Inorg. Chem. **2002**, *41*, 6541–6543

Inorganic Chemistry
Communication

Synthesis of the (Dialkylamino)borate, $[Ph_2B(CH_2NMe_2)_2]^-$, Affords Access to N-Chelated Rhodium(I) Zwitterions

Theodore A. Betley and Jonas C. Peters*

Division of Chemistry and Chemical Engineering,
Arnold and Mabel Beckman Laboratories of Chemical Synthesis,
California Institute of Technology, Pasadena, California 91125

Received August 6, 2002

This paper reports the synthesis of the first bis(amino)borate ligand, $[Ph_2B(CH_2NMe_2)_2]^-$, an anionic equivalent of tertiary diamines. Anionic $[Ph_2B(CH_2NMe_2)_2]$ is an excellent bidentate ligand auxiliary and is used to prepare a series of N-chelated, zwitterionic rhodium(I) complexes.

Poly(pyrazolyl)borate ligands have played a prominent role in chemistry since their introduction by Trofimenko in 1966, evidenced by the fact that nearly 200 bis- and tris(pyrazolyl)borates have now been prepared.[1] Widespread interest in these and other uninegative N-donor ligand sets, such as the increasingly popular diketiminates, stems from their ubiquitous utility for research in bioinorganic model chemistry, C−H activation studies, and many areas of catalysis.[2] Currently absent from the available tool kit of anionic N-donor chelates are simple ligands that present tertiary amine donors to a coordinated metal center. The lack of such ligands is particularly striking given the longstanding interest in neutral tertiary amine chelates (e.g., tetramethylethylenediamine, TMEDA). As part of an interest in developing zwitterionic complexes featuring borate anions fastened to a coordinated metal center by neutral donor ligands that partially insulate the borate charge, we set out to prepare the simple bis(dialkylamino)borate, $[Ph_2B(CH_2NMe_2)_2]^-$, an anionic equivalent to potentially bidentate tertiary diamines. Herein, we report its synthesis and explore some of its initial rhodium coordination chemistry.

Our strategy for the assembly of the $[Ph_2B(CH_2NMe_2)_2]$ anion focused on delivering a nucleophilic carbanion, Me_2NCH_2Li, to a disubstituted borane electrophile, Ph_2BCl. A related strategy has been used recently in the synthesis of (thioether)borate ligands and sterically encumbered (diphenylphosphino)borate ligands.[3−4] Following the method of Tamborski, $[Me_2NCH_2Li]$ was generated by a transmetallation between ^nBuLi and $Me_3SnCH_2NMe_2$.[5] Unfortunately, attempts to smoothly deliver this carbanion to Ph_2BCl were unsuccessful. The complex mixtures that resulted presumably arose from kinetically competitive formation of Lewis acid/base adducts. Analysis of the product mixtures by electrospray MS revealed fragments consistent with small cyclic structures that we tentatively formulated as $\{Ph_2B(CH_2NMe_2)\}_x$ ($x = 2$ or 3).

To circumvent the competitive binding of the amine donor to the borane electrophile, we sought a versatile carbanion reagent in which the N-donor lone pair was protected. While BH_3 protection of tertiary phosphines can be an effective means for the synthesis of alkyl and arylphosphine carbanions (i.e., $R_2P(BH_3)CH_2Li$),[6] similar methods had not, to our knowledge, been explored for tertiary amine precursors.[7] The room temperature addition of ^nBuLi to a THF solution of $Me_3N{\cdot}BH_3$ cleanly afforded $Me_2N(BH_3)CH_2Li(THF)$ (**1**) as a white, microcrystalline solid (Scheme 1). This reagent provides a well-behaved carbanion source of trimethylamine.

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* Author to whom correspondence is addressed. E-mail: jpeters@caltech.edu.

