^{63}Cu NMR Study of Copper(I) Carbonyl Complexes with Various Hydrotris(pyrazolyl)borates: Correlation between ^{63}Cu Chemical Shifts and CO Stretching Vibrations

Sadako Imai,[†] Kiyoshi Fujisawa,*[,†] Takako Kobayashi,[†] Nobuhiko Shirasawa,[†] Hiroshi Fujii,[‡] Tetsuhiko Yoshimura,[‡] Nobumasa Kitajima,[†] and Yoshihiko Moro-oka*[,†]

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226, Japan, and Institute for Life Support Technology, Yamagata Technopolis Foundation, 2-2-1 Matsuei, Yamagata 990, Japan

Received February 6, 1997

Copper(I) carbonyl complexes with a series of hindered $L^{R1,R2}$ ligands (L: hydrotris(pyrazolyl)borate, R1 and R2 are substituents at the 3- and 5-positions of the pyrazole ring, respectively), $L^{R1,R2}$CuCO [R1, R2 = Me, Me (**1**), *i*-Pr, *i*-Pr (**2**), *t*-Bu, Me (**3**), *t*-Bu, *i*-Pr (**4**), Ph, *i*-Pr (**5**), Ph, Ph (**6**)] have been synthesized and characterized by ^{1}H NMR and IR spectroscopy and elemental analysis. The molecular structures of **3** and **6** have been determined by X-ray crystallography. The electronic structures of copper(I) sites are characterized by means of ^{63}Cu NMR spectroscopy and by the C≡O stretching vibration. The sharp ^{63}Cu NMR signals are observed for $L^{R1,R2}$CuCO complexes in toluene at room temperature. The ^{63}Cu NMR signals of copper(I) complexes with alkyl-substituted ligands (**1**−**4**) are observed in lower field than those of the phenyl derivatives (**5**, **6**) correlating with the electron-density at the copper center. This argument is supported by the good correlation between the $\delta(^{63}\text{Cu})$ value and C≡O stretching vibration which is a sensitive indicator of the extent of back-donation of the Cu d electrons to the antibonding C≡O orbitals.

Introduction

Copper is an essential trace element that plays an important role in a variety of biological functions.[1] During last two decades, the structures and functions of copper proteins have been elucidated and these results have been recognized as one of remarkable advances in biochemistry and bioinorganic chemistry.[1] However, little research on the active sites of copper(I)-containing proteins has appeared because of the featureless spectroscopic properties of copper(I) ion. This is due to the filled d^{10} configuration of the copper(I) ion, and therefore it is difficult to detect copper(I) species by visible absorption or EPR spectroscopy. On the other hand, such diamagnetic d^{10} metal ions can be investigated by multinuclear magnetic resonance. This method provides us with direct information on the electronic state of the d^{10} metal centers, and may serve as a powerful tool for characterization of not only metal complexes but also metalloproteins as exemplified by ^{113}Cd NMR for Cd_7-metallothionein[2−5] and by ^{199}Hg NMR for MerR, a metalloregulatory protein.[6] In contrast to these NMR techniques, ^{63}Cu NMR is not always a useful one, because a sharp signal is observed only when a copper(I) center is located in a highly symmetrical environment. The nuclear spin of ^{63}Cu ($I = {}^3/_2$) accelerates the quadrupole relaxation of copper(I) in a lower symmetrical environment. For example, some CuL_4 type tetrahedral complexes show well-shaped signals with narrow line width.[7−19] But digonal and trigonal copper(I) species usually cannot be detected by ^{63}Cu NMR,[11] and even CuL_3L' type tetrahedral complexes give very broad resonance lines because of the reduced symmetry.[7,14,16]

We have been studying coordination chemistry of copper complexes ligated by various hydrotris(pyrazolyl)borates as synthetic models for the active sites of copper proteins. The hydrotris(pyrazolyl)borate may be able to mimic the multiple histidine coordination environment in metalloproteins. Herein, we report the results of ^{63}Cu NMR study of copper(I) carbonyl complexes with various hydrotris(pyrazolyl)borate ligands. The

* Corresponding authors.
[†] Tokyo Institute of Technology.
[‡] Yamagata Technopolis Foundation.

