Reaction of $(C_5H_5)_2NbH_3$ with $(C_5H_5)_2Zn$—Structure of $(C_5H_5)_2NbH_2ZnC_5H_5$[1]

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Three compounds containing niobium–zinc bonds have been obtained from the reaction of Cp_2NbH_3 with Cp_2Zn. When the reaction was carried out in benzene, the use of an excess of Cp_2NbH_3 resulted in formation of the known compound $(Cp_2NbH_2)_2Zn$, while with an excess of Cp_2Zn, $Cp_2NbH(ZnCp)_2$ was formed. In THF, Cp_2NbH_2ZnCp was the sole product whether an equimolar amount or excess of Cp_2Zn was used. The structure of Cp_2NbH_2ZnCp was determined by a single-crystal X-ray diffraction study. The compound forms monoclinic crystals of space group $C2/c$ with four molecules in a cell of dimensions $a = 13.762$ (3) Å, $b = 9.679$ (3) Å, $c = 11.199$ (3) Å, and $\beta = 115.90$ (3)°. The structure was solved by standard Patterson and Fourier methods and refined by full-matrix least-squares techniques. The refinement, with anisotropic thermal parameters for all non-hydrogen atoms, converged at $R_F = 0.023$ ($R_{wF} = 0.025$) for 127 parameters and 924 observed reflections. The molecular structure of Cp_2NbH_2ZnCp resembles that of Cp_2NbH_3, with the central hydrogen atom replaced by a ZnCp group. The Cp(Zn) group, which is disordered in the crystal, is bound to zinc in a nearly symmetrical η^5 fashion. The bonding within the NbH_2Zn fragment is best described as consisting of a normal Nb–Zn single bond and terminal hydrides bound to Nb, with only slight Zn–H interaction.

Introduction

Compounds containing a direct zinc–transition-metal bond have been known for about 40 years; the types of complexes prepared include zinc-bis(transition metal) compounds (e.g., $Zn[Co(CO)_4]_2$[2]), transition-metal zinc halides (e.g., $(CO)_4Fe(ZnCl)_2$[3]), and the more recently prepared organozinc–transition-metal compounds like $CpZnMn(CO)_5$[4] and the cluster compound $Cp_6Ni_2Zn_4$.[5] Nearly all of the compounds described so far contain group 6–8 transition-metal compounds; the only group 5–zinc compounds reported are $Cp_2Nb(CO)H{\cdot}Zn(BH_4)_2$[6] and $(Cp_2NbH_2)_2Zn$.[7] The latter compound was obtained by Tebbe from the reaction between Et_2Zn and Cp_2NbH_3. We have found that Cp_2Zn is a convenient starting material for the preparation of cyclopentadienylzinc–transition-metal compounds.[4,8] It reacts smoothly with transition-metal hydrides, forming direct zinc–metal bonds, under conditions where dialkylzinc compounds either fail to react or react very slowly. We, therefore, decided to investigate the reaction of Cp_2NbH_3 with Cp_2Zn.

Experimental Section

General Remarks. All manipulations were carried out in an atmosphere of dry, oxygen-free nitrogen. All solvents were dried and distilled under nitrogen prior to use. NMR spectra were recorded on Varian EM-390 and CFT-20 and Bruker WP-200 spectrometers. IR spectra were recorded on a Perkin-Elmer 283 spectrometer. Cp_2NbH_3[9] and Cp_2Zn[10] were prepared according

Table I. Crystal Data and Details of the Structure Determination

(a) Crystal Data

formula	$C_{15}H_{17}ZnNb$
mol wt	355.58
cryst system	monoclinic-*b*
space group	No. 15, $C2/c$
a, Å	13.762 (3)
b, Å	9.679 (3)
c, Å	11.199 (3)
β, deg	115.90 (3)
V, Å^3	1341.9 (8)
Z	4
D_{calcd}, g/cm^3	1.760
$F(000)$	712
μ(Mo Kα), cm^{-1}	26.4
approx cryst size, mm	0.5 × 0.18 × 0.22