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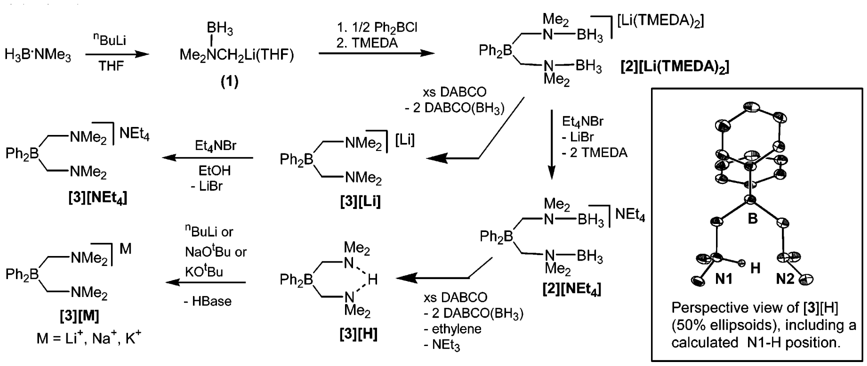
10.1021/ic0259336 CCC: $22.00

Scheme 1



Addition of isolated **1** to half an equivalent of diphenylchloroborane (25 °C; toluene) generated the borane-protected amino(borate) complex [$Ph_2B(CH_2N(BH_3)Me_2)_2$][Li], [**2**][Li]. This species was conveniently precipitated from diethyl ether by addition of TMEDA to produce [**2**][Li(TMEDA)$_2$] as a white solid. To derive the target ligand, we canvassed myriad potentially suitable methods to remove the borane protecting group from [**2**]. Borane liberation from alkylamines is traditionally accomplished by transfer to another strong Lewis base, acidification, or oxidation.[6,8] Unfortunately, [**2**] degraded to $Me_3N{\cdot}BH_3$ on exposure to strong acid (e.g. HCl) and resisted borane oxidation in the presence of Pd/C in methanol (25 wt % Pd/C, 3 days, 25 °C). We thus focused on a Lewis base deprotection strategy.

Because the target ligand [$Ph_2B(CH_2NMe_2)_2$] should itself be an extremely good Lewis base, most reagents proved ineffective. For example, incubation of [**2**] in neat solutions of morpholine, pyrrolidine, piperidine, or tributylphosphine at 100 °C for a period of days afforded no deprotection. A large excess of less encumbered phosphines, such as PMe_3 and PEt_3, did provide a modest degree of deprotection above 80 °C over several days; however, clean product was not isolable with these reagents. The system of choice proved to be a 25-fold excess of 1,4-diazabicyclo[2.2.2]octane (DABCO) (toluene, 100 °C, complete and quantitative after 10 h as determined by ^{11}B NMR). The excess DABCO was effectively recovered by sublimation (60 °C, 10 Torr), and the target ligand [$Ph_2BN^{Me}{}_2$] was isolated as its lithium salt [$Ph_2B(CH_2NMe_2)_2$][Li], [**3**][Li], in yields that typically exceeded 80%. The ammonium salt [**3**][NEt_4] formed readily upon addition of an ethanolic solution of Et_4NBr to [**3**] [Li].

An initial attempt to deprotect the ammonium salt [**2**]-[NEt_4] under similar conditions resulted in a Hoffmann degradation reaction that led to the formation of [**3**][H],[9] whose solid-state structure is represented in Scheme 1.[10] The fortuitous formation of this free acid derivative provided ready access to a range of other salts, [**3**][M^+], by simple base deprotonation (where M^+ = Li, Na, K from ^{n}BuLi, NaO^{t}Bu, and KO^{t}Bu, respectively; see Scheme 1).

Having established the synthesis of several useful salts of the target [$Ph_2B(CH_2NMe_2)_2$] anion, we have begun to examine its utility to support metal complexes and wish to introduce this by way of its initial rhodium(I) chemistry. The lithium salt [**3**][Li] underwent facile transmetallation with {(NBD)RhCl}$_2$ to afford the crystalline yellow rhodium complex [$Ph_2B(CH_2NMe_2)_2$]Rh(NBD) (**4**) (NBD = norbornadiene) in 86% isolated yield. Complex **4** was thoroughly characterized, and it is noteworthy that the parent ion was detected by electrospray mass spectroscopy (ES-MS). NBD adduct **4** is formally zwitterionic, and unlike related (pyrazolyl)borate ligands, simple resonance contributors that delocalize the anionic borate charge to the amine donor groups are not available. To a first approximation, this is also true of (phosphino)- and (thioether)borate ligands, though it seems likely that different donor arms would insulate the tethered borate unit to varying degrees. To ascertain whether any ion-pairing of the borate unit to the partially "cationic" rhodium center would be observed in the solid state, we performed an X-ray diffraction study on a single crystal of **4**.[11] Figure 1 depicts two views of **4** and reveals that the diphenylborate unit resides at a position quite removed from the rhodium metal center (Rh−B = 3.672 Å, Figure 2a). In fact, the borate unit appears to be fastened as far from the rhodium center as possible: a vector bisects the molecule that contains the bridgehead methylene of the NBD ligand, the Rh center, and the borate itself. This conformation is very different from that typically adopted by square planar bis(pyrazolyl)borate complexes, where appreciable canting of the chelate ring forces the borate unit much closer to the coordinated metal center. For example, the previously reported bis(ethylene) derivative [$H_2B(pz)_2$]-Rh(C_2H_4)$_2$, also represented in Figure 2, adopts a puckered ligand confirmation that places the borate unit 2.998 Å away from the bound rhodium atom. This distance is 0.67 Å shorter than the Rh−B distance in **4**.[12]

