structure, shown in Figure 1, which is based on an octadeca-
hedron missing two adjacent vertices.

The formation of the complex I can be envisaged as the
direct insertion of the metal atom above the B (5, 9, 8, 1)
face of the anion with the loss of two hydrogens, followed
by the rearrangement of the cage-framework. However, it
is surprising that complex II is the only product of the (CO)2
MnBr reaction since its formation requires degradation of
the starting hypho-Sb2B10.

The reaction of [Cp*RhCl(pz)] with
hypho-Sb2B10 also resulted in cage degradation, and gave
the six-boron cluster archachno-7-Cp*Rh-8,8-Sb2B10. III. Thus
the reaction leading to the formation of the compounds involves
either the direct insertion or the degradative insertion of
a metal atom to the cage-framework.

The work presented here has resulted in the production of
a variety of new metalladithiaborane clusters with cage
framework compositions including S2B4 and S3B5. These
results also suggest that an even wider range of metalla dithi-
aborane clusters are possible.

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3. In a typical experiment, a solution of Na+ S2B4H4 was
prepared by the reaction in vacuo of excess NaH (~0.1
g. 4.2 mmol) with archachno-6,8-S2B4H9 (0.45 g, 3.0 mmol)
in dimethoxyethane (~25 mL) at ~ -20°C. The solution
was allowed to warm slowly to room temperature and
refluxed overnight. 11B-NMR spectra taken at this point
confirmed the exclusive formation of hypho-Sb2B10. The
solvent was removed in vacuo and the residue dissolved
in 20 mL of methylene chloride. This suspension was
maintained at ~5°C while 5 mL of 1 M HCl in EtOH was
added. The solution was stirred for 30 min and the
methylene chloride layer then filtered. Subsequent vacuum
sublimation of the resulting mixture gave 0.21 g
(0.9 mmol) of hypho-Sb2B10. This corresponds to a 67.75%
yield based on consumed archachno-6,8-S2B4H9.
4. 11B-NMR (64.2 MHz, ppm, C6D6) 14.2 (d, B2, JBB = 150 Hz),
-2.0 (d, B6, JBB = 180 Hz), -4.9 (d, B6, JBB = 200 Hz),
-8.0 (d, B6, JBB = 170 Hz), -21.8 (d, B6, JBB = 180 Hz),
-26.1 (d, B6, JBB = 150 Hz), -40.8 (d, B6, JBB = 180 Hz),
2D 11B-11B COSY NMR (64.2 MHz, ppm, C6D6, 11B spin-
decoupled) B2-B6, B2-B5, B5-B6, B5-B4, B4-B6, B4-B5,
B5-B4, B3-B2; 11B-NMR (200.13 MHz, ppm, C6D6, 11B spin-
decoupled) 3.9 (s, CH of C6H3), -0.7 (s, HBB); Exact mass
called for 11B2C16H20Mn6O4S8, 367.8054, found 367.8051; Rf =
0.76 in Benzene; Mp = 79-82°C; IR spectrum (KBr pellet, cm-1)
2960s, 2920s, 2860s, 2550s, 2530s, 1470m, 1420m, 1380m, 1270m,
1200v, 1100v, 1030m, 980v, 880v, 840v, 820w, 780w, 760w, 700v,
650w, 610w, 570w, 540w, 380v.
5. 11B-NMR (64.2 MHz, ppm, C6D6) 4.0 (d, B2, JBB = 150 Hz),
-20.1 (d, B6, JBB = 130 Hz), -22.1 (dt, B6, JBB = 120 Hz),
-52.8 (d, B6, JBB = 150 Hz); 2D 11B-11B COSY NMR (64.2
MHz, ppm, C6D6, 11B spin-decoupled) B2-B6, B2-B5, B5-B4,
B6-B1, B3-B2; 11H-NMR (200.13 MHz, ppm, C6D6, 11B spin-
decoupled) -0.6 (t, HBB), -1.6 (s, HBB); Exact mass called
called for 11B2C16H20Mn6O4S8, 367.8054, found 367.8051; Rf =
0.57 in hexane; Mp = 95-96°C; IR spectrum (KBr pellet,
cm-1) 2970s, 2940s, 2910s, 2860s, 2600m, 2590m, 2580m,
2560m, 2100s, 2020s, 2000s, 1980s, 1960s, 1940w, 1550w,
1470w, 1460w, 1270w, 1100w, 1050w, 1010m, 990m, 870m,
850w, 820w, 770w, 740w, 700w, 670m, 620m, 450m, 430m.
6. 11B-NMR (64.2 MHz, ppm, C6D6) 3.9 (d, B6, JBB = 160 Hz),
-9.4 (d, B6, JBB = 170 Hz), -35.0 (dt, B6, JBB = 130 Hz),
-40.8 (d, B6, JBB = 130 Hz); 2D 11B-11B COSY NMR (64.2
MHz, ppm, C6D6, 11B spin-decoupled) B2-B6, B2-B5, B5-B4,
B6-B1; 11H-NMR (200.13 MHz, ppm, C6D6, 11B spin-decoupled)
0.3 (s, CH of C6H3), -0.7 (s, HBB); Exact mass called
called for 11B2C16H20Mn6O4S8, 376.8054, found 376.8051; Rf =
0.76 in Benzene; Mp = 90-92°C; IR spectrum (KBr pellet, cm-1)
2960s, 2920s, 2860s, 2570w, 2550s, 2530s, 1470m,
1420m, 1380m, 1270m, 1200v, 1100v, 1030m, 980v, 880v,
810s, 750w, 670w, 580w, 420w, 410w.
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Preparation of N-Carbethoxymethyl-C-alkyl(or aryl)nitrone
and Their 1,3-Dipolar Cycloaddition to Alkenes

