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Synthesis and Characterization of Binuclear Palladium(I) Complexes of Isocyanides with Phenyl-Substituted Cyclopentadienyl and Tris(pyrazol-1-yl)borate Ligands[†]

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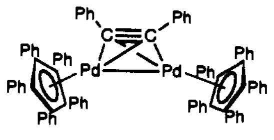
The reactions of $PdCl_2(RNC)_2$ with potassium pentaphenylcyclopentadienide ($K\{C_5Ph_5\}$) and potassium tetraphenylcyclopentadienide ($K\{C_5HPh_4\}$) gave binuclear palladium(I) complexes, $Pd_2(\eta\text{-}C_5Ph_5)_2(\mu\text{-}RNC)_2$ (**3**; R = 2,6-$Me_2C_6H_3$) and $Pd_2(\eta\text{-}C_5HPh_4)_2(\mu\text{-}RNC)_2$ (**4a**, R = 2,6-$Me_2C_6H_3$; **4b**, R = 2,4,6-$Me_3C_6H_2$), in good yields. Complexes **3** and **4** were characterized by elemental analysis, IR, UV–vis, and ^1H and ^{13}C NMR spectroscopies, and X-ray crystallography. Compound **3** crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 13.391(8)$ Å, $b = 23.793(9)$ Å, $c = 13.681(6)$ Å, $\alpha = 90.24(4)^\circ$, $\beta = 118.13(4)^\circ$, $\gamma = 90.30(4)^\circ$, and $Z = 2$ ($R = 0.085$ and $R_w = 0.088$ for 2886 independent reflections with $I > 4\sigma(I)$), and compound **4b** crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 14.907(3)$ Å, $b = 18.794(3)$ Å, $c = 11.769(2)$ Å, $\alpha = 101.88(2)^\circ$, $\beta = 97.33(2)^\circ$, $\gamma = 89.40(2)^\circ$, and $Z = 2$ ($R = 0.047$ and $R_w = 0.038$ for 5808 independent reflections with $I > 3\sigma(I)$). Complexes **3** and **4** consist of two palladium atoms bridged by two isocyanides having the C–N–C linear structure. The Pd_2C_2 core is folded with the dihedral angles of 121.6° (**3**) and 137.5° (**4b**) between the two Pd_2C planes. The Pd–Pd bond lengths are 2.632(5) Å (**3**) and 2.673(1) Å (**4b**), and the phenyl-substituted cyclopentadienyl groups coordinate to the metal in the distorted η^5-fashion. Complex **4** readily reacted with isocyanide to yield the ketenimine compound, $Ph_4C_4C{=}C{=}NR$ (**5**). When potassium 1,2,4-triphenylcyclopentadienide ($K\{C_5H_2Ph_3\}$) was used, the binuclear palladium(I) complex of isocyanide with bridging $\eta^3\text{-}C_5H_2Ph_3$ anions, $Pd_2(\mu\text{-}\eta^3\text{-}C_5H_2Ph_3)_2(RNC)_2$ (**6a**, R = 2,6-$Me_2C_6H_3$; **6b**, R = 2,4,6-$Me_3C_6H_2$), was obtained instead of the isocyanide-bridged dimer. Complex **6b** crystallizes in the triclinic system, space group $P\bar{1}$ with $a = 11.511(4)$ Å, $b = 12.768(3)$ Å, $c = 10.157(2)$ Å, $\alpha = 103.23(2)^\circ$, $\beta = 91.71(2)^\circ$, $\gamma = 96.83(2)^\circ$, and $Z = 2$ ($R = 0.034$ and $R_w = 0.033$ for 5572 independent reflections with $I > 3\sigma(I)$). In the dimer **6**, two $\eta\text{-}C_5H_2Ph_3$ groups are parallel in an *anti* arrangement. The Pd–Pd bond length is 2.6309(9) Å. The reaction of $Pd_2Cl_2(RNC)_4$ with $Na\{HB(pz)_3\}$ (pz = pyrazol-1-yl) produced the dipalladium(I) compound, $Pd_2\{HB(pz)_3\}_2(\mu\text{-}RNC)_2$ (**8**, R = 2,4,6-$Me_3C_6H_2$), which crystallizes in the monoclinic system, space group $P2_1/n$, with $a = 11.243(3)$ Å, $b = 15.871(6)$ Å, $c = 12.035(2)$ Å, $\beta = 91.99(2)^\circ$, and $Z = 2$ ($R = 0.062$ and $R_w = 0.073$ for 1142 independent reflections with $I > 3\sigma(I)$). Complex **8** consists of two palladium atoms bridged by two isocyanides, and the Pd_2C_2 core is crystallographically planar. The $HB(pz)_3$ anion coordinates to the metal in an asymmetrical tridentate manner. The Pd–Pd bond length is considerably elongated to 2.757(4) Å. A linear correlation between the Pd–Pd bond length and the dihedral angle between the two PdC_2 planes was observed in the series of $Pd_2(\mu\text{-}RNC)_2$ dimers. The present work provides an efficient route to a new series of binuclear palladium(I) complexes containing cyclopentadienyl analogues and isocyanides.