(b) Data Collection

θ_{min}, θ_{max}, deg	0.1, 25.0
radiation	Mo Kα, Zr filtered, 0.710 69 Å
$\omega/2\theta$ scan, deg	$0.60 + 0.35 \tan\theta$
max time/reflctn, min	0.5
horizontal and vertical aperture,mm	3, 3
ref reflctns	$\bar{5}33$, $\bar{5}1\bar{1}$
total data	1143
total unique	1058
obsd data ($I > 2.5\sigma(I)$)	924
total X-ray exp time, h	11.2

(c) Refinement

no. of refined parameters	127
wtg scheme	$w^{-1} = (\sigma^2(F) + 0.001F^2)/0.79$
final $R_F = \Sigma \lvert F_o - \lvert F_c \rvert\rvert / \Sigma F_o$	0.023
final $R_{wF} = [\Sigma w(F_o - \lvert F_c \rvert)^2 / \Sigma w F_o^2]^{1/2}$	0.025
rms dev of reflctn of unit wt	1.03

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Table II. ^1H and ^{13}C NMR Data for Niobium-Zinc Compounds[a]

	^1H NMR			^{13}C NMR	
compd	Cp(Zn)	Cp(Nb)	H(Nb)	Cp(Zn)	Cp(Nb)
$(Cp_2NbH_2)_2Zn$		4.75	−9.07		83.2
Cp_2NbH_2ZnCp	6.55	4.45	−8.23	105.4	81.3
$Cp_2NbH(ZnCp)_2$	6.50	4.17	−9.04	106.0, 105.8	77.7
Cp_2NbH_3		4.92	−2.54, −3.55		86.4
Cp_2Zn	6.33			114.4	

[a] C_6D_6, δ in ppm relative to internal Me_4Si.

Table III. Fractional Atomic Coordinates for Cp_2NbH_2ZnCp

atom	*x/a*	*y/b*	*z/c*
Nb(1)	0 (–)	0.13720 (4)	0.25 (–)
Zn(1)	0 (–)	0.39970 (6)	0.25 (–)
C(11)	0.1250 (3)	0.1171 (4)	0.1559 (4)
C(12)	0.1762 (3)	0.1887 (4)	0.2767 (4)
C(13)	0.1869 (3)	0.0972 (4)	0.3785 (4)
C(14)	0.1413 (3)	−0.0274 (4)	0.3199 (4)
C(15)	0.1030 (3)	−0.0144 (4)	0.1822 (4)
C(21)	−0.095 (2)	0.601 (2)	0.207 (4)
C(22)	−0.015 (4)	0.609 (2)	0.334 (3)
C(23)	0.081 (3)	0.611 (2)	0.326 (4)
C(24)	0.060 (3)	0.608 (3)	0.195 (5)
C(25)	−0.052 (2)	0.601 (2)	0.116 (1)
H(1)	0.037 (3)	0.248 (3)	0.379 (4)
H(11)	0.108 (3)	0.153 (4)	0.076 (4)
H(12)	0.201 (3)	0.277 (4)	0.281 (4)
H(13)	0.220 (4)	0.123 (4)	0.462 (5)
H(14)	0.141 (3)	−0.097 (4)	0.365 (4)
H(15)	0.072 (3)	−0.080 (4)	0.123 (4)
H(21)	−0.171	0.597	0.185
H(22)	−0.024	0.611	0.414
H(23)	0.152	0.614	0.399
H(24)	0.112	0.613	0.159
H(25)	−0.091	0.594	0.021

to literature methods. The reactions of Cp_2Zn with Cp_2NbH_3 afford virtually quantitative yields of Nb–Zn products. The actual isolated yields are of the order of 70% due to workup losses. This loss is larger in the case of Cp_2NbH_2ZnCp because the reaction is carried out in THF and the THF-washing step is necessary.

$(Cp_2NbH_2)_2Zn$. A 0.45-g (2-mmol) sample of Cp_2NbH_3 was added to a suspension of 0.2 g (1 mmol) of Cp_2Zn in 15 mL of benzene. After the solution was stirred for 15 min, the benzene was removed in vacuo, and the residue was crystallized from pentane (30 °C/−40 °C) to give red crystals of $(Cp_2NbH_2)_2Zn$.