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Nitrones are valuable synthetic intermediates and excel-
 lent 1,3-dipoles. They have been utilized for the synthesis of
various nitrogen containing biologically active compounds,
e.g., alkaloids1 and β-lactams2. Preparation of nitrones has
usually been achieved either by condensation of aldehydes
with hydroxylamines3 or by oxidation of N,N-dialkylhydroxyl-
amines4.

During the preparation of various 1,3-dipolar cycloadducts
as the possible starting materials for the construction of car-
bapenem skeleton, we thought that it would be interesting
to develop a method for the preparation of N-carbethoxymeth-
nitrilones (2). Examination of literature did not reveal any
reported method. Recently, we found that N-carbethoxyme-

thyl nitrones (2) could be synthesized easily by the condensation of N-hydroxyglycine ethyl ester (1) with aldehydes. Furthermore, the nitrones reacted with various alkenes very well to give 1,3-dipolar cycloadducts in good yields. In this communication we would like to report the results.

N-Hydroxyglycine ethyl ester (1) was synthesized following the method reported by the Herscheld. Reduction of ethyl N-hydroxyiminocetate was achieved with 5 eq. borane-pyridine complex in 54% yield. The condensation of N-hydroxyglycine ethyl ester with aldehydes at refluxing benzene gave the corresponding nitrones in good yields. Thus, refluxing of N-hydroxyglycine ethyl ester (1) (0.28 g, 2.35 mmol) with 2,2-dimethyl-3-hydroxypropanol (0.24 g, 2.35 mmol) in benzene (10 mL) for 3 hr under nitrogen gave the nitrone 2 (0.43 g, yield 90%): 1H-NMR (CDCl3), δ 1.22 (s, 1H), 1.28 (t, 3H), 3.57 (s, 2H), 4.23 (q, 2H), 4.50 (s, 2H), 4.85 (brs, 1H), 6.55 (s, 1H); IR (KBr) 3500, 1745, 1605, 1420, 1205 cm⁻¹; UV (95% EtOH), λmax = 236 nm (ε = 36,000).

When acetaldehyde, propionaldehyde or butyraldehyde was stirred with N-hydroxyglycine ethyl ester in benzene in the presence of molecular seives 3 Å at room temperature, nitrones 2a-2c were produced in good yields also. The nitrones obtained by these methods are summarized in Table 1.

Refuxing of the N-carboxbenzoxymethyl nitrones (2) with alkenes in benzene gave 1,3-cycloadducts (3) in good yields. Thus, refluxing of N-carboxbenzoxymethyl-C-ethyl nitrone (2b) (0.159 g, 1.0 mmol) with diethyl fumarate (0.344 g, 2.00 mmol) in benzene (10 mL) for 8 hr under nitrogen gave a pale green liquid after removing solvent. It was purified by chromatography on silica gel using hexane-ethyl acetate (6:1) as an eluent to give 2-carboxbenzoxymethyl-4,5-diethoxycarbonyl-3-ethylisoxazolidine (3a) (0.28 g, yield 84%): 1H-NMR (CDCl3), δ 0.70-1.72 (m, 14H), 3.00-3.86 (m, 3H), 3.90-4.66 (m, 7H), 4.87 (d, J=8.4 Hz, 1H); IR (neat), 2990, 1745, 1480, 1380, 1200, 1040 cm⁻¹. The isoxazolidine derivatives obtained by this method are summarized in Table 2.

Currently, the transformation of the 1,3-dipolar cycloadducts to carbapenem skeletons is under investigation.

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References


Molecular Recognition of Butylamines by Calix[4]-crown Ethers

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Numerous attempts have been made to modify and endow unique binding characteristics to the crown ethers. Of these,