preparation procedure to produce the (2×1) reconstruction of Pt(110). Hence, our conclusion is that the rate of CO bond scission varies very strongly with surface structure and the details of the sample preparation procedure. This may explain why bond scission was observed by Levis et al.[1,3] and Madix[4] but not by Guo et al.,[2] Sexton,[5] or Gibson.[29]

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Registry No. CH_3OH, 67-56-1; Pt, 7440-06-4.

Communications to the Editor

Synthesis of the First Distillable α-Boranyldiazomethane. Direct Evidence of Lithioboranyldiazomethane–Lithioboranylisodiazomethane [(>BCNN⁻,Li⁺)–(>BNNC⁻,Li⁺)] Rearrangement

Marie-Pierre Arthur, Antoine Baceiredo, and Guy Bertrand*

Laboratoire de Chimie de Coordination du CNRS
205 route de Narbonne, 31077 Toulouse Cêdex, France

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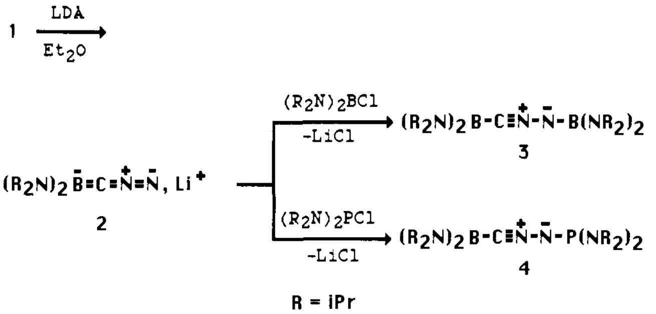
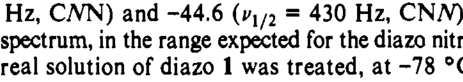
Main group element substituted diazo compounds have been widely studied[1] except in the boron series. Indeed, only two examples of C-substituted α-boranyldiazomethanes, characterized by IR in solution, have been reported so far.[2] The lack of examples of this class of compounds is probably due to the ability of Lewis acids to catalyze the decomposition of diazo derivatives.[1] Boron-stabilized carbanions A have been widely used in organic synthesis, and X-ray diffraction studies have shown that they present a boron–carbon double bond character.[3] We have recently shown that (diazomethylene)phosphoranes B are stable at room temperature and that they are diazocarbene (:C=N$_2$) or naked carbon atom generators, as well as powerful building blocks in heterocyclic chemistry.[4] Thus it was of interest to try preparing a new type of cumulene C, featuring both a diazo group and a borataalkene moiety.

A B C

In the hope of obtaining a stable C-unsubstituted α-boranyldiazomethane, and to further produce a carbanion α to boron, we chose to synthesize [bis(diisopropylamino)boranyl]diazomethane (**1**). The attachment to boron of heteroatoms that are capable of π-donation is of primary importance to decrease the Lewis acidity and to prevent, in the second step, attack on the boron atom itself by the base, which would lead to a coordinatively saturated borate complex. Compound **1** is easily available by addition of a stoichiometric amount of bis(diisopropylamino)chloroborane[5] to an ethereal solution of the lithium salt of diazomethane,[6] at −78 °C.

Scheme I





$$(R_2N)_2BCl + HCN_2Li \xrightarrow[-78°C]{Et_2O} (R_2N)_2B-\underset{\underset{N_2}{\|}}{C}-H$$

R : iPr **1**

Diazoborane **1** is thermally stable and was obtained in 54% yield as a yellow oil after distillation (bp 70–74 °C/10^{-1} mmHg). The spectroscopic data[7] allowed exclusion of all its possible structural isomers; of particular interest were a strong IR absorption at 2071 cm^{-1} (ν CN$_2$), a signal at 36.5 ppm (J_{CH} = 169.5 Hz) broadened by the proximity of boron in the ^{13}C NMR spectrum, a signal at +34.5 in the ^{11}B NMR spectrum, and two signals at −114.2 ($\nu_{1/2}$ = 80 Hz, C*N*N) and −44.6 ($\nu_{1/2}$ = 430 Hz, CN*N*) in the ^{14}N NMR spectrum, in the range expected for the diazo nitrogens.[8]

An ethereal solution of diazo **1** was treated, at −78 °C, with a slight excess of lithium diisopropylamide (LDA). After stirring for a few hours at room temperature, the sharp IR absorption due to the diazo **1** was replaced by a broad band at 2080 cm^{-1}, and a new broad signal appeared at 26 ppm in the ^{11}B NMR spectrum. Addition of bis(diisopropylamino)chloroborane and bis(diisopropylamino)chlorophosphane to this ethereal solution of **2** af-