Introduction

Binuclear transition metal complexes of the cyclopentadienyl anion and its derivatives ($C_5R_5^-$; R = H, Me, Ph) have widely been studied in relevance to catalytic reactions and photo- and electrochemistry and as useful precursors to cluster compounds. However, the corresponding chemistry of platinum and palladium has been very slow to develop due to a lack of suitable synthetic routes.[1-3] In particular, the binuclear palladium system had been limited to $Pd_2(\eta^5\text{-}C_5Ph_5)_2(\mu\text{-}PhC{\equiv}CPh)$ (**1**),[1] which was primarily associated with alkyne oligomerization. The phenyl-substituted cyclopentadienyl group, C_5Ph_5, is known to stabilize various oxidation states, and the $\eta^5\text{-}C_5Ph_5$ complexes of palladium are more stable than their $\eta^5\text{-}C_5H_5$ analogues. However, the steric bulk of the C_5Ph_5 anion reduces the access with respect to ligand substitution at metal centers, and consequently many synthetic routes in the cyclopentadienyl chemistry are not available when the C_5Ph_5 ligand is used. Recently, the second example, $Pd_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}CO)_2$ (**2**), was prepared by the reaction of $[PdCl(CO)_n]$ with C_5Me_5MgCl, and the binuclear compound **2** was transformed to a trinuclear palladium cluster $[Pd_3(\eta^5\text{-}C_5Me_5)_3(\mu^3\text{-}CO)_2]^+$ by an action of HBF_4 or CF_3SO_3H.[2]



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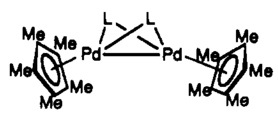

2 L = CO

We have studied the synthesis and characterization of palladium and platinum clusters of isocyanides also including binuclear

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[®] Abstract published in *Advance ACS Abstracts,* December 1, 1993.

(1) (a) Ban, E.; Cheng, P.; Jack, T.; Nyburg, S. C.; Powell, J. *J. Chem. Soc., Chem. Commun.* **1973,** 368. (b) Jack, T. R.; May, C. J.; Powell, J. *J. Am. Chem. Soc.* **1977,** *99,* 4707. (c) Broadley, K.; Connelly, N. G.; Lane, G. A.; Geiger, W. G. *J. Chem. Soc., Dalton Trans.* **1986,** 373.

(2) Boag, N. M.; Boucher, D.; Davies, J. A.; Miller, B. W.; Pinkerton, A. A.; Syed, R. *Organometallics* **1988,** *7,* 791.

(3) (a) Dixon, A. J.; Firth, S.; Haynes, A.; Poliakoff, M.; Turner, J. J.; Boag, N. M. *J. Chem. Soc., Dalton Trans.* **1988,** 1501. (b) Boag, N. M. *Organometallics* **1988,** *7,* 1446.

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complexes.[4-9] Recently, bidentate diphosphines were introduced as a supporting ligand for metal–metal bonds, and it was revealed that the length of the methylene chain of the diphosphines dramatically influenced the structure of platinum clusters.[10-12] Further, by using the indenyl group instead of diphosphines, the binuclear palladium(I) dimer $Pd_2(\mu\text{-}\eta^3\text{-indenyl})_2(RNC)_2$ (RNC = isocyanide) was prepared by the reaction of $PdCl_2(RNC)_2$ with lithium indenyl, where the two η^3-indenyl groups coordinated to the Pd_2 center in a wedge-shaped *syn*-arrangement.[13,14] Here, we wish to report a direct synthesis of binuclear palladium complexes containing phenyl-substituted cyclopentadienyl groups ($C_5H_{5-n}Ph_n$, $n = 3$–5), which are characterized by X-ray crystallography. In comparison with the dimers of phenyl-substituted cyclopentadienyl groups, a binuclear palladium complex of tris(pyrazol-1-yl)borate anion was also prepared.

