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Preparations of Copper(I) Complexes Ligated with Novel Hindered Pyrazolylborates

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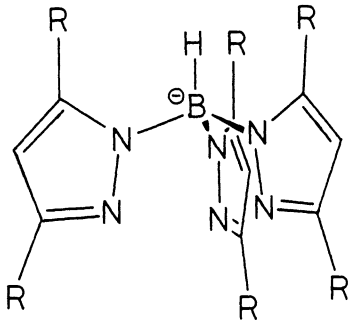
Novel hindered pyrazolylborates, $HB(3,5\text{-}Ph_2pz)_3^-$ and $HB(3,5\text{-}iPr_2pz)_3^-$ were synthesized. Several copper(I) complexes ligated with these ligands were prepared and their properties are compared with the corresponding complexes with conventional pyrazolylborate as ligand.

The use of tripod nitrogen ligands, hydrotris(1-pyrazolyl)borate, $HBpz_3^-$ and hydrotris(3,5-dimethyl-1-pyrazolyl)borate, $HB(3,5\text{-}Me_2pz)_3^-$, is very effective for preparation of a variety of transition metal complexes.[1] Especially, the geometry (as well as strong electron donating property of $HB(3,5\text{-}Me_2pz)_3^-$) is favorable for the synthesis of model compounds of several metalloproteins since coordination of multi-histidyl nitrogen atoms is often observed in metalloproteins, e.g., superoxide dismutase, hemerythrin, hemocyanin, cytochrome c oxidase. Recent successes by Lippard et al.[2] and us[3] for the synthesis of model complexes of methemerythrin and oxyhemocyanin clearly prove that this is the case. We have now developed novel hindered pyrazolylborates $HB(3,5\text{-}Ph_2pz)_3^-$ (**1**) and $HB(3,5\text{-}iPr_2pz)_3^-$ (**2**). The preparation and characterization of several copper(I) complexes using **1** and **2** are described herein.



1 R=Ph
2 R=iPr

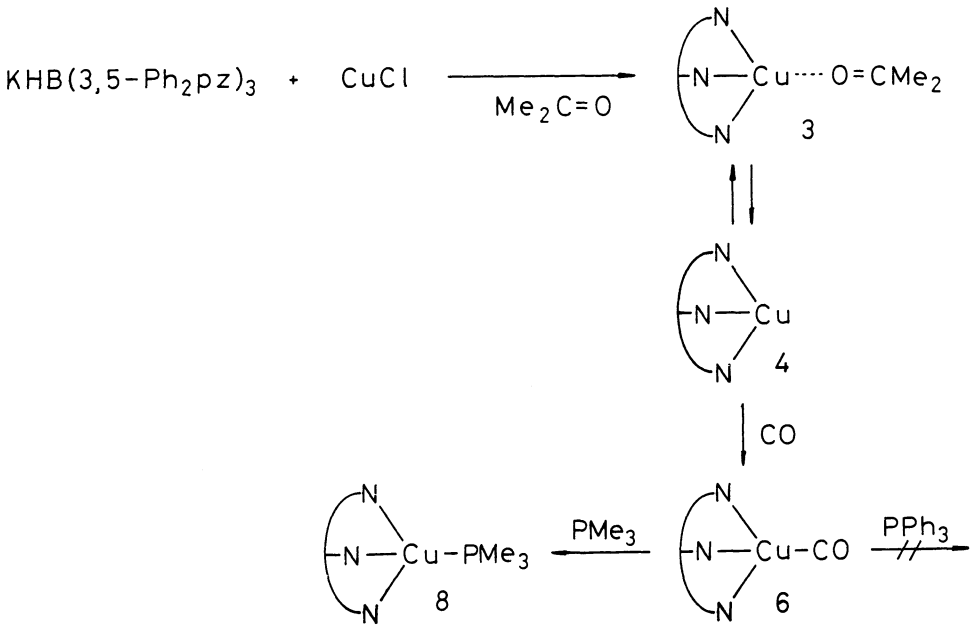
The potassium salts of **1** and **2** were prepared in a manner analogous to that for $KHBpz_3$.[4] 3,5-Diphenylpyrazol and 3,5-diisopropylpyrazol were synthesized by the reaction of dibenzoylmethane and diisobutyrylmethane with hydrazine,[5] respectively. KBH_4 was heated in the presence of 4.0 equiv. 3,5-diphenylpyrazol at 270 °C for 2 h, when the evolution of 3 equiv. amount of H_2 was observed. Filtration followed by washing with hot toluene several times, affords white crystalline $KHB(3,5\text{-}Ph_2pz)_3$[6] in 45% yield. $KHB(3,5\text{-}iPr_2pz)_3$[7] was prepared by the reaction of KBH_4 with 3.2 equiv. 3,5-diisopropylpyrazol at 260 °C for 2 h. In this case, the purification was accomplished by careful recrystalli-

tion from pentane solution several times (48% yield after purification).

