Organic LETTERS
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# Synthesis of 2,6-Hexa-*tert*-butylterphenyl Derivatives, 2,6-$(2,4,6\text{-}t\text{-}Bu_3C_6H_2)_2C_6H_3X$, where X = I, Li, OH, SH, $N_3$, or $NH_2$

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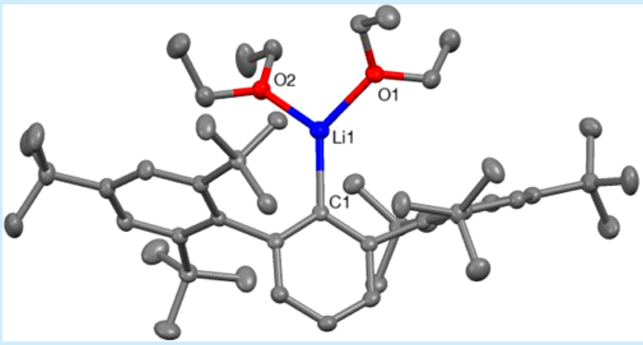
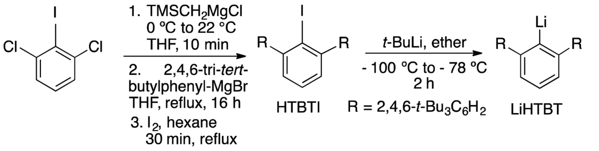
S Supporting Information

**ABSTRACT:** A "double benzyne" reaction between 1,3-dichloro-2-iodobenzene and 2,4,6-*t*-$Bu_3C_6H_2MgBr$ followed by the addition of iodine led to 2,6-(2,4,6-*t*-$Bu_3C_6H_2)_2C_6H_3I$ (HTBTI) in 65% yield. Lithiation of HTBTI with Li-*t*-Bu gave $Li(Et_2O)_2$HTBT from which HTBTSH, $HTBTN_3$, $HTBTNH_2$, and HTBTOH were prepared. An X-ray structure of $W(OHTBT)_2Cl_4$ shows that the two HTBTO ligands are *trans* to one another with the *t*-$Bu_3C_6H_2$ groups on one HTBTO interdigitated with the *t*-$Bu_3C_6H_2$ groups on the other HTBTO.



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 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*-Pr; HMT or HIPT, respectively). There are many examples of compounds in which $[2,6\text{-}(2,4,6\text{-}R_3C_6H_2)_2C_6H_3]^-$ or $[2,6\text{-}(2,4,6\text{-}R_3C_6H_2)_2C_6H_3X]^-$ is bound to a transition or main group metal or metalloid where X = O,[3] S,[4] or N (amido or imido[5]). In terms of catalysis, molybdenum- or tungsten-based alkylidene complexes in the past 10 years that contain a $[2,6\text{-}(2,4,6\text{-}R_3C_6H_2)_2C_6H_3O]^-$ ligand (and variations) have led to olefin metathesis catalysts that provide kinetic control of *Z*[6] or *E* selectivity[7] 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*-Bu. It arguably would be the most sterically demanding in the $[2,6\text{-}(2,4,6\text{-}R_3C_6H_2)_2\text{-}C_6H_3]^-$ 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-$(2,4,6\text{-}t\text{-}Bu_3C_6H_2)_2C_6H_3X$ (HTBTX) derivatives (X = I, Li, OH, SH, $N_3$, or $NH_2$) along with X-ray structures of $Li(Et_2O)_2$HTBT 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-$(2,4,6\text{-}t\text{-}Bu_3C_6H_2)_2$-4-$BrC_6H_2MgX$ (X = Br or Cl), which was then hydrolyzed to yield the desired 3,5-$(2,4,6\text{-}t\text{-}Bu_3C_6H_2)_2C_6H_3Br$.[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 HTBTH 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*-Bu in diethyl ether at −78 °C gave $Li(Et_2O)_2$HTBT in 67% yield. An X-ray structural study (Figure 1) of $Li(Et_2O)_2$HTBT revealed the lithium to be trigonally coordinated with a Li−C1 bond length of 2.137(4) Å,