Experimental Section

Benzene, dichloromethane, tetrahydrofuran, and hexane were distilled over calcium hydride and diethyl ether was distilled over lithium aluminum hydride prior to use. Other reagents were of the best commercial grade and were used without further purifications. Isocyanide,[15] $PdCl_2(RNC)_2$,[16] and $Pd_2Cl_2(RNC)_4$[4] were prepared by the known methods. Potassium phenyl-substituted cyclopentadienides ($K\{C_5Ph_5\}$, $K\{C_5HPh_4\}$, or $K\{C_5H_2Ph_3\}$) were prepared by the reaction of 1,2,3,4,5-pentaphenyl-1,3-cyclopentadiene, 1,2,3,4-tetraphenyl-1,3-cyclopentadiene,[17] or 1,2,4-triphenyl-1,3-cyclopentadiene,[18] respectively, with KH in a THF–benzene mixed solvent. All manipulations were carried out under a nitrogen atmosphere.

NMR spectroscopy was carried out on a JEOL GX-400 instrument; ^1H NMR spectra were measured at 400 MHz in $CDCl_3$ or C_6D_6, and ^{13}C NMR spectra were measured at 100 MHz in C_6D_6. Infrared and electronic absorption spectra were recorded with Jasco A-100 and Ubest-30 spectrometers, respectively. Mass spectra were measured on a Hitachi M-80 spectrometer. HPLC analysis was performed on a TSK-CCPM system using a reversed-phase column of ODS-80TM and a detector of UV-8011.

Preparation of $Pd_2(\eta^5\text{-}C_5Ph_5)_2(\mu\text{-}2,6\text{-}Me_2C_6H_3NC)_2\cdot1.5C_6H_6$ (3). A suspension of $PdCl_2(RNC)_2$ ($R = 2,6\text{-}Me_2C_6H_3$) (0.2 mmol) in 20 mL of benzene was treated at 0 °C dropwise with $K\{C_5Ph_5\}$ (0.4 mmol) in 10 mL of a THF–benzene mixed solvent. The reaction mixture was warmed to room temperature and stirred for 1 h. The solvent was removed in vacuo, and the residue was extracted with benzene. The solution was chromatographed on alumina (deactivated with 10 wt % of H_2O) and eluted with benzene. The violet eluate was concentrated to about 10 mL, and an addition of hexane gave violet crystals of $Pd_2(\eta^5\text{-}C_5Ph_5)_2(\mu\text{-}2,6\text{-}Me_2C_6H_3NC)_2\cdot1.5C_6H_6$ (3) in a yield of 51%. Anal. Calcd for $C_{88}H_{68}N_2Pd_2\cdot1.5C_6H_6$: C, 78.53; H, 5.23; N, 1.89. Found: C, 79.25; H, 5.43; N, 1.75. IR (Nujol): $\nu_{N\equiv C}$ 1956 cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (log ϵ) 581 (4.42), 484 (4.24), 378 (4.74) nm. ^1H NMR (C_6D_6): δ 1.94 (s, *o*-Me), 6.6~7.3 (m, H–Ar). ^{13}C NMR (C_6D_6): δ 20.33 (*o*-Me), 116.86 (C—Cp), 145.46 (N≡C).

Preparation of $Pd_2(\eta^5\text{-}C_5HPh_4)_2(\mu\text{-}RNC)_2$ (4) and the Ketenimine Compound $Ph_4C_4C{=}C{=}NR$ (5). A suspension of $PdCl_2(RNC)_2$ (0.2 mmol) in 20 mL of benzene was treated at 0 °C dropwise with $K\{C_5HPh_4\}$ (0.4 mmol) in 10 mL of a THF–benzene mixed solvent. The reaction mixture was warmed to room temperature and stirred for 1 h. The solvent was removed in vacuo, and the residue was extracted with benzene. The solution was chromatographed on alumina (deactivated with 10 wt % of H_2O) and eluted with benzene. The eluate was concentrated to about 10 mL, and an addition of hexane gave violet crystals of **4**, which were recrystallized from a benzene–hexane or CH_2Cl_2–Et_2O mixed solvent. $Pd_2(\eta^5\text{-}C_5HPh_4)_2(\mu\text{-}2,6\text{-}Me_2C_6H_3NC)_2$ (**4a**): yield 21%. Anal. Calcd for $C_{76}H_{60}N_2Pd_2$: C, 75.18; H, 4.98; N, 2.31. Found: C, 74.72; H, 4.91; N, 2.41. IR (Nujol): $\nu_{N\equiv C}$ 1992, 1953s cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (log ϵ) 550 (4.19), 469 (4.08), 369 (4.53) nm. ^1H NMR (C_6D_6): δ 1.82 (s, *o*-Me), 6.46 (s, H–Cp), 6.7~7.3 (m, H–Ar). $Pd_2(\eta^5\text{-}C_5HPh_4)_2(\mu\text{-}2,4,6\text{-}Me_3C_6H_2NC)_2\cdot CH_2Cl_2$ (**4b**): yield 69%. Anal. Calcd for $C_{78}H_{64}N_2Pd_2\cdot CH_2Cl_2$: C, 71.50; H, 5.01; N, 2.11. Found: C, 71.77; H, 5.02; N, 2.31. IR (Nujol): $\nu_{N\equiv C}$ 2001^{sh}, 1977 s, 1942^{sh} cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (log ϵ) 555 (4.19), 463 (4.08), 365 (4.53) nm. ^1H NMR (C_6D_6): δ 1.86 (s, *o*-Me), 2.04 (s, *p*-Me), 4.31 (s, CH_2Cl_2), 6.48 (s, H–Cp), 6.5~7.4 (m, H–Ar). ^{13}C NMR (C_6D_6): δ 19.36 (*o*-Me), 21.40 (*p*-Me), 95.10, 115.75 (C–Ph of Cp), 118.57 (C–H of Cp), 146.85 (N≡C).