$Cp_2NbH(ZnCp)_2$. A 0.45-g (2-mmol) sample of Cp_2NbH_3 was added to a suspension of 1.17 g (6 mmol) of Cp_2Zn in 15 mL of benzene. After the solution was stirred for 30 min, the excess of Cp_2Zn was removed by centrifugation and the solvent was removed in vacuo. The resulting solid was washed once with 10 mL of pentane and crystallized from boiling benzene (80 °C/20 °C) to yield orange-yellow crystals of $Cp_2NbH(ZnCp)_2$.

Cp_2NbH_2ZnCp. This compound could not be obtained pure from Cp_2Zn and Cp_2NbH_3 in benzene: from equimolar amounts of reactants, a mixture of $(Cp_2NbH_2)_2Zn$, $Cp_2NbH(ZnCp)_2$, and Cp_2NbH_2ZnCp was obtained. Using THF as a solvent, Cp_2NbH_2ZnCp was the sole product whether an equimolar amount or an excess of Cp_2Zn was used: 0.75 g (4 mmol) of Cp_2Zn in 10 mL of THF was added to a solution of 0.45 g (2 mmol) of Cp_2NbH_3 in 9 mL of THF. After being stirred for 30 min at room temperature, the solution was stored overnight at −30 °C. The following day, the solution was decanted and the yellow residue was washed first with cold THF (5 mL) and then with pentane (5 mL) and dried in vacuo. Crystallization from benzene afforded orange crystals of Cp_2NbH_2ZnCp, suitable for X-ray diffraction analysis.

Data Collection and Structure Determination of Cp_2NbH_2ZnCp. An orange crystal was sealed under nitrogen in a Lindemann capillary and transferred to an Enraf-Nonius CAD4F diffractometer. Unit cell dimensions and standard deviations were determined in the usual way[11] from the setting angles of 13 carefully centered reflections. The crystal data and details of the structure determination are summarized in Table I.

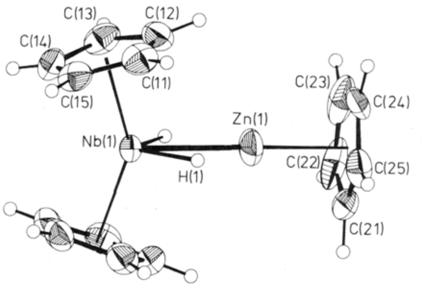

Figure 1. ORTEP drawing of Cp_2NbH_2ZnCp, showing 40% probability thermal ellipsoids. Hydrogen atoms are represented by artificially small spheres. Only one conformation of the disordered Cp(Zn) ring is shown.

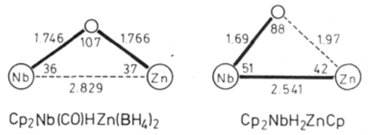

Figure 2. Bond distances (Å) and angles (deg) in the NbHZn moiety of $Cp_2Nb(CO)H{\cdot}Zn(BH_4)_2$[6] and Cp_2NbH_2ZnCp.

The intensities of one quadrant of the reflection sphere (−*h*,+*k*,±*l*) were collected in the ω/2θ scan mode, with use of Zr-filtered Mo Kα radiation. The intensities of two reference reflections were monitored every hour of X-ray exposure time. There was no indication for decay during the data collection; the (random) fluctuations in the control reflections were less than 4%. The data were subsequently corrected for Lorentz and polarization effects and fluctuations in the control reflections in the previously described way.[11] A ψ scan for a close to axial reflection showed variations of less than 10% about the mean. Correction for absorption was therefore not considered necessary.

The space groups *Cc* and *C*2/*c* were compatible with the observed systematic extinctions. The structure determination was initiated in the lower space group symmetry *Cc*. The two metal atoms were located from a Patterson map, and the Cp(Nb) carbon atoms were located from the first difference Fourier. At this point, it became apparent that the positions of all atoms located so far conformed to the higher symmetry *C*2/*c*, with the two metal atoms located on the twofold axis. Therefore, the six maxima that were found in the difference Fourier at positions corresponding to Cp(Zn) carbon atoms should be interpreted as either a pseudosymmetry artifact or a disorder of the Cp(Zn) ring. In view of the occurrence of disordered Cp(Zn) rings in CpZnMe[12] and $Cp_6Ni_2Zn_4$,[5] the disorder model was adopted and further refinement was carried out in the space group *C*2/*c*, assuming a statistical twofold axis through the Cp(Zn) ring. Potential refinement instabilities due to partial overlap of the electron densities could be successfully controlled by constraining the C–C bond lengths in the Cp(Zn) ring to be equal. The Cp(Nb) hydrogen atoms and the niobium-bound hydrides could easily be located from a difference Fourier and refined satisfactorily. The hydrogen atoms of the Cp(Zn) ring were assigned a common isotropic thermal parameter; the thermal parameters of all other