(1) Kaim, W.; Rall, J. *Angew. Chem., Int. Ed. Engl*. **1996**, *35*, 43.
(2) Otvos, J. D.; Armitage, I. M. *Proc. Natl. Acad. Sci. U.S.A.* **1980**, *77*, 7094.
(3) Frey, M. H.; Wagner, G.; Vašák, M.; Sørensen, O. W.; Neuhaus, D.; Wörgötter, E.; Kägi, J. H. R.; Ernst, R. R.; Wüthrich, K. *J. Am. Chem. Soc*. **1985**, *107*, 6847.
(4) Arseniev, A.; Schultze, P.; Wörgötter, E.; Braun, W.; Wagner, G.; Vašák, M.; Kägi, J. H. R.; Wüthrich, K. *J. Mol. Biol*. **1988**, *201*, 637.
(5) Schultze, P.; Wörgötter, E.; Braun, W.; Wagner, G.; Vašák, M.; Kägi, J. H. R.; Wüthrich, K. *J. Mol. Biol*. **1988**, *203*, 251.
(6) Utschig, L. M.; Bryson, J. W.; O'Halloran, T. V. *Science* **1995**, *268*, 380.
(7) Goodfellow, R. J. *Multinuclear NMR*; Mason, J., Ed.; Plenum Press: New York, 1987; Chapter 21.
(8) Yamamoto, T.; Haraguchi, H.; Fujiwara, S. *J. Phys. Chem*. **1970**, *74*, 4369.
(9) Lutz, O.; Oehler, H.; Kroneck, P. *Z. Phys. A* **1978**, *288*, 17.
(10) Lutz, O.; Oehler, H.; Kroneck, P *Z. Naturforsch* **1978**, *33A*, 1021.
(11) Kroneck, P.; Lutz, O.; Nolle, A.; Oehler, H. *Z. Naturforsch* **1980**, *35A*, 221.
(12) Marker, A.; Gunter, M. J. *J. Magn. Reson.* **1982**, *47*, 118.
(13) Kroneck, P.; Kodweiss, J.; Lutz, O.; Nolle, A.; Zepf, D. *Z. Naturforsch* **1982**, *37A*, 186.
(14) Geerts, R. L.; Huffman, J. C.; Folting, K.; Lemmen, T. H.; Caulton, K. G. *J. Am. Chem. Soc*. **1983**, *105*, 3503.
(15) Kitagawa, S.; Munakata, M. *Inorg. Chem*. **1984**, *23*, 4388.
(16) Kitagawa, S.; Munakata, M. Sasaki, M. *Inorg. Chim. Acta* **1986**, *120*, 77.
(17) Endo, K.; Yamamoto, K.; Deguchi, K.; Matsushita, K. *Bull. Chem. Soc. Jpn*. **1987**, *60*, 2803.
(18) Mohr, B.; Brooks, E. E.; Rath, N.; Deutsch, E. *Inorg. Chem*. **1991**, *30*, 4541.
(19) Black, J. R.; Levason, W. *J. Chem. Soc., Dalton Trans* **1994**, 3225.

S0020-1669(97)00138-9 CCC: $15.00
Published on Web 05/20/1998

present study has been carried out to investigate the applicability of ^{63}Cu NMR to $L^{R1,R2}CuCO$ complexes [L: hydrotris(pyrazolyl)borate, where R1 and R2 are substituents at the 3- and 5-positions of the pyrazole ring, respectively, Me, Me (**1**), *i*-Pr, *i*-Pr (**2**), *t*-Bu, Me (**3**), *t*-Bu, *i*-Pr (**4**), Ph, *i*-Pr (**5**), Ph, Ph (**6**)]. We show that $L^{R1,R2}CuCO$ complexes show sharp signals and that the good correlation between the δ (^{63}Cu) value and C≡O stretching vibration exists.

Experimental Section

Instrumentation. ^{1}H NMR spectra were recorded on JEOL GX-270 (270 MHz), JEOL EX-400 (400 MHz), and Bruker AC-200 (200 MHz) NMR spectrometers using Me_4Si as an internal reference. ^{63}Cu NMR spectra were recorded on a JEOL α-620 (164.3 MHz) NMR spectrometer using $[Cu(CH_3CN)_4]PF_6$ as an external reference. IR spectra were recorded on a JASCO FT/IR-5300. Elemental analyses were performed at the analytical facility of the Research Laboratory of Resource Utilization, Tokyo Institute of Technology.

Materials. All operations were performed under an argon atmosphere by standard Schlenk tube techniques. All solvents were carefully purified[20] and distilled under argon. All deuterated solvents for NMR spectroscopy were dried over molecular sieves and distilled prior to use. CuCl purchased from Wako was purified according to the described method.[21] $[Cu(CH_3CN)_4]PF_6$,[22] $KL^{t-Bu,Me}$,[23] $L^{Me,Me}CuCO$ (**1**),[24] $L^{i-Pr,i-Pr}CuCO$ (**2**),[21] and $L^{Ph,Ph}CuCO$ (**6**)[21,25] were prepared as described in the literature. All other chemicals of analytical grade were used as purchased.

Preparation of 3-*tert*-Butyl-5-isopropylpyrazole. A solution of pinacolin (273.4 g, 2.73 mol) in 150 mL of diethyl ether was added dropwise to a stirred suspension of lithium amide (100.0 g, 4.36 mol) in diethyl ether (1200 mL) over 1 h. Methyl isobutylate (389.1 g, 3.81 mol) dissolved in diethyl ether (300 mL) was then added dropwise to the resulting mixture over 1 h. After the mixture was refluxed for 13 h, the thick sludge was hydrolyzed by a dilute HCl aqueous solution. The ether layer was treated with a saturated NaCl aqueous solution several times, and, after drying over $MgSO_4$, diethyl ether was removed by evaporation. The resulting solution was distilled under reduced pressure (at 75 °C, 10 mmHg), affording 307.0 g (1.81 mol, 66% yield) of 2,2-dimethyl-6-methyl-3,5-heptanedione.