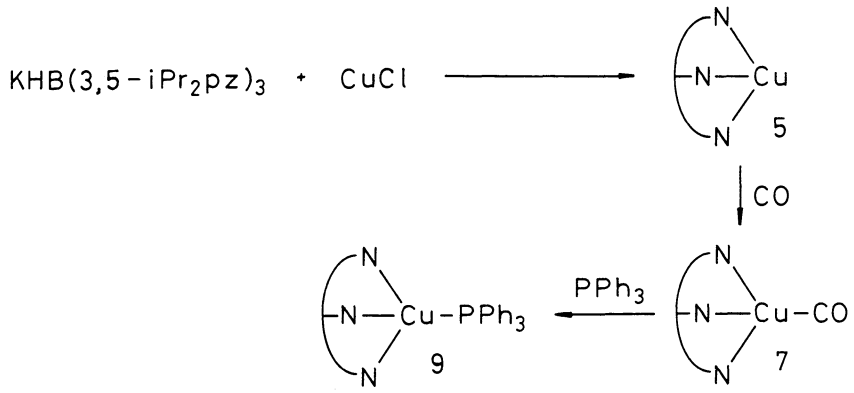
$KHB(3,5\text{-}Ph_2pz)_3$ was reacted with 1 equiv. CuCl in degassed acetone for 2 h. Filtration followed by reduction of the solvent affords pale yellow crystals, $Cu(Me_2CO)(HB(3,5\text{-}Ph_2pz)_3)$[8] (**3**). **3** is moderately stable even in air at room temperature in crystalline state, however, in non-coordinative solvent such as CH_2Cl_2, the readily dissociation of the coordinated acetone occurs to generate the coordinatively unsaturated copper(I) species, $Cu(HB(3,5\text{-}Ph_2pz)_3)$[9] (**4**). The reaction of $KHB(3,5\text{-}iPr_2pz)_3$ with CuCl in acetone does not give the acetone adduct, but gives $Cu(HB(3,5\text{-}iPr_2pz)_3)$[10] (**5**) directly.

Reaction of **4** with CO readily proceeds in CH_2Cl_2 to give $Cu(CO)(HB(3,5\text{-}Ph_2pz)_3)$[11] (**6**) in almost quantitative yield. $Cu(CO)(HB(3,5\text{-}iPr_2pz)_3)$[12] (**7**) is also prepared easily by CO treatment of **5** or by the reaction of $KHB(3,5\text{-}iPr_2pz)_3$ with CuCl in acetone under a CO atmosphere. The vibration frequencies of CO for **6** and **7** are 2086 and 2056 cm^{-1}, respectively, besides the frequencies for $Cu(CO)HBpz_3$[13] and $Cu(CO)(HB(3,5\text{-}Me_2pz)_3)$[14] are 2083 and 2065 cm^{-1}. Thus the order of the frequencies for $Cu(CO)(HB(3,5\text{-}R_2pz)_3)$ is R=Ph≳H>Me>iPr as expected from the electron donating property of the ligand. To our knowledge, the value of **7**, 2056 cm^{-1}, is the lowest one reported for Cu(I) carbonyl complex known to date, and very close to the values of the Cu(I)-CO adducts found in biological systems;hemocyanins,[15] 2063 for Molluscs, 2043 for Crustacea, and 2062 cm^{-1} for cytochrome c oxidase.[16]

The PMe_3 treatment of **6** in CH_2Cl_2 results in the fast displacement of CO to give the precipitate of $Cu(PMe_3)(HB(3,5\text{-}Ph_2pz)_3)$[17] (**8**). However, PPh_3 displacement does not occur even after 3 days stirring of PPh_3 with **6**, whereas **7** easily reacts with PPh_3 to genarate $Cu(PPh_3)(HB(3,5\text{-}iPr_2pz)_3)$ (**9**).[18] These facts sug-



Scheme 1.



Scheme 2.

gest that the size of the pocket like cage on the copper side of **4** consisting of three phenyl rings are smaller than that of **5** and is not accessible to PPh_3 (the cone angle: PPh_3, 145°; PMe_3, 118°).

In summary, the reactions to derive the Cu(I) complexes described in this communication are illustrated in Scheme 1 and 2. The unique charaters of **1** and **2** owing to the bulkiness and the electronic property are effective in design and synthesis of novel transition metal complexes of unusual structure, which will be the subject of our future reports.

