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Authors

Bukhryakov, Konstantin V
Schrock, Richard R
Hoveyda, Amir H
[et al.](#)

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Synthesis of 2,6-Hexa-*tert*-butylterphenyl Derivatives, 2,6-(2,4,6-*t*-Bu₃C₆H₂)₂C₆H₃X, where X = I, Li, OH, SH, N₃, or NH₂

Konstantin V. Bukhryakov[†], Richard R. Schrock^{†,*}, Amir H. Hoveyda[‡], Peter Müller[†], and Jonathan Becker[†]

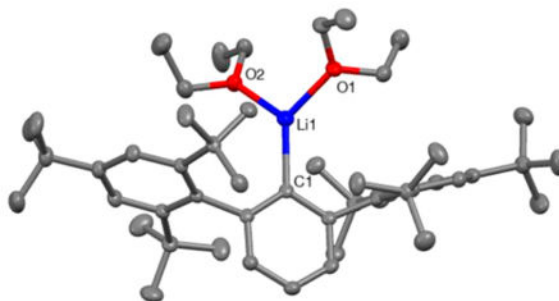
[†]Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

[‡]Department of Chemistry, Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467, United States

Abstract

A “double benzyne” reaction between 1,3-dichloro-2-iodobenzene and 2,4,6-*t*-Bu₃C₆H₂MgBr followed by the addition of iodine led to 2,6-(2,4,6-*t*-Bu₃C₆H₂)₂C₆H₃I (HTBTI) in 65% yield. Lithiation of HTBTI with Li-*t*-Bu gave Li(Et₂O)₂HTBT from which HTBTSH, HTBTN₃, HTBTNH₂, and HTBTOH were prepared. An X-ray structure of W(OHTBT)₂Cl₄ shows that the two HTBTO ligands are *trans* to one another with the *t*-Bu₃C₆H₂ groups on one HTBTO interdigitated with the *t*-Bu₃C₆H₂ groups on the other HTBTO.

Graphical Abstract



One of the most significant advances in the chemistry of a large fraction of elements in the periodic table in the past 50 years has been the synthesis of compounds that contain

*Corresponding Author: rrs@mit.edu.

ORCID

Richard R. Schrock: 0000-0001-5827-3552

Amir H. Hoveyda: 0000-0002-1470-6456

Notes

The authors declare no competing financial interest.

ASSOCIATED CONTENT

Supporting Information

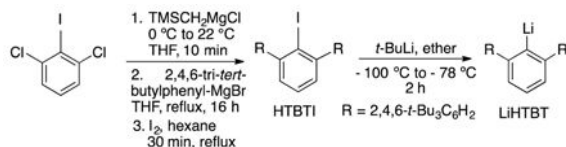
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b01062.

Experimental details for the syntheses of all compounds (PDF)

X-ray crystallographic files for the two structural studies (CIF)

sterically demanding groups.¹ In inorganic and organometallic chemistry, bulky mono-, di-, or trianionic ligands have allowed the synthesis of compounds in which the element is in an unusual oxidation state or bonding state or catalysts whose function critically depends upon the size, shape, and electronics of the sterically dominating ligand.² In inorganic chemistry, bulky anionic ligands include (among many others) those based on the 2,6-terphenyl motif in which the phenyl groups in the 2 and 6 positions are sterically demanding 2,4,6- $R_3C_6H_2$ groups ($R = Me$ or $i\text{-Pr}$; HMT or HIPT, respectively). There are many examples of compounds in which $[2,6-(2,4,6-R_3C_6H_2)_2C_6H_3]^-$ or $[2,6-(2,4,6-R_3C_6H_2)_2C_6H_3X]^-$ is bound to a transition or main group metal or metalloid where $X = O$,³ S ,⁴ or N (amido or imido⁵). In terms of catalysis, molybdenum- or tungsten-based alkylidene complexes in the past 10 years that contain a $[2,6-(2,4,6-R_3C_6H_2)_2C_6H_3O]^-$ ligand (and variations) have led to olefin metathesis catalysts that provide kinetic control of Z^6 or E selectivity⁷ or that initiate the formation of *cis,syndiotactic* polymers in ring-opening metathesis polymerization reactions,⁸ including those that generate *cis,syndiotactic*-(**A-alt-B**) copolymers.⁹ A 2,6-terphenyl that is largely absent in the 2,6-terphenyl class of compounds is that in which $R = t\text{-Bu}$. It arguably would be the most sterically demanding in the $[2,6-(2,4,6-R_3C_6H_2)_2C_6H_3]^-$ series of 2,6-terphenyls or their derivatives and could provide additional insight into bonding and reactivity in view of that increased steric bulk. We report here the synthesis of 2,6-(2,4,6- $t\text{-Bu}_3C_6H_2$)₂C₆H₃X (HTBTX) derivatives ($X = I, Li, OH, SH, N_3, \text{ or } NH_2$) along with X-ray structures of $Li(Et_2O)_2HTBT$ and *trans*- $W(OHTBT)_2Cl_4$.