Hydrazine monohydrate (29.3 g, 0.59 mol) was added dropwise to a solution of 2,2-dimethyl-6-methyl-3,5-heptanedione (66.5 g, 0.39 mol) in 200 mL of ethanol. After 5 h of refluxing, diethyl ether was added to the mixture and then the solution was treated with a saturated NaCl aqueous solution. After drying over $MgSO_4$ overnight, the solvent was evaporated to dryness. The resulting white solid was dissolved in acetonitrile and allowed to stand overnight at −20 °C. The white needles (48.0 g, 0.29 mol, 74% yield) were filtered off and dried under vacuum. ^{1}H NMR ($CDCl_3$, 270 MHz): δ 1.28 (d, J = 7 Hz, 6H, CH*Me*$_2$), 1.32 (s, 9H, C*Me*$_3$), 2.96 (sept, J = 7 Hz, 1H, C*H*Me$_2$), 5.89 (s, 1H, Pz), 9.05 (br, 1H, NH). IR (KBr, cm^{-1}): 3173 (NH), 3098 (NH), 2963 (CH), 2930 (CH), 2905 (CH), 2872, 1572, 1487, 1464, 1363, 1317, 1284, 1236, 1209, 1134, 1010, 789. Anal. Calcd for $C_{10}H_{18}N_2$: C, 72.24; H, 10.91; N, 16.85. Found: C, 71.79; H, 11.14; N, 16.53.

Preparation of 3-Phenyl-5-isopropylpyrazole. 2-Methyl-5-phenyl-3,5-pentanedione was prepared by the literature method.[26]

Hydrazine monohydrate (15.3 g, 0.31 mol) was added dropwise to a solution of 2-methyl-5-phenyl-3,5-pentanedione (38.8 g, 0.20 mol) in 100 mL of ethanol. After 8 h of refluxing, diethyl ether was added to the mixture, and then the solution was washed with a saturated NaCl aqueous solution several times. After drying over $MgSO_4$ overnight, the solvent was evaporated to dryness. The resulting white solid was dissolved in acetonitrile and allowed to stand overnight at −20 °C. The white product (24.5 g, 0.13 mol, 65% yield) was filtered off and dried under vacuum. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.30 (d, J = 7 Hz, 6H, CH*Me*$_2$), 3.00 (sept, J = 7 Hz, 1H, C*H*Me$_2$), 6.36 (s, 1H, Pz), 7.24−7.75 (m, 5H, Ph), 10.85 (br, 1H, NH). IR (KBr, cm^{-1}): 3172 (NH), 3126 (NH), 3072 (NH), 2963 (CH), 2873 (CH), 1605, 1570, 1464, 1343, 1075, 1009, 767, 695. Anal. Calcd for $C_{12}H_{14}N_2$: C, 77.38; H, 7.58; N, 15.04. Found: C, 77.11; H, 7.44; N, 15.24.

Preparation of Potassium Hydrotris(3-*tert*-butyl-5-isopropyl-1-pyrazolyl)borate ($KL^{t-Bu,i-Pr}$). A mixture of 3-*tert*-butyl-5-isopropylpyrazole (23.6 g, 0.14 mol) and KBH_4 (2.39 g, 0.044 mol) was heated in an oil bath with stirring. The temperature was elevated gradually. After the temperature of the oil bath reached 260 °C, heating was continued at the same temperature until no hydrogen evolution had been observed. The mixture was allowed to cool to room temperature, and the resulting solid was extracted with CH_2Cl_2. After the extract was evaporated under vacuum, the resultant white solid was dissolved in 25 mL of acetonitrile and allowed to stand overnight at −20 °C. $KL^{t-Bu,i-Pr}\cdot CH_3CN$ (17.5 g, 0.030 mol) was filtered off and dried under vacuum (64% yield). ^{1}H NMR ($CDCl_3$, 270 MHz): δ 1.00 (d, J = 7 Hz, 18H, CH*Me*$_2$), 1.15 (s, 27H, C*Me*$_3$), 2.00 (s, 3H, *Me*CN), 3.09 (sept, J = 7 Hz, 3H, C*H*Me$_2$), 5.75 (s, 3H, Pz). IR (KBr, cm^{-1}): 2962 (CH), 2930 (CH), 2905 (CH), 2469 (BH), 1672, 1531, 1464, 1361, 1300, 1240, 1184, 1047, 1003, 785, 713, 648. Anal. Calcd for $C_{32}H_{55}N_7BK$: C, 65.39; H, 9.43; N, 16.68. Found: C, 64.89; H, 9.52; N, 16.34.

Preparation of Potassium Hydrotris(3-phenyl-5-isopropyl-1-pyrazolyl)borate ($KL^{Ph,i-Pr}$). A mixture of 3-phenyl-5-isopropylpyrazole (24.5 g, 0.13 mol) and KBH_4 (2.16 g, 0.040 mol) was heated in an oil bath with stirring. The temperature was elevated gradually. After the temperature of the oil bath reached 260 °C, heating was continued at the same temperature until no hydrogen evolution had been observed. The mixture was allowed to cool to room temperature and the resulting solid was extracted with CH_2Cl_2. After the extract was evaporated under vacuum, the resultant white solid was dissolved in 10 mL of CH_2Cl_2 and 20 mL of heptane and allowed to stand overnight at −20 °C. The white powder (12.5 g, 0.021 mol, 46% yield) was filtered off and dried under vacuum. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 1.13 (d, J = 7 Hz, 18H, CH*Me*$_2$), 3.27 (sept, J = 7 Hz, 3H, C*H*Me$_2$), 6.33 (s, 3H, Pz), 7.12−7.56 (m, 15H, Ph). IR (KBr, cm^{-1}): 2964 (CH), 2931 (CH), 2868 (CH), 2458 (BH), 1605, 1502, 1463, 1420, 1359, 1297, 1182, 1142, 1359, 1297, 1182, 1142, 1073, 1051, 764, 697. Anal. Calcd for $C_{36}H_{42}N_6BKO(KL^{Ph,i-Pr}\cdot H_2O)$: C, 69.22; H, 6.78; N, 13.45. Found: C, 69.51; H, 6.37; N, 13.73.