The mother liquor mentioned above was chromatographed on silica gel eluted with hexane, to give yellow compounds of formula $Ph_4C_4C{=}C{=}NR$. **5a**: $R = 2,6\text{-}Me_2C_6H_3$, yield 22% for Pd. MS: *m/e* = 500 (M^+). IR (Nujol): $\nu_{C=C=N}$ 2069 cm^{-1}. ^1H NMR (C_6D_6): δ 1.80 (s, *o*-Me), 6.59, 6.67 (A_2B, H–Xyl), 6.9–7.5 (m, H–Ph). **5b**: $R = 2,4,6\text{-}Me_3C_6H_2$, yield 32% for Pd. MS: *m/e* = 514 (M^+). IR (Nujol): $\nu_{C=C=N}$ 2094, 2131^{sh} cm^{-1}. ^1H NMR (C_6D_6): δ 1.83 (s, *o*-Me), 1.87 (*p*-Me), 6.39 (s, H–Mes), 6.9~7.5 (m, H–Ph).

Preparation of $Pd_2(\mu\text{-}\eta^3\text{-}C_5H_2Ph_3)_2(RNC)_2$ (6) and the Ketenimine Compound 2,3,5-$Ph_3HC_4C{=}C{=}NR$ (7). A suspension of $PdCl_2(RNC)_2$ (0.2 mmol) in 20 mL of benzene was treated at 0 °C dropwise with $K\{C_5H_2Ph_3\}$ (0.4 mmol) in 10 mL of THF–benzene mixed solvent. The reaction mixture was warmed to room temperature and stirred for 1 h. The solvent was removed in vacuo, and the residue was extracted with benzene. The dark red solution was chromatographed on alumina (deactivated with 10 wt % of H_2O) and eluted with benzene. The eluate was concentrated to about 10 mL, and an addition of hexane gave dark red crystals of **6**, which were recrystallized from a benzene–hexane or CH_2Cl_2–Et_2O mixed solvent. $Pd_2(\mu\text{-}\eta^5\text{-}C_5H_2Ph_3)_2(2,6\text{-}Me_2C_6H_3NC)_2\cdot{}^1/_2CH_2Cl_2$ (**6a**): yield 25%. Anal. Calcd for $C_{64}H_{52}N_2Pd_2\cdot{}^1/_2CH_2Cl_2$: C, 70.15; H, 4.84; N, 2.54. Found: C, 70.07; H, 4.81; N, 2.77. IR (Nujol): $\nu_{N\equiv C}$ 2097 s, 2026^{sh}, 1937^{sh} cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (log ϵ) 535 (4.07), 339^{sh} (4.92) nm. ^1H NMR (C_6D_6): δ 2.04 (s, *o*-Me), 4.31 (s, CH_2Cl_2), 6.47 (s, H–Cp), 6.6–7.4 (m, H–Ar). $Pd_2(\mu\text{-}\eta^5\text{-}C_5H_2Ph_3)_2(2,4,6\text{-}Me_3C_6H_2NC)_2$ (**6b**): yield 55%. Anal. Calcd for $C_{66}H_{56}N_2Pd_2$: C, 72.73; H, 5.18; N, 2.57. Found: C, 72.40; H, 5.17; N, 2.83. IR (Nujol): $\nu_{N\equiv C}$ 2111s cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (log ϵ) 525^{sh} (3.63), 450^{sh} (3.94), 325^{sh} (4.74) nm. ^1H NMR (C_6D_6): δ 1.95 (s, *p*-Me), 2.06 (*o*-Me), 6.47 (s, H–Cp), 6.8–7.4 (m, H–Ar). Yellow compounds of 2,3,5-$Ph_3HC_4C{=}C{=}NR$ (7) were obtained from the mother liquids. **7a**: $R = 2,6\text{-}Me_2C_6H_3$, yield 12% for Pd. MS: *m/e* = 424 (M^+). IR (Nujol): $\nu_{C=C=N}$ 2130^{sh}, 2061 cm^{-1}. **7b**: $R = 2,4,6\text{-}Me_3C_6H_2$, yield 10% for Pd. MS: *m/e* = 438 (M^+). IR (Nujol): $\nu_{C=C=N}$ 2063 cm^{-1}.