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6) IR (KBr-disc) ν_{BH} 2527 cm^{-1}; ^{1}H-NMR ($(CD_3)_2CO$) δ ppm 7.13 (s, 3H, pz), 7.32-7.54 (m, 18H, Ph), 7.85-7.95 (m, 12H, Ph); Anal Found: C, 76.25; H, 5.01; N, 11.88%. Calcd for $C_{45}H_{34}N_6BK$: C, 76.26; H, 4.84; N, 11.86%.
7) IR (KBr-disc) ν_{BH} 2467 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ ppm 5.76 (s, 3H, pz), 3.14 (m, 3H, $C\underline{H}Me_2$), 2.66 (m, 3H, $C\underline{H}Me_2$), 1.05 (d, 18H, $CH\underline{Me}_2$), 1.00 (d, 18H, $CH\underline{Me}_2$); Anal Found: C, 64.27; H, 9.24; N, 16.68%. Calcd for $C_{27}H_{46}N_6BK$: C, 64.27; H, 9.19; N, 16.65%.
8) IR (KBr-disc) ν_{BH} 2599, ν_{CO} 1676 cm^{-1}; Anal Found: C, 72.40; H, 5.01; N, 10.22%. Calcd for $C_{48}H_{40}N_6BOCu$: C, 72.86; H, 5.10; N, 10.62%.
9) **4** was not isolated because of its high air sensitivity. The NMR and IR spectrum of **3** in CH_2Cl_2 established the dissociation of the coordinated acetone

to generate **4**; ^{1}H-NMR (CD_2Cl_2) δ ppm 6.72-6.80 (m, 9H, Ph), 6.87-6.90 (m, 6H, Ph), 7.09-7.11 (m, 9H, Ph), 7.40-7.43 (m, 6H, Ph), 6.30 (s, 3H, pz), 2.08 (s, 6H, free $\underline{Me}_2CO$); IR (in CH_2Cl_2) ν_{CO} 1716 cm^{-1}.

10) IR (KBr-disc) ν_{BH} 2523 cm^{-1}; ^{1}H-NMR ($C_6D_5CD_3$) δ ppm 6.08 (s, 3H, pz), 3.90 (m, 3H, $C\underline{H}Me_2$), 3.03 (m, 3H, $C\underline{H}Me_2$), 1.42 (d, 18H, $CH\underline{Me}_2$), 1.35 (d, 18H, $CH\underline{Me}_2$); Anal Found: C, 62.10; H, 9.01; N, 15.19%. Calcd for $C_{27}H_{46}N_6BCu$: C, 61.30; H, 8.76; N, 15.88%.

11) IR (KBr-disc) ν_{BH} 2635, ν_{CO} 2086 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ ppm 6.94-7.81 (m, 30H, Ph), 6.45 (s, 3H, pz); Anal Found: C, 71.98; H, 4.21; N, 11.18%. Calcd for $C_{46}H_{34}N_6BOCu$: C, 72.59; H, 4.50; N, 11.04%.

12) IR (KBr-disc) ν_{BH} 2525, ν_{CO} 2056 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ ppm 5.74 (s, 3H, pz) ;3.41 (m, 3H, $C\underline{H}Me_2$); 3.03 (m, 3H, $C\underline{H}Me_2$); 1.25 (d, 18H, $CH\underline{Me}_2$); 1.21 (d, 18 H, $CH\underline{Me}_2$); Anal Found: C, 60.09; H, 8.21; N, 15.00%. Calcd for $C_{28}H_{46}N_6BO$ Cu: C, 60.37; H, 8.32; N, 15.09%.

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17) IR (KBr-disc) ν_{BH} 2620 cm^{-1}; Anal Found: C, 66.11; H, 4.75; N, 9.64; Cl, 7.75%. Calcd for $C_{49}H_{45}N_6BCl_2PCu$ (**8** CH_2Cl_2): C, 65.82; H, 5.07; N, 9.40; Cl,7.93%. FD-MS (m/e) 808 (M^+). No accurate ^{1}H-NMR was obtained because of the low solubility of **8** in any solvent.

18) IR (KBr-disc) ν_{BH} 2526 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ ppm 7.3-7.7 (m, 15H, Ph), 5.67 (s, 3H, pz), 3.53 (m, 3H, $C\underline{H}Me_2$), 2.69 (m, 3H, $C\underline{H}Me_2$), 1.24 (d, 18H, $CH\underline{Me}_2$), 0.72 (d, 18H, $CH\underline{Me}_2$); Anal Found: C, 67.96; H, 8.08; N, 10.52%. Calcd for $C_{45}H_{61}N_6BPCu$: C, 68.30; H, 7.77; N, 10.62%.

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