Preparation of Carbonyl[hydrotris(3-*tert*-butyl-5-methyl-1-pyrazolyl)borate]copper(I) ($L^{t-Bu,Me}CuCO$) (3). CuCl (118 mg, 1.190 mmol) and $KL^{t-Bu,Me}$ (550 mg, 1.190 mmol) were dissolved in CH_2Cl_2 (8 mL) and acetone (4 mL). The mixture was stirred for 30 min and filtered through Celite. After the colorless filtrate was stirred under CO atmosphere overnight, the solvent was evaporated under vacuum. The resulting solid was dissolved in CH_2Cl_2 (3 mL) and allowed to stand overnight at −20 °C. The white product (232 mg, 0.450 mmol, 38% yield) was filtered off and dried under vacuum. ^{1}H NMR ($C_6D_5CD_3$, 400 MHz): δ 1.40 (s, 27H, C*Me*$_3$), 2.34 (s, 9H, C*Me*), 5.76 (s, 3H, Pz). IR (KBr, cm^{-1}): 2966 (CH), 2927 (CH), 2863 (CH), 2519 (BH), 2059 (CO), 1541, 1473, 1426, 1562, 1263, 1189, 1067, 784, 769. Anal. Calcd for $C_{25}H_{40}N_6BCuO$: C, 58.31; H, 7.83; N, 16.32. Found: C, 58.47; H, 8.22; N, 16.32.

Preparation of Carbonyl[hydrotris(3-*tert*-butyl-5-isopropyl-1-pyrazolyl)borate]copper(I) ($L^{t-Bu,i-Pr}CuCO$) (4). Complex **4** was prepared in a manner similar to the preparation of **3** starting from CuCl (47 mg, 0.475 mmol) and $KL^{t-Bu,i-Pr}\cdot CH_3CN$ (279 mg, 0.475 mmol). Recrystallization from CH_2Cl_2 (3 mL) at −20 °C gave 135 mg (0.225 mmol, 47% yield) of white crystalline product. ^{1}H NMR ($C_6D_5CD_3$, 200 MHz): 1.18 (d, J = 7 Hz, 18H, CH*Me*$_2$), 1.51 (s, 27H, C*Me*$_3$),

(20) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals;* Pergamon: New York, 1980.
(21) Kitajima, N.; Fujisawa, K.; Fujimoto, C.; Moro-oka, Y.; Hashimoto, S.; Kitagawa, T.; Toriumi, K.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc*. **1992**, *114*, 1277.
(22) Kubas, G. J. *Inorg. Synth*. **1979**, *19*, 90.
(23) Torofimenko, S.; Calabrese, J. C.; Kochi, J. K.; Welowiec, S.; Hulsbergen, F. B.; Reedijk, J. *Inorg. Chem*. **1992**, *31*, 3943.
(24) Abusalah, O. M.; Bruce, M. I.; Hameister, C. *Inorg. Synth*. **1982**, *21*, 107.
(25) Kitajima, N.; Fujisawa, K.; Fujimoto, C.; Moro-oka, Y. *Chem. Lett*. **1989**, 421.
(26) Murdoch, H. D.; Nonhebel, D. C. *J. Chem. Soc*. **1962**, 2153.

Table 1. Crystallographic Data for $L^{t-Bu,Me}CuCO$ (**3**) and $L^{Ph,Ph}CuCO$ (**6**)

	3	**6**
empirical formula	$C_{25}H_{40}N_6BOCu$	$C_{46}H_{34}N_6BOCu$
crystal system	monoclinic	trigonal
mol wt	514.99	761.17
space group	*Pc*	*R*3*c*
a/Å	15.493(3)	16.141(3)
b/Å	9.675(2)	
c/Å	19.058(3)	26.432(2)
β /deg	95.87(1)	
V/Å^3	2842(1)	5964(2)
Z	4	6
D_{calcd}/g·cm^{-3}	1.20	1.27
μ(Mo Kα)/cm^{-1}	7.95	5.92
temp/°C	23	25
no. of measd reflctions	5337	1311
no. of observs	4206 ($I > 3\sigma(I)$)	822 ($I > 1.5\sigma(I)$)
no. of variable params	611	165
R/%[a]	3.28	5.85
*R*w/%[b]	2.51	3.00
goodness-of-fit indicator	1.84	1.68
max peak, e/Å^3	0.25	0.32
min peak, e/Å^3	−0.26	−0.34

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $Rw = [\sum[w(|F_o| - |F_c|)^2]/\sum w|F_o|^2]^{1/2}$, $w = 1/\sigma^2(|F_o|)$.

3.61 (sept, J = 7 Hz, 3H, C*H*Me$_2$), 6.00 (s, 3H, Pz). IR (KBr, cm^{-1}): 2967 (CH), 2928 (CH), 2869 (CH), 2541 (BH), 2057 (CO), 1533, 1458, 1376, 1362, 1303, 1182, 1061, 1049, 793, 789, 754, 715, 642. Anal. Calcd for $C_{31}H_{52}N_6BCuO$: C, 62.14; H, 8.75; N, 14.03. Found: C, 61.79; H, 8.73; N, 14.07.