The approach to the synthesis of the hexa-*tert*-butyl-2,6-terphenyl is a “double benzyne” reaction analogous to that discovered by Hart.¹⁰ In 2004 a variation of the Hart reaction was used to prepare 2,6-(2,4,6- $t\text{-Bu}_3C_6H_2$)₂-4- BrC_6H_2MgX ($X = Br$ or Cl), which was then hydrolyzed to yield the desired 3,5-(2,4,6- $t\text{-Bu}_3C_6H_2$)₂C₆H₃Br.¹¹ We prepared HTBTMgX ($X = Br$ or I) in an analogous manner and treated it with iodine in hexane to obtain HTBTI (eq 1) in 65% yield. The iodide is typically an isolable and useful intermediate in syntheses of well-known hexamethylterphenyl or hexaisopropylterphenyl analogs of HTBT. Hexane is necessary to form HTBTI from HTBTMgX, since refluxing a solution of HTBTMgX in the presence of iodine in THF gave a mixture of HTBTI and HTBTI in an ~1:1 ratio from the radical reaction of iodine with THF and generation of HI.¹²



(1)

Lithiation of HTBTI with $Li-t\text{-Bu}$ in diethyl ether at -78°C gave $Li(Et_2O)_2HTBT$ in 67% yield. An X-ray structural study (Figure 1) of $Li(Et_2O)_2HTBT$ revealed the lithium to be trigonally coordinated with a $Li-C1$ bond length of $2.137(4) \text{ \AA}$, which is significantly longer than that in $Li(Et_2O)HIPT$ ($Li-C = 2.017(7) \text{ \AA}$), where only one ether is coordinated to lithium,¹³ or in $(Et_2O)_2Li-2,6-(2,4,6-Ph_3C_6H_2)_2C_6H_3$ ($Li-C = 2.074(16) \text{ \AA}$).¹⁴ A repulsive

interaction probably leads to some bending back of the *t*-Bu₃C₆H₂ rings from the plane of the six carbon atoms in the *t*-Bu₃C₆H₂ rings. We conclude that the lithium in Li(Et₂O)₂HTBT, in comparison to that in Li(Et₂O)HIPT, is more prone to bind a second ether than be attracted to the electron density in the more sterically demanding *t*-Bu₃C₆H₂ rings.

Treatment of LiHTBT with elemental sulfur followed by reduction with LiAlH₄ afforded HTBTSH in 88% overall yield, while treatment of LiHTBT with tosyl azide gave HTBTN₃, which was then reduced to HTBTNH₂ in 85% overall yield (Scheme 1). Refluxing LiHTBT in the presence of B(OMe)₃ in toluene produced HTBTB(OMe)₂, which was converted *in situ* to HTBTOH upon treatment with NaOH/H₂O₂ in 75% overall yield. The reaction between LiHTBT and PhNO₂ in ether at -78 to 22 °C (overnight) gave only ~20% of the desired HTBTOH.

The reaction between tungsten hexachloride and 2 equiv of LiOHTBT in benzene or toluene at room temperature produced black *trans*-W(OHTBT)₂Cl₄, which was recrystallized from pentane in 43% overall yield. An X-ray structure shows that the *t*-Bu₃C₆H₂ groups on one HTBTO are interdigitated with the *t*-Bu₃C₆H₂ groups on the other HTBTO (Figure 2). *Cis* HTBTO ligands, as found for the terphenoxides in *cis*-W(O-2,6-Ph₂C₆H₃)₂Cl₄,¹⁵ would not seem to be possible for steric reasons. The W1–O2 and W1–O2 bond lengths in *trans*-W(OHTBT)₂Cl₄ (1.813(3) and 1.896(3) Å) are comparable to the W–O bond lengths in *cis*-W(O-2,6-Ph₂C₆H₃)₂Cl₄ (1.824(6) and 1.855(7) Å). Addition of a third HTBTO group to *trans*-W(OHTBT)₂Cl₄ would not seem to be possible either. In fact, heating a solution of W(OHTBT)₂Cl₄ in benzene in the presence of several equivalents of LiOHTBT at 80 °C led only to slow decomposition to unidentified products.