To obtain comparative data pertaining to the donor strength of anionic [**3**], we prepared the dicarbonyl complex [$Ph_2B(CH_2NMe_2)_2$]Rh(CO)$_2$ (**5**), which proceeded quantitatively upon

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(10) [**3**][H] ($C_{18}H_{27}BN_2$): MW = 282.23, colorless prism, collection temperature = 98 K, monoclinic, space group $P2_{1/n}$, a = 7.787(3) Å, b = 13.571(1) Å, c = 15.931 Å, α = 90°, β = 91.47(2)°, γ = 90°, V = 1683.15(3) Å^3, Z = 4, R_1 = 0.0855 [$I > 2\sigma(I)$], GOF = 1.158.

(11) **4** ($C_{25}H_{34}BN_2Rh$): MW = 476.27, yellow plate, collection temperature = 98 K, monoclinic, space group $P2_{1/n}$, a = 12.233(1) Å, b = 9.538(2) Å, c = 18.599(5) Å, α = 90°, β = 91.504(4)°, γ = 90°, V = 2194.12(3) Å^3, Z = 4, R_1 = 0.0805 [$I > 2\sigma(I)$], GOF = 1.102.

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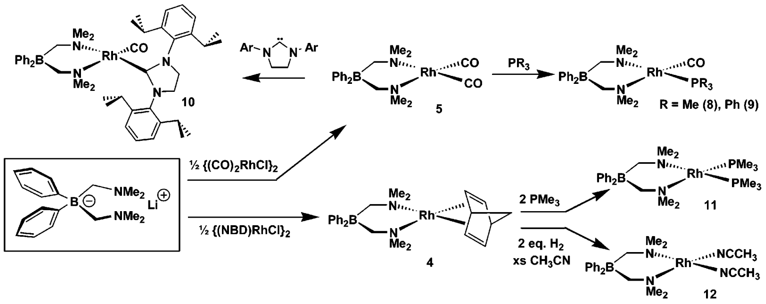
Scheme 2



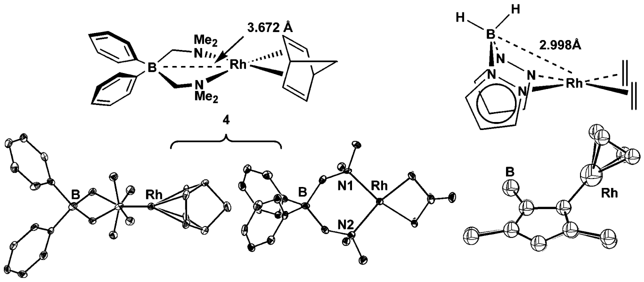
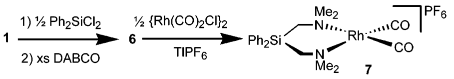


Figure 1. 50% displacement ellipsoid representation of **4** (two perspectives) and a structural representation of the previously reported complex $[H_2B(Pz)_2]Rh(C_2H_4)_2$. Rh−B bond distances are indicated.