Preparation of Carbonyl[hydrotris(3-phenyl-5-isopropyl-1-pyrazolyl)borate]copper(I) ($L^{Ph,i-Pr}CuCO$) (5). Complex **5** was prepared in a manner similar to the preparation of **4** starting from CuCl (38 mg, 0.383 mmol) and $KL^{Ph,i-Pr}$ (233 mg, 0.383 mmol). Recrystallization from CH_2Cl_2 (0.5 mL) and octane (3 mL) at −20 °C gave 120 mg (0.182 mmol, 48% yield) of white crystalline product. ^{1}H NMR (C_6D_5-CD_3, 200 MHz): δ 1.29 (d, J = 7 Hz, 18H, CH*Me*$_2$), 3.71 (sept, J = 6.9 Hz, 3H, C*H*Me$_2$), 6.15 (s, 3H, Pz), 7.02−7.63 (m, 15H, Ph). IR (KBr, cm^{-1}): 2969 (CH), 2929 (CH), 2870 (CH), 2537 (BH), 2075 (CO), 1541, 1501, 1464, 1427, 1374, 1297, 1171, 1048, 794, 767, 699. Anal. Calcd for $C_{37}H_{40}N_6BCuO$: C, 67.42; H, 6.12; N, 12.75. Found: C, 67.82; H, 6.40; N, 12.75.

X-ray Data Collection. Single crystals of **3** and **6** were obtained by recrystallization from CH_2Cl_2 at −20 °C and at room temperature, respectively. The crystals were sealed in thin-walled glass capillaries. The data for **3** and **6** were collected at room temperature. A Mo X-ray source equipped with a graphite monochromator (Mo Kα, λ = 0.710 68 Å) was used. Relevant crystallographic information is given in Table 1. Cell constants were obtained from a least squares refinement of the setting angles for 25 (**3**) and 20 (**6**) carefully centered reflections in the range of $20 \le 2\theta \le 25°$. The intensity data was collected using $\omega-2\theta$ scan technique. The intensities of three standard reflections monitored every 150 reflections showed no serious decay. The initial positional parameter of the copper atom in **3** and **6** was determined by the direct method, SAPI91.[27] Subsequent difference Fourier synthesis easily locates all non-hydrogen atoms, which were refined anisotropically by TEXSAN.[28] The hydrogen atoms were calculated and included in the final refinement. The final structure refined by full-matrix least-squares refinements (TEXSAN) was based on 4206 observed reflections ($I > 3\sigma(I)$) with 611 variable parameters for **3**, 822 observed reflections ($I > 1.5\sigma(I)$) with 165 variable parameters for **6**. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.25 and −0.26 e/Å^3 for **3** and 0.32 and −0.34 e/Å^3 for **6**. ORTEP drawings of the structure of **3** and **6** appear in Figures 1 and 2, respectively. Selected bond lengths and angles are presented in Table 2. Full tables of bond lengths and angles, atomic coordinates, and temperature factors are given in the Supporting Information.

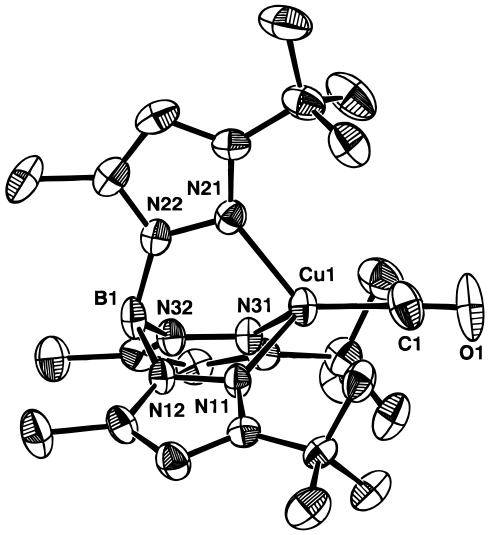

Figure 1. ORTEP drawing of $L^{t-Bu,Me}CuCO$ (**3**).

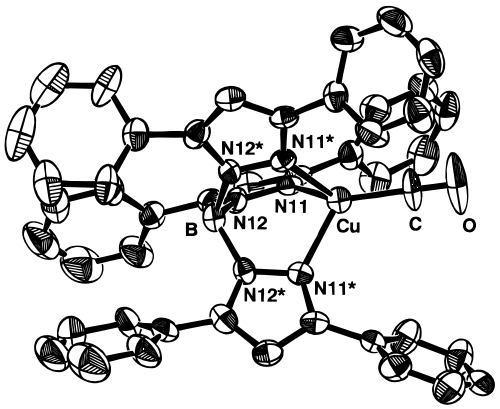

Figure 2. ORTEP drawing of $L^{Ph,Ph}CuCO$ (**6**).