**Received:** April 8, 2017
**Published:** May 1, 2017

DOI: 10.1021/acs.orglett.7b01062
*Org. Lett.* 2017, 19, 2607−2609

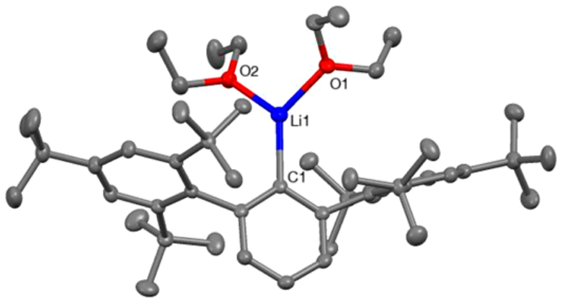
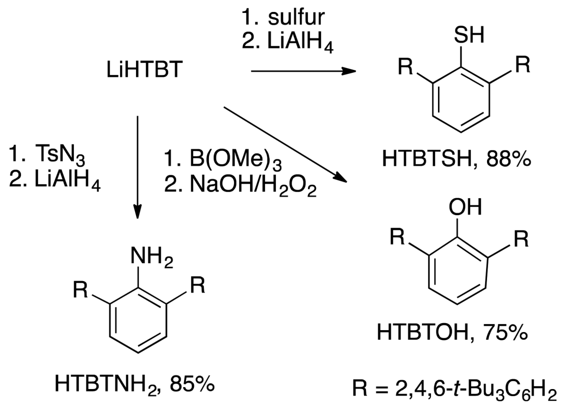


**Figure 1.** Structure of Li$(Et_2O)_2$HTBT. Hydrogen atoms have been omitted for clarity. Ellipsoids are shown at 50% probability.

which is significantly longer than that in Li$(Et_2O)$HIPT (Li–C = 2.017(7) Å), where only one ether is coordinated to lithium,[13] or in $(Et_2O)_2$Li-2,6-(2,4,6-$Ph_3C_6H_2)_2C_6H_3$ (Li–C = 2.074(16) Å).[14] A repulsive interaction probably leads to some bending back of the *t*-$Bu_3C_6H_2$ rings from the plane of the six carbon atoms in the *t*-$Bu_3C_6H_2$ rings. We conclude that the lithium in Li$(Et_2O)_2$HTBT, in comparison to that in Li$(Et_2O)$HIPT, is more prone to bind a second ether than be attracted to the electron density in the more sterically demanding *t*-$Bu_3C_6H_2$ rings.

Treatment of LiHTBT with elemental sulfur followed by reduction with $LiAlH_4$ afforded HTBTSH in 88% overall yield, while treatment of LiHTBT with tosyl azide gave $HTBTN_3$, which was then reduced to $HTBTNH_2$ 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/$H_2O_2$ in 75% overall yield. The reaction between LiHTBT and $PhNO_2$ in ether at −78 to 22 °C (overnight) gave only ~20% of the desired HTBTOH.

**Scheme 1. Syntheses of HTBTSH, $HTBTNH_2$, and HTBTOH**



The reaction between tungsten hexachloride and 2 equiv of LiOHTBT in benzene or toluene at room temperature produced black *trans*-W$(OHTBT)_2Cl_4$, which was recrystallized from pentane in 43% overall yield. An X-ray structure shows that the *t*-$Bu_3C_6H_2$ groups on one HTBTO are interdigitated with the *t*-$Bu_3C_6H_2$ groups on the other HTBTO (Figure 2). *Cis* HTBTO ligands, as found for the terphenoxides in *cis*-W(O-2,6-$Ph_2C_6H_3)_2Cl_4$,[15] would not seem to be possible for steric reasons. The W1–O2 and W1–O2 bond lengths in *trans*-W$(OHTBT)_2Cl_4$ (1.813(3) and 1.896(3) Å) are comparable to the W–O bond lengths in *cis*-W(O-2,6-$Ph_2C_6H_3)_2Cl_4$ (1.824(6) and 1.855(7) Å). Addition of a third HTBTO group to *trans*-W$(OHTBT)_2Cl_4$ would not seem to be possible either. In fact, heating a solution of W$(OHTBT)_2Cl_4$ in benzene in the presence of several equivalents of LiOHTBT at 80 °C led only to slow decomposition to unidentified products.

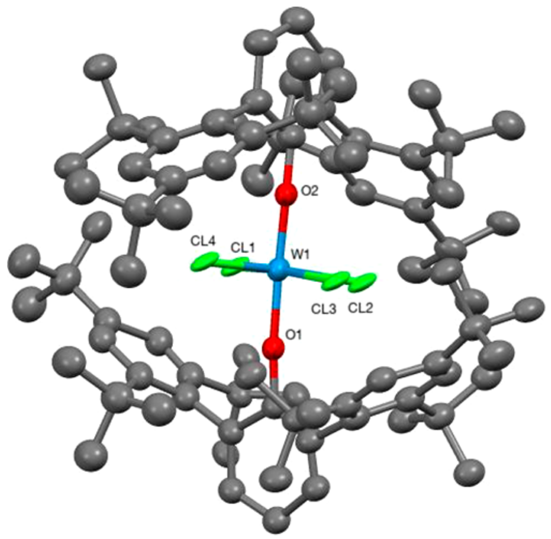


**Figure 2.** Structure of W$(OHTBT)_2Cl_4$. Hydrogen atoms have been omitted for clarity. Ellipsoids are shown at 50% probability.

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.

## ■ 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)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

R.R.S. and A.H.H. are grateful for financial support from the National Institutes of Health (GM-59426).

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DOI: 10.1021/acs.orglett.7b01062
*Org. Lett.* 2017, 19, 2607−2609