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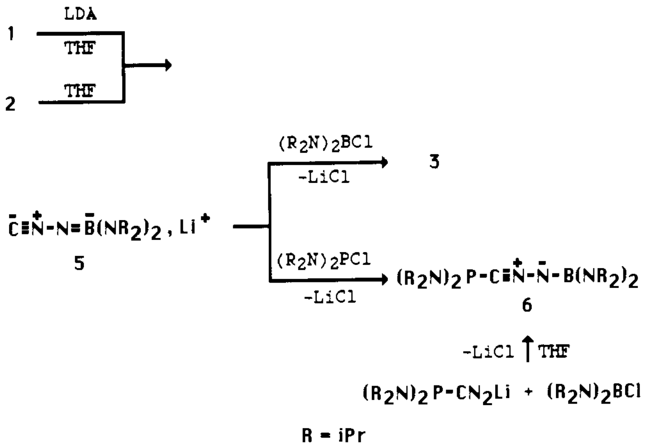
(6) The lithium salt of diazomethane was prepared by a modification of the published procedure: (a) Müller, E.; Ludsteck, D. *Chem. Ber.* **1954**, *87*, 1887. (b) Müller, E.; Rundel, W. *Chem. Ber.* **1955**, *88*, 917; **1957**, *90*, 1299, 1302, 2673.

(7) All isolated compounds afforded satisfactory elemental analysis. Selected physical data are the following. **1**: ^{1}H NMR (C_7D_8, 298 K) 1.05 (d, J_{HH} = 6.6 Hz, 24 H, CH$_3$), 3.17 (s, 1 H, CN$_2$H), 3.47 (sept, J_{HH} = 6.6 Hz, 4 H, CH); ^{13}C NMR (C_7D_8, 223 K) 22.90 (s, CH$_3$), 36.51 (s, CN$_2$), 45.89 (s, CH). **3**: yellow oil, bp 110–120 °C/10^{-3} mmHg; ^{11}B NMR (C_7D_8, 363 K) +23.5, +27.8; ^{13}C NMR (C_7D_8, 223 K) 65.8 (br s, CNN); ^{14}N NMR (C_7D_8, 348 K) −186.4 ($\nu_{1/2}$ = 140 Hz, C*N*N), −285 ($\nu_{1/2}$ = 1300 Hz, NR$_2$); IR (ether) 2160 cm^{-1}. **4**: yellow oil, bp 105–110 °C/10^{-3} mmHg; ^{11}B NMR (C_6D_6) +22; ^{31}P NMR (C_6D_6) +96.6; ^{13}C NMR (C_6D_6) 67.0 (br s, CNN); ^{14}N NMR (C_6D_6, 298 K) −184.4 ($\nu_{1/2}$ = 220 Hz, C*N*N), −320 ($\nu_{1/2}$ = 1500 Hz, NR$_2$); IR (ether) 2145 cm^{-1}. **6**: yellow oil, bp 110–115 °C/0.2 mmHg; ^{11}B NMR (CDCl$_3$) +29; ^{31}P NMR (CDCl$_3$) +45.1; ^{13}C NMR (C_6D_6) 61.87 (d, J_{PC} = 48.3 Hz, CNN); IR (CDCl$_3$) 2113 cm^{-1}.

(8) The ^{14}N NMR signals of diazo compounds are in the range −110 to −125 for C*N*N and −20 to −74 for CN*N*, while for nitrilimines only one nitrogen (C*N*N) is observable between −170 and −215: Horchler v. Locquenghien, K.; Reau, R.; Bertrand, G., submitted for publication.

0002-7863/91/1513-5856$02.50/0

Scheme II



forded nitrilimines **3** and **4** in 85 and 80% yield, respectively. These first boranyl nitrilimines were stable enough to be purified by distillation and were unambiguously characterized by spectroscopy.[7] The isolation of **3** and **4** strongly supports the formation of lithioboranyldiazomethane **2**, since we have already shown that the lithium salts of various α-heterosubstituted diazomethanes react with bulky electrophiles at the nitrogen end, rather than at carbon, to give nitrilimines[9] (Scheme I). Whether compound **2** has a linear or slightly bent structure remains an open question as in the case of (diazomethylene)phosphoranes.[4]

Surprisingly, when the reaction of diazo **1** with LDA was carried out in THF, instead of ether, a different species (**5**), characterized by IR (2048 cm^{-1}, weak) and ^{11}B NMR (+25, broad), was obtained. Addition of bis(diisopropylamino)chloroborane to a THF solution of **5** led again to *C*- and *N*-boranyl nitrilimine **3** (80% yield), but interestingly the addition of bis(diisopropylamino)-chlorophosphane did not give rise to the *C*-boranyl *N*-phosphanyl nitrilimine **4**, but to its isomer the *C*-phosphanyl *N*-boranyl nitrilimine **6**, in 70% yield. The structure of **6** was confirmed by comparison of its spectroscopic data[7] with those of a sample prepared by reacting the lithium salt of [bis(diisopropylamino)-phosphanyl]diazomethane with bis(diisopropylamino)chloroborane (Scheme II).