Table 2. Selected Bond Distances (Å) and Angles (deg) for $L^{t-Bu,Me}CuCO$ (**3**) and $L^{Ph,Ph}CuCO$ (**6**)

3		**6**	
Cu1−N11	2.070(4)	Cu−N	2.059(6)
Cu1−N21	2.067(4)		
Cu1−N31	2.058(4)		
Cu2−N41	2.057(4)		
Cu2−N51	2.057(4)		
Cu2−N61	2.065(4)		
Cu1−C1	1.789(6)	Cu−C	1.78(1)
Cu2−C2	1.805(6)		
C1−O1	1.113(6)	C−O	1.08(1)
C2−O2	1.106(6)		
N11−Cu1−C1	122.8(2)	N−Cu−C	125.0(2)
N21−Cu1−C1	126.8(2)		
N31−Cu1−C1	120.6(2)		
Cu1−C1−O1	177.6(6)	Cu−C−O	180.0(1)
N41−Cu2−C2	123.0(2)		
N51−Cu2−C2	123.1(2)		
N61−Cu2−C2	123.7(2)		
Cu1−C1−O1	177.6(6)		
Cu2−C2−O2	177.6(6)		

Results and Discussion

Synthesis of Copper(I) Carbonyl Complexes (1−6). To get insights into the electronic influences of the substituents in

(27) Fan Hai-Fu 1991. Structure Analysis Programs with Intelligent Control, Rigaku Corporation, Tokyo, Japan.
(28) *TEXSAN: Single-Crystal Structure Analysis Software*, Version 1.6; Molecular Structure Corporation, The Woodlands, TX, 77381, 1993.

the pyrazolyl rings, asymmetrically substituted ligands, $KL^{t-Bu,i-Pr}$ and $KL^{Ph,i-Pr}$, were newly synthesized. *tert*-Butyl and phenyl groups at the 3-position of the pyrazolyl ring in these ligands are expected to show the thermal stability by their steric protection of the metal center when compared with the $L^{i-Pr,i-Pr}$ ligand bearing isopropyl groups. The $L^{t-Bu,Me}$ ligand, which is the *tert*-butyl substituent of the $L^{Me,Me}$ ligand, is also used for this purpose.

The copper(I) carbonyl complexes $L^{Me,Me}CuCO$ (**1**),[24] $L^{i-Pr,i-Pr}CuCO$ (**2**),[21] and $L^{Ph,Ph}CuCO$ (**6**)[21,25] were prepared according to the published procedures. The new copper(I) carbonyl complexes, $L^{t-Bu,Me}CuCO$ (**3**), $L^{t-Bu,i-Pr}CuCO$ (**4**) and $L^{Ph,i-Pr}CuCO$ (**5**), were also prepared following the published method, the reaction between $KL^{R1,R2}$ and CuCl with CO atmosphere in polar solvents such as acetone and CH_2Cl_2. These complexes could be isolated from CH_2Cl_2 or CH_2Cl_2/octane in 40−80% yield.

The obtained complexes **1**−**6** have been identified by ^{1}H NMR and IR spectroscopy and elemental analysis. For the asymmetrically substituted complexes **3**−**5**, the substitution pattern cannot be determined by spectroscopic methods alone. The structure of **3** was determined by X-ray crystallography, and the substitution pattern of complex **4** assigned on the basis of the molecular structure of the superoxide copper(II) complex, $L^{t-Bu,i-Pr}Cu(O_2)$.[29] Although no crystal structure determination of a complex with the $L^{Ph,i-Pr}$ ligand has been reported so far,[30] the substitution pattern of $L^{Ph,i-Pr}CuCO$ (**5**) can be assigned by comparison of the ^{1}H NMR data. The isopropyl-methine protons of $L^{i-Pr,i-Pr}CuCO$ (**2**) and $L^{t-Bu,i-Pr}CuCO$ (**4**) are observed at δ 3.21, 3.58 (**2**), and 3.61 (**4**) in toluene-d_8, respectively. These data suggest that the methine proton of the isopropyl group at the 5-position of the pyrazolyl ring appears in lower field. Since the isopropyl-methine proton of **5** is located at δ 3.71, it is concluded that isopropyl group occupies the 5-position. These assignments are consistent with the general trend that a bulkier substituent tends to occupy the 3-position far from the B−H moiety.

Crystal Structures of 3 and 6. The crystals of **3** and **6** were obtained from CH_2Cl_2 and their molecular structures have been determined by X-ray crystallography. ORTEP drawings are presented in Figures 1 and 2, respectively.

A unit cell of complex **3** contains two independent molecules with similar geometries. The complex **6** has the crystallographic C_3 symmetry with the B−Cu−C−O axis. The crystallographic data and selected structural parameters are summarized in Tables 1 and 2, respectively.

The Cu−C and C−O bond lengths are comparable to those of related carbonyl complexes, and the Cu−C−O linkages are linear as expected.[21] The geometry of the copper centers can be described as a distorted tetrahedron coordinated by an N_3C ligand set.

Substituent Effect of the Pyrazolyl Groups: Estimation of Electron Density at the Copper Center. In Table 3, the ν(C≡O) values (KBr pellet) of the $L^{R1,R2}CuCO$ complexes are listed together with their Cu−C and C−O bond lengths.