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Table IV. Bond Distances (Å) for Cp_2NbH_2ZnCp

Nb(1)-Zn(1)	2.5407 (7)	Zn(1)-H(1)	1.97 (4)	C(13)-C(14)	1.385 (6)
Nb(1)-H(1)	1.69 (4)	Zn(1)-C(21)	2.28 (2)	C(14)-C(15)	1.401 (7)
Nb(1)-C(11)	2.386 (4)	Zn(1)-C(22)	2.28 (3)	C(15)-C(11)	1.370 (6)
Nb(1)-C(12)	2.363 (4)	Zn(1)-C(23)	2.31 (3)	C(11)-H(11)	0.89 (4)
Nb(1)-C(13)	2.367 (4)	Zn(1)-C(24)	2.36 (4)	C(12)-H(12)	0.92 (4)
Nb(1)-C(14)	2.367 (4)	Zn(1)-C(25)	2.37 (2)	C(13)-H(13)	0.87 (6)
Nb(1)-C(15)	2.383 (4)	C(11)-C(12)	1.405 (6)	C(14)-H(14)	0.84 (4)
		C(12)-C(13)	1.400 (6)	C(15)-H(15)	0.88 (4)

Table V. Selected Bond Angles (deg) for Cp_2NbH_2ZnCp

Zn(1)-Nb(1)-H(1)	51 (1)	C(13)-C(14)-C(15)	108.6 (4)	C(22)-C(23)-C(24)	108 (4)
Nb(1)-Zn(1)-H(1)	42 (1)	C(14)-C(15)-C(11)	107.9 (4)	C(23)-C(24)-C(25)	110 (4)
Nb(1)-H(1)-Zn(1)	88 (2)	C(15)-C(11)-C(12)	108.4 (4)	C(24)-C(25)-C(21)	104 (3)
C(11)-C(12)-C(13)	107.6 (4)	C(21)-C(22)-C(23)	107 (4)	C(25)-C(21)-C(22)	111 (3)
C(12)-C(13)-C(14)	107.5 (4)				

atoms were refined independently, using anisotropic thermal parameters for the non-hydrogen atoms. Weights were introduced in the final refinement stages. The refinement converged at $R_F = 0.023$ ($R_{wF} = 0.025$) for 127 parameters, 924 reflections, and $w^{-1} = (\sigma^2(F) + 0.001F^2)/0.79$. The highest features in the final difference Fourier were two peaks of ca. 0.4 e/Å^3 at ca. 1 Å from Nb and were considered to be absorption artifacts. Neutral atom scattering factors were taken from ref 13 and corrected for anomalous dispersion.[14] All calculations were carried out on the Cyber 175 of the University of Utrecht Computer Center. Programs used include SHELX-76 (structure determination and refinement),[15] PLATO (geometry analysis),[16] and ORTEP (plotting program).[17]

Results and Discussion

Tebbe obtained $(Cp_2NbH_2)_2Zn$ as the sole reaction product from Cp_2NbH_3 and Et_2Zn.[7] The greater reactivity of Cp_2Zn appears from the fact that it is able to effect substitution of a second hydrogen atom of Cp_2NbH_3. The product of the reaction of Cp_2Zn with Cp_2NbH_3 in 2:1 molar ratio is a yellow-orange crystalline compound, formed in quantitative yield, the ^1H NMR spectrum of which shows the presence of Cp(Zn), Cp(Nb), and H(Nb) groups in 2:2:1 ratio, in accordance with the stoichiometry $Cp_2NbH(ZnCp)_2$.[18] Hydrolysis of the product affords Cp_2NbH_3 quantitatively, indicating that it is a true substitution product and not an adduct like $Cp_2HNb{\rightarrow}ZnCp_2$. We have been unable to prepare $Cp_2Nb(ZnCp)_3$ by substitution of the third hydrogen atom of Cp_2NbH_3. Any excess Cp_2Zn over the 2:1 molar ratio used in the reaction described above is recovered unchanged, and $Cp_2Nb(ZnCp)_2$ remains the sole reaction product. It is possible to decrease the reactivity of Cp_2Zn by carrying out the reaction in a coordinating solvent (THF); this makes isolation of Cp_2NbH_2ZnCp possible. ^1H and ^{13}C NMR data for the three niobium-zinc compounds are given in Table II.