We conclude that the 2,6-hexa-*tert*-butylterphenyl group is as accessible as the hexamethyl and hexaisopropyl analogs and look forward to its comparison with “smaller” 2,6-hexamethylterphenyl or 2,6-hexa-isopropylterphenyl and their derivatives in some of the many circumstances that have been explored to date.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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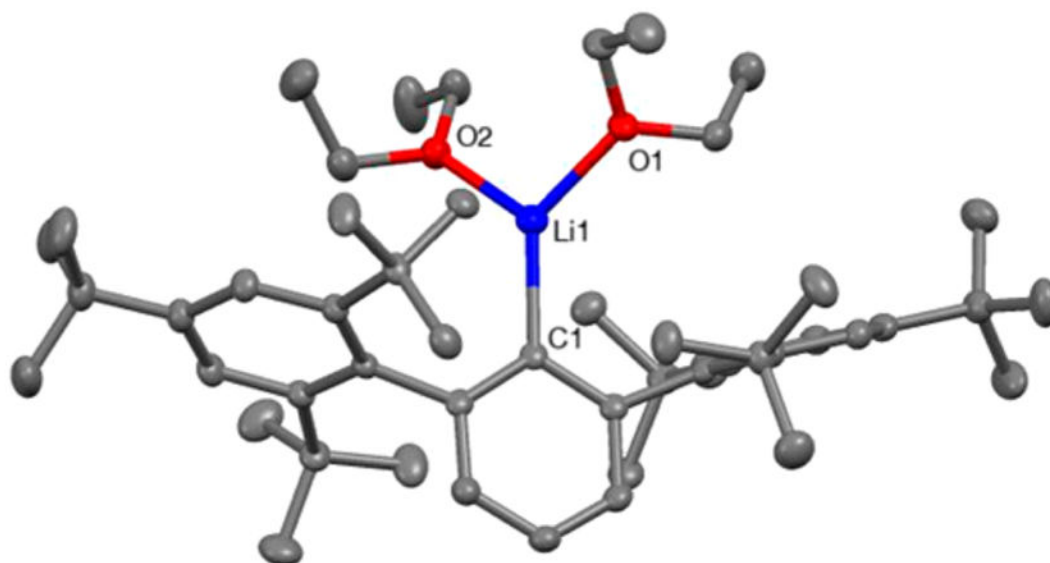


Figure 1. Structure of Li(Et₂O)₂HTBT. Hydrogen atoms have been omitted for clarity. Ellipsoids are shown at 50% probability.