The copper(I) carbonyl complexes are stabilized by the back-donation of copper d electrons to the antibonding C≡O orbital, and the ν(C≡O) value is a sensitive indicator of the extent of back-donation, i.e., electron density at the metal center. The copper(I) carbonyl complexes show intense absorption around 2050 cm^{-1} assignable to C≡O stretching vibration. As is expected, ν(C≡O) values of $L^{R1,R2}CuCO$ complexes are observed at the lower region (2056−2137 cm^{-1}) than free CO (2143 cm^{-1}).[34,35] As pyrazolyl substituents become more electron-donating from CF_3 to alkyl, the ν(C≡O) value shifts to lower energy. In other words, the electron density at the copper center increases in this order. However, the bond lengths of the Cu−C−O part do not change significantly and are the same within the range of the experimental errors. Thus, it has proved that electron density at copper center can be estimated by ν(C≡O) values better than by the structural parameters. On the basis of the extent of the red shift, the electron-density at copper center increases in the following order: $L^{i-Pr,i-Pr} \approx L^{t-Bu,Me} > L^{H,H} > L^{Ph,Ph} > L^{CF_3,CF_3}$ (see Table 3).[36]

Table 3. Selected Structural and Spectroscopic Data for $L^{R1,R2}CuCO$ Complexes

	Cu−C/Å	C−O/Å	ν(C≡O)/cm^{-1} (KBr pellet)	ref
$L^{i-Pr,i-Pr}CuCO$ (**2**)	1.769(8)	1.118(10)	2056	21
$L^{t-Bu,Me}CuCO$ (**3**)	1.789(6)	1.113(6)	2059	this work
	1.805(6)	1.106(6)		
$L^{H,H}CuCO$	1.755(11)	1.120(13)	2083	31, 32
	1.775(5)	1.120(6)		
$L^{Ph,Ph}CuCO$ (**6**)	1.78(1)	1.08(1)	2080	this work
$L^{CF3,CF3}CuCO$	1.808(4)	1.110(5)	2137	33

^{63}Cu NMR Spectroscopy of 1−6. As discussed in Introduction, measurement of the ^{63}Cu NMR has been limited by the requirement that the structure around the copper center is highly symmetrical. Sharp signals are observed only for tetrahedral complexes due to this limitation. For example, the line width of the standard reference, $[Cu(CH_3CN)_4]PF_6$, is 540 Hz,[9] and the most narrow line width, 137 Hz, is observed for $Cu[P(OC_2H_5)]_4ClO_4$.[11]

^{63}Cu NMR shift of a solution sample appears over the range of 600 ppm. Previous studies have indicated that ^{63}Cu NMR chemical shift is dependent on the π-accepting ability of the coordinated ligands,[15] that is, δ(^{63}Cu) value becomes larger, as ligands become more π-acidic: CuS_4 (S = thioether), 70−80 ppm;[19] CuP_4, 70−250 ppm;[11] CuN_4 (N = pyridine), 100−110 ppm;[15] $Cu(RNC)_4$, 450−550 ppm.[15] Other complexes having a low symmetry, even tetrahedral CuL_3L' complexes, give very broad signals. Therefore, ^{63}Cu NMR of only two CuL_3L' complexes, $[CuCl(P(OC_2H_5)_3)]$[16] and $[CuCO(t\text{-}BuO)]_4$,[14] have been reported so far.

The $L^{R1,R2}CuCO$ complexes exhibit sharp signals in the range of 580−730 ppm, as shown in Figure 3, despite their tetrahedral C_3 symmetrical CuL_3L' type structures.

In particular, $L^{alkyl,alkyl}CuCO$ complexes give very sharp signals. The line widths of $L^{alkyl,alkyl}CuCO$ complexes range between 70 and 250 Hz. On the other hand, phenyl derivatives exhibit the broader signals (2900 Hz for $L^{Ph,i-Pr}CuCO$ (**5**) and 4200 Hz for $L^{Ph,Ph}CuCO$ (**6**)). As discussed above, no significant structural difference has been observed for the alkyl and

(29) Fujisawa, K.; Tanaka, M.; Moro-oka, Y.; Kitajima, N. *J. Am. Chem. Soc.* **1994**, *116*, 12079.
(30) Fujisawa, K. Unpublished result. Very recently, the molecular structure of $L^{Ph,i-Pr}Cu(II)NO_3$ has been determined by X-ray crystallography. This result strongly indicates that isopropyl group occupies the 5-position of the pyrazole ring.
(31) Bruce, M. I.; Ostazewski, A. P. P. *J. Chem. Soc., Dalton Trans* **1973**, 2433.
(32) Churchill, M. R.; DeBoer, B. G.; Rotella, F. J.; Abu Salah, O. M.; Bruce, M. *Inorg. Chem.* **1975**, *14*, 2051.
(33) Dias, H. V. R.; Lu, H. L. *Inorg. Chem.* **1995**, *34*, 5380.
(34) Braterman, P. S. *Metal Carbonyl Spectra*; Academic Press: New York, 1975; 177.
(35) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley-Interscience: New York, 1986; p 291.
(36) Kitajima, N.; Tolman, W. B. *Prog. Inorg. Chem.* **1995**, *43*, 419.

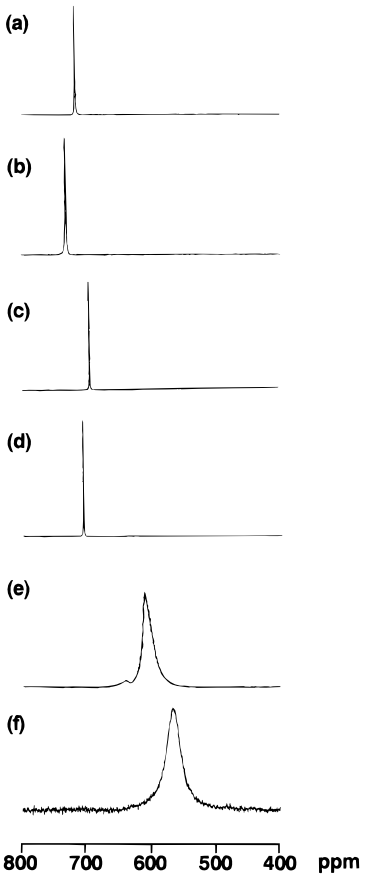

Figure 3. ^{63}Cu NMR spectra of $L^{R1,R2}CuCO$ complexes: (a) $L^{Me,Me}$-CuCO (**1**), (b) $L^{i-Pr,i-Pr}CuCO$ (**2**), (c) $L^{t-Bu,Me}CuCO$ (**3**), (d) $L^{t-Bu,i-Pr}CuCO$ (**4**), (e) $L^{Ph,i-Pr}CuCO$ (**5**), and (f) $L^{Ph,Ph}CuCO$ (**6**).