An ORTEP drawing of the Cp_2NbH_2ZnCp molecule, along with the adopted numbering scheme, is shown in Figure 1. Final atomic coordinates and thermal parameters are given in Table III, bond distances in Table IV, and selected bond angles in Table V. The molecule resembles that of Cp_2NbH_3,[19] with the central hydrogen atom replaced by a ZnCp group.[20] The Cp_2Nb fragment has a rather large bending angle of 145 (1)° (cf. Cp_2NbH_3, 141.6°;[19] $Cp_2Nb(CO)H$, 143°;[21] $Cp_2Nb(CO)H{\cdot}Zn(BH_4)_2$, 140.7°;[6] $[CpNb(C_5H_4)H]_2$, 140.4°;[22] $Cp_2Nb(C_2H_4)C_2H_5$, 132.4°[23]) but otherwise has a normal geometry, with a perpendicular metal-ring distance of 2.056 (8) Å and average Nb-C and C-C distances of 2.373 (5) and 1.392 (7) Å. The Cp(Zn) ring is bound in a nearly symmetrical η^5 fashion, with its center displaced slightly off the Nb-Zn axis (0.15 Å). The zinc-ring distance of 2.00 (5) Å resembles those in $(CpZn)_2Co(Cp)PPh_3$[8] (2.01 (1) and 2.02 (2) Å).

The most interesting feature of this structure is the bonding within the NbH_2Zn fragment. A structure with bridging hydrogen atoms and no direct Nb-Zn interaction has been proposed for $(Cp_2NbH_2)_2Zn$.[7] In $Cp_2Nb(CO)H{\cdot}Zn(BH_4)_2$ the presence of a hydrogen atom bridging a Nb-Zn dative bond has been established by X-ray diffraction analysis.[6] In Cp_2NbH_2ZnCp, the Nb-Zn distance of 2.5407 (7) Å indicates the presence of a normal Nb-Zn single bond; also, the Nb-H distance of 1.69 (4) Å is equal to the average Nb-H distance in Cp_2NbH_3[19] and somewhat shorter than the Nb-H distance (unrefined) of 1.75 Å in the hydrogen-bridged $Cp_2Nb(CO)H{\cdot}Zn(BH_4)_2$[6] (Figure 2). More significantly, the Zn-H distance of 1.97 (4) Å is larger than this distance in $Cp_2Nb(CO)H{\cdot}Zn(BH_4)_2$ (1.77 Å) and the terminal Zn-H distance in $[HZnN(Me)C_2H_4NMe_2]_2$ (1.62 Å by neutron diffraction[24]). Some Zn-H interaction is, however, indicated by the HNbZn angle of 51 (1)°, which is considerably smaller than the inner HNbH angles in Cp_2NbH_3 (61 (3) and 65 (3)°[19]). In accord with this, the Nb-H stretch vibration is shifted to longer wavelengths on going from Cp_2NbH_3 (1670, 1710 cm^{-1}) to Cp_2NbH_2ZnCp (1625 cm^{-1}); this shift is, however, far smaller than the one observed on going from $Cp_2Nb(CO)H$ (ν_{NbH} = 1682 cm^{-1} [25]) to $Cp_2Nb(CO)H{\cdot}Zn(BH_4)_2$ (ν_{NbH} = 1400 cm^{-1} [6]). For $(Cp_2NbH_2)_2Zn$, for which a structure with bridging hydrogen atoms has been proposed,[7] the Nb-H stretch vibrations are found at 1510 and 1560 cm^{-1}, which is more in accord with a structure intermediate between that found in Cp_2NbH_2ZnCp and a pure hydrogen-bridged structure.