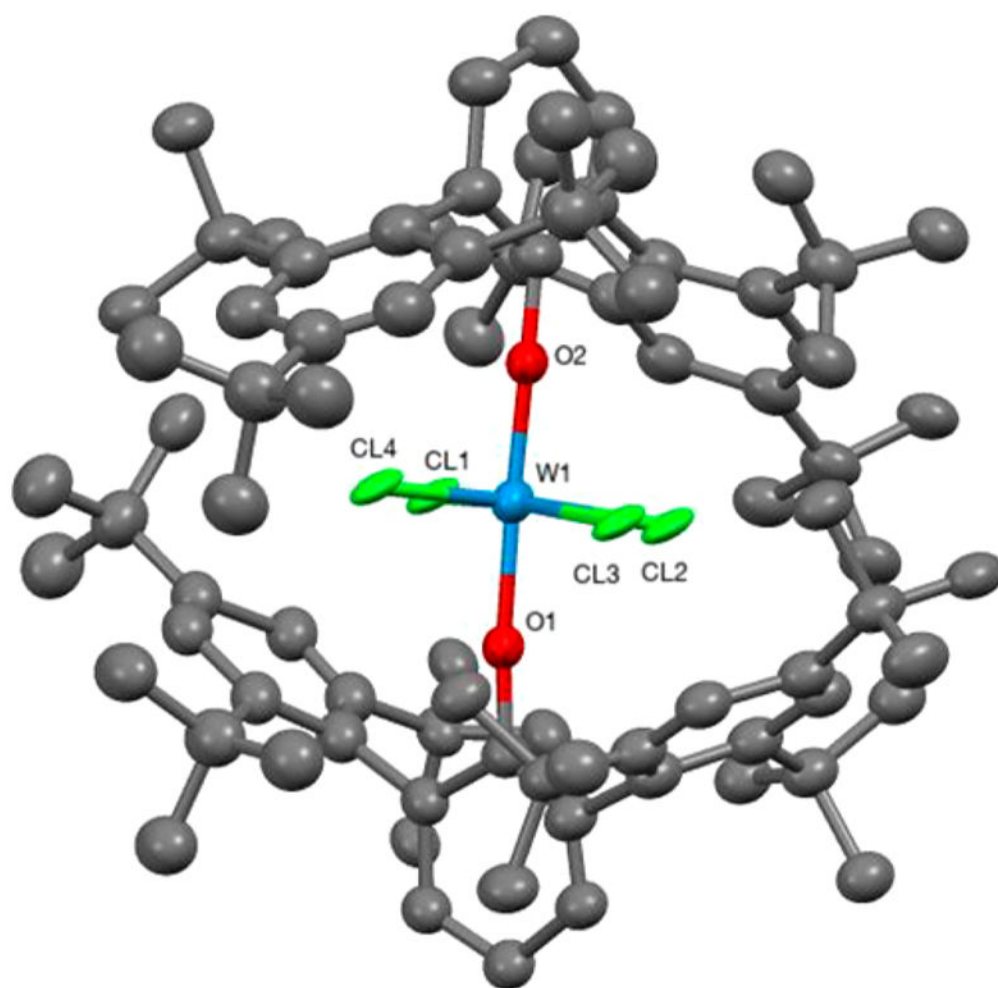
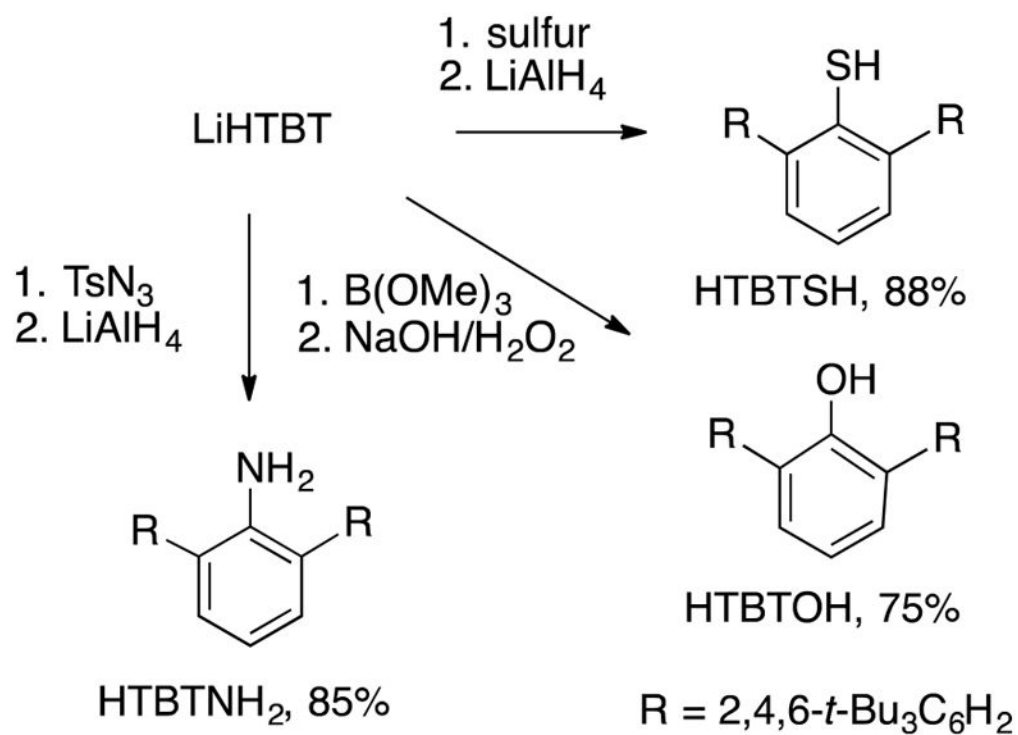


Figure 2. Structure of W(OHTBT)₂Cl₄. Hydrogen atoms have been omitted for clarity. Ellipsoids are shown at 50% probability.



Scheme 1.
Syntheses of HTBTSH, HTBTNH₂, and HTBTOH