Table 4. Vibrational Data, ^{63}Cu Chemical Shifts, and Line Widths of $L^{R1,R2}CuCO$ Complexes (**1**−**6**) in Toluene Solutions

	ν(C≡O)/ cm^{-1}	δ(^{63}Cu)/ ppm	line width/ Hz
$L^{Me,Me}CuCO$ (**1**)	2062	716	110
$L^{i-Pr,i-Pr}CuCO$ (**2**)	2061	730	205
$L^{t-Bu,Me}CuCO$ (**3**)	2064	700	70
$L^{t-Bu,i-Pr}CuCO$ (**4**)	2064	703	75
$L^{Ph,i-Pr}CuCO$ (**5**)	2077	603	2900
$L^{Ph,Ph}CuCO$ (**6**)	2079	585	4200

phenyl substituted complexes. Kroneck and co-workers reported the dependence of the line width on temperature and solvents.[13] They also described the effect of water. However, in the present case, addition of water did not cause broadening of the line width. It is unlikely that these factors effect the line widths of the ^{63}Cu NMR signals. Therefore, the broad resonance lines of the phenyl derivatives may be attributed to the asymmetric charge distribution at copper center due to the π-acceptor property of the phenyl ligand.[10,11]

As going from alkyl to phenyl substituted ligands, the acceptor ability increases and influences the charge distribution of the copper(I) ion. Table 4 shows the ν(C≡O) vibrations, the δ(^{63}Cu) values and line widths of complexes **1**−**6** in toluene solution.

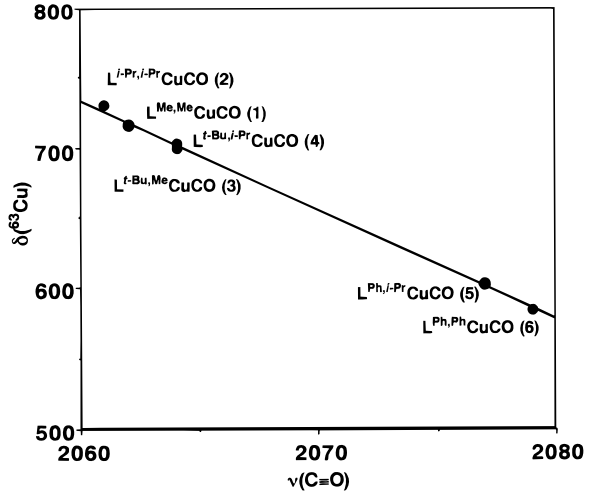

Figure 4. Correlation between ^{63}Cu NMR chemical shifts and C≡O stretching vibrations of $L^{R1,R2}CuCO$ (**1**-**6**)

The solution IR spectra were also recorded using the same solvent used for the ^{63}Cu NMR. When the δ(^{63}Cu) values for **1**−**6** are plotted against the ν(C≡O) values (Figure 4), a good correlation is observed. As the ν(C≡O) value increases, the ^{63}Cu NMR signal shifts toward lower field.

Conclusions

In this article, we have synthesized copper(I) carbonyl complexes with various hydrotris(pyrazolyl)borate ligands and characterized their electronic states of the metal centers by means of ^{63}Cu NMR. A series of $L^{R1,R2}CuCO$ complexes exhibit the sharp ^{63}Cu NMR signals in contrast to other CuL_3L' type complexes and the chemical shifts are found to be related to the electron donating or withdrawing capabilities of the hydrotris(pyrazolyl)borate ligands as supported by the dependence of the C≡O stretching vibration. The good correlation between the δ(^{63}Cu) value and the C≡O stretching vibration is observed as shown in Figure 4. According to this result, the ^{63}Cu NMR measurement, which is a more sensitive indicator than IR spectroscopy to estimate the metal electron density, allows us to compare the electronic properties of hydrotris(pyrazolyl)-borates and other N_3 ligands such as triazacyclononanes.[37]

This study also shows the possibility that ^{63}Cu NMR can be applied to the dinuclear complexes and other $L^{R1,R2}CuX$ type complexes.

Acknowledgment. This research was supported in part by Grants-in-Aids for Scientific Research from the Japanese Ministry of Education, Science, Sports, and Culture (06403010 and 08102006).

Supporting Information Available: Tables of atomic coordinates, temperature factors, and bond lengths and angles (Tables S1−S4) are available (19 pages). See any current masthead page for order and Internet access instructions.

IC970138R

(37) Haselhorst, G.; Stoetzel, S.; Strassburger, A.; Walz, W.; Weighardt, K.; Nuber, B. *J. Chem. Soc., Dalton Trans.* **1993**, 83.