, coordination of $[\text{LNbO}]^{4-}$ to $\{\text{Cp}_2\text{Zr}\}^{2+}$ has no apparent effect on the structure of either moiety.^{21,22}

Both the lability of the Zr–O bond in $[(\text{LNbO})_2\text{ZrCp}_2]^{6-}$ and its ability to act as a $[\text{LNbO}]^{4-}$ transfer reagent are borne out by the reactions summarized in Scheme 1. Facile Zr–O bond cleavage occurs when $[(\text{LNbO})_2\text{ZrCp}_2]^{6-}$ reacts with excess $n\text{-Bu}_4\text{NX}$ ($\text{X} = \text{Cl}, \text{Br}$) to form quantitatively $[\text{LNbO}]^{4-}$ and $\text{Cp}_2\text{-ZrX}_2$ as observed by ^1H NMR and IR spectroscopy. The reaction between $n\text{-Bu}_4\text{NCl}$ and the singly substituted species $[\text{LNbOZrClCp}_2]^{3-}$ ²³ also yielded $[\text{LNbO}]^{4-}$ and Cp_2ZrCl_2 . The $[(\text{LNbO})_2\text{ZrCp}_2]^{6-}$ ion reacts likewise with $n\text{-Bu}_4\text{NOAc}$ and $n\text{-Bu}_4\text{NF}$ to produce $[\text{LNbO}]^{4-}$.

Hydrolysis of $[(\text{LNbO})_2\text{ZrCp}_2]^{6-}$ with excess ^{17}O enriched H_2^*O in acetonitrile produces $[\text{LNb}^*\text{O}]^{4-}$ and the acid condensa-

tion product $[(\text{LNb})_2^*\text{O}]^{6-}$ detected by ^{17}O NMR spectroscopy (^{17}O δ , 512 ppm).²⁴ These results are consistent with hydrolysis studies of $[\text{LNbO}]^{4-}$ with the noncoordinating counterion $n\text{-Bu}_4\text{N}^+$ which undergoes oxo ligand exchange with H_2^*O only in the presence of a catalytic amount of acid.¹³ Presumably the coordinated $\{\text{Cp}_2\text{Zr}\}^{2+}$ fragment hydrolyzes initially to form zirconium hydroxide or aquo species²⁵ which, acting as source of protons, mediate the oxo ligand exchange reaction. The lability of $[\text{LNbO}]^{4-}$ in $[(\text{LNbO})_2\text{ZrCp}_2]^{6-}$ corroborates earlier studies of the rapid exchange of $[\text{MW}_5\text{O}_{19}]^{3-}$ ($\text{M} = \text{Nb}, \text{Ta}$) fragments in $[\text{Cp}_3\text{M}'(\text{MW}_5\text{O}_{19})_2]^{3-}$ ($\text{M}' = \text{Th}, \text{U}$).⁷

Reactions of $[(\text{LNbO})_2\text{ZrCp}_2]^{6-}$ with main group covalent halides result in transfer of $[\text{LNbO}]^{4-}$ to form main group derivatives functionalized solely on the terminal ONb oxygen atom also shown in Scheme 1. The reaction of $[(\text{LNbO})_2\text{ZrCp}_2]^{6-}$ with excess R_3SiX ($\text{R} = \text{Me}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) resulted in quantitative formation of Cp_2ZrX_2 and $[\text{LNbOSiR}_3]^{3-}$,^{3–26} an example of a silyl derivative of a complete polyoxometalate.^{4c} An ^{17}O NMR spectroscopic study of the reaction with enriched $[(\text{LNb}^*\text{O})_2\text{ZrCp}_2]^{6-}$ confirmed complete retention of the label in $[\text{LNb}^*\text{OSiMe}_3]^{3-}$ consistent with transfer of the $[\text{LNbO}]^{4-}$ group to the $\{\text{R}_3\text{Si}\}^+$ group. In contrast, no reaction is observed between trialkylsilyl halides and $(n\text{-Bu}_4\text{N})_4[\text{LNbO}]$. The monosubstituted product $[\text{LNbOZrClCp}_2]^{3-}$, a putative intermediate in the reaction, also reacted with Me_3SiCl to form $[\text{LNbOSiMe}_3]^{3-}$ cleanly. Preliminary results indicate that the reaction of $[(\text{LNbO})_2\text{ZrCp}_2]^{6-}$ with PcAlCl ($\text{Pc} = 29\text{H}, 31\text{H-phthalocyaninato}$) yields $[\text{LNbOZrClCp}_2]^{3-}$ and the novel blue polyoxometalate phthalocyanine conjugate $[\text{LNbOAlPc}]^{3-}$.²⁷

The reactions in Scheme 1 feature the activation of the terminal ONb oxygen atom toward derivatization by coordination to the strong Lewis acid fragment $\{\text{Cp}_2\text{Zr}\}^{2+}$. The ready displacement of this group from $[(\text{LNbO})_2\text{ZrCp}_2]^{6-}$ illustrates a potential general method for derivatizing polyoxometalates with a larger variety of main group and transition metal reagents than investigated previously and exemplifies the lability of the Zr–O bond when the $\{\text{Cp}_2\text{Zr}\}^{2+}$ fragment coordinates to a metal oxo species.^{12b} Since polyoxometalate surface oxygens resemble solid-state metal oxide surfaces,^{1,2,5i} these reactions could be applied to the Group 4 metalocene chemistry²⁸ and functionalization²⁹ of oxide materials.

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Supporting Information Available: Preparative and spectroscopic data (PDF) plus additional crystallographic tables and figures (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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