Scheme 3



addition of [**3**][Li] to $\{Rh(CO)_2Cl\}_2$. Dicarbonyl **5** exhibits the two expected bands in the carbonyl region (ν(CO), CH_2Cl_2/KBr: 2070, 1992 cm^{-1}). These bands are appreciably lower in frequency than those previously reported for the cationic complex $[(TMEDA)Rh(CO)_2][ClO_4]$ (ν(CO), CH_2Cl_2/KBr: 2080, 2010 cm^{-1}). To provide an electronic comparison to an isostructural cation, we also prepared the salt $[Ph_2Si(CH_2NMe_2)_2]Rh(CO)_2][PF_6]$, **7**.[13] Addition of a THF solution of $\{Rh(CO)_2Cl\}_2$ to a solution of $Ph_2Si(CH_2NMe_2)_2$ (**6**) and $[Tl][PF_6]$ produced **7** for spectroscopic comparison (Scheme 3). The ν(CO) vibrations for **7** (KBr/CH_2Cl_2) were observed at 2097 and 2030 cm^{-1}, much higher in frequency than for zwitterionic **5** and somewhat higher than those observed for $[(TMEDA)Rh(CO)_2][ClO_4]$. The difference in ν(CO) between **5** and **7** likely arises from differences in electrostatic polarization effects for the two systems, in addition to some delocalization of the borate charge through the σ-framework for zwitterionic **5**. It is also interesting to compare the carbonyl stretches for **5** with those of a related bis(pyrazolyl)borate complex, $[H_2B(pz)_2]Rh(CO)_2$, which exibits ν(CO) stretches at 2088 and 2022 cm^{-1}.[14] That the ν(CO) bands of **5** are so much lower in frequency than those of $[H_2B(pz)_2]Rh(CO)_2$ is somewhat surprising given the increased potential for anionic charge delocalization in the latter, but is consistent with the notion that a trialkylamine ligand is a stronger σ-donor and also a poorer π-acid than a pyrazolyl ligand.

While the reactivities of "$[Ph_2B(CH_2NMe_2)_2]Rh(I)$" fragments have yet to be thoroughly explored, we can report on the synthesis of several promising synthons for future study. For example, the room temperature addition of the tertiary phosphines PMe_3 and PPh_3 to **5** provided the monocarbonyl derivatives $[Ph_2B(CH_2NMe_2)_2]Rh(CO)(PMe_3)$, **8**, and $[Ph_2B(CH_2NMe_2)_2]Rh(CO)(PPh_3)$, **9**, respectively. Likewise, the substitution of one carbonyl ligand on **5** by a bulky, saturated Arduengo-type carbene, (1,3-bis-(2,6-diisopropylphenyl)-imidazole-2-ylidene), gave rise to the monocarbonyl complex $[Ph_2B(CH_2NMe_2)_2]Rh(CO)$(carbene), **10**. The bis(phosphine) complex $[Ph_2B(CH_2NMe_2)_2]Rh(PMe_3)_2$, **11**, formed on stirring **4** in the presence of 2 equiv of phosphine. All of these substitutions proceeded quantitatively according to their crude NMR spectra, and isolated yields generally exceeded 80% (Scheme 2). To derive a precursor with relatively labile coligands, norbornadiene adduct **4** was subjected to hydrogenative conditions in the presence of excess acetonitrile. This led rapidly and in good yield to the isolable solvento complex $[Ph_2B(CH_2NMe_2)_2]Rh(CH_3CN)_2$, **12**. The stability of zwitterionic **12** is to be contrasted with its cationic analogue $[Ph_2Si(CH_2NMe_2)_2]Rh(CH_3CN)_2][PF_6]$, which we could not isolate. An attempt to hydrogenate $[Ph_2Si(CH_2NMe_2)_2]Rh(NBD)][PF_6]$ (**13**) in the presence of excess acetonitrile, first prepared by a method analogous to that used in the generation of **4** using $\{(NBD)RhCl\}_2$, resulted in the rapid precipitation of rhodium(0). Finally, we note the encouraging result that complex **12** mediated the rapid catalytic reduction of styrene in d_6-acetone (see Supporting Information). Studies are underway to further probe the reactivity of the amine-chelated zwitterions described here.

Acknowledgment. We thank the NSF (Grant CHE-0132216), the ACS Petroleum Research Fund, and the Dreyfus Foundation for financial support. T.A.B. thanks the Department of Defense for a graduate research fellowship.

Supporting Information Available: Experimental protocols and characterization data; crystallographic data for complex [**3**]-[H] and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) Neutral amine ligand $Ph_2Si(CH_2NMe_2)_2$ was prepared first by delivery of **1** to Ph_2SiCl_2 to form $Ph_2Si(CH_2N(BH_3)Me_2)_2$ in 95% yield. $Ph_2Si(CH_2N(BH_3)Me_2)_2$ was then deprotected by DABCO to provide $Ph_2Si(CH_2NMe_2)_2$ in 92% isolated yield.

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