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Conclusions

It is clear that hydrogen bridge formation is more important in $(Cp_2NbH_2)_2Zn$ than in Cp_2NbH_2ZnCp. In the former compound, the zinc atom is coordinatively unsaturated and tries to relieve this unsaturation by the formation of hydrogen bridges. In the latter compound, however, the zinc atom is already coordinatively saturated through η^5-coordination of the Cp(Zn) group, and hydrogen bridge formation is unnecessary.

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Registry No. $(Cp_2NbH_2)_2Zn$, 39430-61-0; $Cp_2NbH(ZnCp)_2$, 87432-58-4; Cp_2NbH_2ZnCp, 87432-59-5; Cp_2NbH_3, 11105-67-2; Cp_2Zn, 11077-31-9.

Supplementary Material Available: Listings of thermal parameters and structure factor amplitudes (7 pages). Ordering information is given on any current masthead page.

Tantalum–Zinc Compounds—Structure of $(CH_3C_5H_4)_2TaH(ZnC_5H_5)_2$

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From the reaction of $Cp'TaH_3$ ($Cp' = CH_3C_5H_4$) with Cp_2Zn, four different compounds containing tantalum–zinc bonds have been isolated: $(Cp'_2TaH_2)_2Zn$, Cp'_2TaH_2ZnCp, and two isomers of $Cp'_2TaH(ZnCp)_2$. The crystal structure of the most stable of the two isomers was determined by a single-crystal X-ray diffraction study. The compound crystallizes in the monoclinic space group $P2_1/n$ with four molecules in a cell of dimensions $a = 15.519$ (3) Å, $b = 8.461$ (4) Å, $c = 15.52$ (1) Å, and $\beta = 99.99$ (4)°. The least-squares refinement, with anisotropic thermal parameters for all non-hydrogen atoms, converged at $R_F = 0.036$ ($R_{wF} = 0.041$) for 1845 observed reflections and 293 parameters. The molecule resembles that of Cp_2TaH_3, with two adjacent hydrogen atoms replaced by ZnCp groups. The geometry of the Cp'_2Ta fragment is normal, with the methyl groups located approximately above and below the tantalum-bound hydride. The Cp(Zn) rings are bound in a somewhat asymmetrical η^5 fashion. On the basis of NMR evidence, a similar structure with the remaining hydride now occupying a central position is assigned to the less stable isomer of $Cp'_2TaH(ZnCp)_2$. The reaction of Cp_2Ta(olefin)H with Cp_2Zn proceeds with loss of olefin to give $Cp_2Ta(ZnCp)_3$ as the final product. According to NMR data, this compound has a structure analogous to that of Cp_2TaH_3, with all three hydrides replaced by ZnCp groups.

Introduction

In the preceding paper[1] we reported the synthesis and characterization of the two new niobium–zinc compounds, obtained from the reaction of Cp_2NbH_3 with Cp_2Zn. Attempts to extend these reactions to derivatives of other niobium hydrides were, however, hampered by the reactivity of these niobium compounds and their zinc derivatives. Therefore, we extended our investigations in transition-metal–zinc compounds[1-3] to the heavier group 5B metal tantalum. Several mixed-metal tantalum compounds are known: $Cp_2TaH_2SnMe_3$,[4] $\{[Cp_2Ta(\mu\text{-}SMe)_2]_2Pt\}Cl_2$,[5,6] and some salt-like derivatives of the hexacarbonyltantalate anion.[7,8]

No tantalum–zinc compounds have been reported up to now. Although Cp_2NbH_3 reacted with Et_2Zn to form $(Cp_2NbH_2)_2Zn$, reaction of Cp_2TaH_3 with Et_2Zn resulted only in formation of a loose adduct.[9] We have found that Cp_2Zn is generally more reactive toward transition-metal hydrides than dialkyl- and diarylzinc compounds.[1,2] Therefore, we decided to investigate the reactions of Cp'_2TaH_3 ($Cp' = CH_3C_5H_5$) and Cp_2Ta(olefin)H with Cp_2Zn.

Experimental Section

General Remarks. All manipulations were carried out in an atmosphere of dry, oxygen-free nitrogen. All solvents were dried and distilled under nitrogen prior to use. NMR spectra were

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