The striking difference observed in the reaction of **1** with LDA, depending on the solvent, could only be rationalized by postulating the rearrangement of the first-formed species **2** into its structural isomer **5**, induced by the basicity of THF compared with that of ether. Indeed, it was possible to prepare **2** in ether and then to remove the solvent under vacuum, and the subsequent addition of THF gave rise to **5**. This rearrangement appeared to be irreversible since **5**, prepared in THF, did not isomerize into **2** in ether (Scheme II).

It is of interest to note that Hart[10] has calculated that HCNN$^-$ would be more stable than CNNH$^-$ by approximately 6 kcal/mol. These calculations also predicted that protonation of CNNH$^-$ was more likely to occur at the nitrogen atom to give isocyanamide CNNH$_2$, while protonation of HCNN$^-$ should occur at the carbon atom to give diazomethane. In other words, the proton affinity for nitrogen over carbon in CNNH$^-$ would be exactly reversed in HCNN$^-$. Since nitrilimine has been calculated[10,11] to be the least stable isomer of diazomethane, from thermodynamic and kinetic considerations the nitrilimine should never be obtained from HCNN$^-$ or CNNH$^-$. We have already shown that the use of heteroatoms such as phosphorus and silicon allows the preparation of stable nitrilimines;[9] the results reported here demonstrate that the use of boron totally reverses the scale of kinetic behavior of diazomethane salts and greatly modifies their thermodynamic behavior.

Acknowledgment. Thanks are due to the CNRS for financial support of this work.

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[2 + 2] Cycloaddition of Re–Re Quadruple Bonds. Structural Characterization of the First Cyclotetrarhenium Diynes, $(n\text{-Bu}_4\text{N})_2\text{Re}_4\text{Cl}_8(\mu\text{-O})_2(\mu\text{-OMe})(\mu\text{-X})$ (X = Cl or OMe)

Jhy-Der Chen and F. Albert Cotton*

Department of Chemistry and
Laboratory for Structure and Bonding
Texas A&M University, College Station, Texas 77843

Received April 19, 1991

Quadruply bonded dinuclear complexes containing a Mo–Mo,[1,2] W–W,[3] or Mo–W[4] unit have been found to be able to dimerize to form rectangular clusters. A detailed report describing the preparative route for the molybdenum compounds has also been published.[5] The quadruply bonded complexes undergo [2 + 2] cycloaddition by loss of the δ components. Two single bonds are then formed to join the triply bonded dimers together.[5,6] The reactions were believed to be initiated by dissociation of phosphine ligands from the dinuclear complexes, with subsequent coupling of the coordinatively unsaturated dimer through bridging chloride.[5] Such complexes are interesting because they result from an important new type of reactivity of complexes containing metal–metal quadruple bonds. Previous efforts in this laboratory to prepare analogous rhenium compounds, i.e., four-membered Re$_4$ rings with Re–Re triple bonds and Re–Re single bonds bridged by Cl atoms, all failed. However, we have now succeeded in obtaining compounds that differ in having bridging oxygen atoms.

The complex $(n\text{-Bu}_4\text{N})_2\text{Re}_4\text{Cl}_8(\mu\text{-O})_2(\mu\text{-OMe})(\mu\text{-Cl})$ (**1**) was obtained by refluxing the quadruply bonded complex $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ in MeOH and H$_2$O for 6 h.[7] The reaction proceeded according to eq 1.

$$2(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8 + \text{MeOH} + 2\text{H}_2\text{O} \rightarrow (n\text{-Bu}_4\text{N})_2\text{Re}_4\text{Cl}_8(\mu\text{-O})_2(\mu\text{-OMe})(\mu\text{-Cl}) + 2(n\text{-Bu}_4\text{N})\text{Cl} + 5\text{HCl} \quad (1)$$

Crystals of this complex conform to the space group *Pbca* with eight molecules in the unit cell.[8] Figure 1 shows an ORTEP

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[7] $(n\text{-Bu}_4\text{N})_2\text{Re}_2\text{Cl}_8$ (0.2 g) was placed in a flask containing 40 mL of methanol and 0.05 mL of water. The mixture was heated to reflux for 6 h, resulting in a deep brown solution. The solvent was evaporated and the solid dissolved in THF. The solution was filtered, and an excess of *n*-hexane was added to precipitate the deep brown product. Yield: 0.06 g (35%). Crystals suitable for X-ray crystallographic analysis were obtained by layering a CH$_2$Cl$_2$/THF solution of the product with *n*-hexane.