Preparation of $Pd_2\{HB(pz)_3\}_2(\mu\text{-}2,4,6\text{-}Me_3C_6H_2NC)_2$ (8). To a dichloromethane solution of $Pd_2Cl_2(2,4,6\text{-}Me_3C_6H_2NC)_4$ (0.2 mmol) was added 0.4 mmol of $Na\{HB(pz)_3\}$ (pz = pyrazol-1-yl). The reaction mixture was stirred for 48 h at room temperature and was chromatographed on deactivated alumina eluted with CH_2Cl_2. The yellow fraction was collected, and concentrated to about 5 mL. An addition of THF and hexane to the solution gave yellow crystals of $Pd_2\{HB(pz)_3\}_2(\mu\text{-}2,4,6\text{-}Me_3C_6H_2NC)_2$ (8) in a yield of 52%. Anal. Calcd. for $C_{38}H_{42}N_{14}Pd_2B_2$: C, 49.11; H, 4.56; N, 21.10. Found: C, 50.08; H, 4.24; N, 21.21. IR (Nujol): ν_{BH} 2452, $\nu_{C=N}$ 1997, 1978^{sh} cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} (log ϵ) 398 (3.78), 383^{sh} (3.77) nm.

Reaction of 4a with $2,6\text{-}Me_2C_6H_3NC$. A benzene solution containing **4a** (0.01 mmol) and $2,6\text{-}Me_2C_6H_3NC$ (0.02 mmol) was refluxed for 1 h. Then, the solution was cooled and passed through a short silica gel column eluted with hexane. The ketenimine compound **5a** in the eluate was analyzed by HPLC (yield 51% for Pd).

Crystal Data and Intensity Measurements for $Pd_2(\eta^5\text{-}C_5Ph_5)_2(\mu\text{-}2,6\text{-}Me_2C_6H_3NC)_2\cdot1.5C_6H_6$ (3), $Pd_2(\eta^5\text{-}C_5HPh_4)_2(\mu\text{-}2,4,6\text{-}Me_3C_6H_2NC)_2\cdot CH_2Cl_2$ (4b), $Pd_2(\mu\text{-}\eta^3\text{-}C_5H_2Ph_3)_2(2,4,6\text{-}Me_3C_6H_2NC)_2\cdot C_6H_6$ (6b), and

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(4) Yamamoto, Y.; Yamazaki, H. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 1843.

(5) Yamamoto, Y.; Yamazaki, H. *Inorg. Chem.* **1986**, *25*, 3327.

(6) Yamamoto, Y.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1986**, 677.

(7) (a) Yamamoto, Y.; Takahashi, K.; Yamazaki, H. *Chem. Lett.* **1985**, 201. (b) Yamamoto, Y.; Takahashi, K.; Matsuda, K.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1987**, 1833.

(8) (a) Yamamoto, Y.; Aoki, K.; Yamazaki, H. *Chem. Lett.* **1979**, 391. (b) Yamamoto, Y.; Aoki, K.; Yamazaki, H. *Organometallics* **1983**, *2*, 1377.

(9) (a) Yamamoto, Y.; Yamazaki, H.; Sakurai, T. *J. Am. Chem. Soc.* **1982**, *104*, 2329. (b) Yamamoto, Y.; Yamazaki, H. *J. Chem. Soc., Dalton Trans.* **1989**, 2161.

(10) (a) Yamamoto, Y.; Takahashi, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1986**, *108*, 2458. (b) Yamamoto, Y.; Yamazaki, H. *Organometallics*, **1993**, *12*, 933.

(11) Tanase, T.; Kudo, Y.; Ohno, M.; Kobayashi, K.; Yamamoto, Y. *Nature* **1990**, *344*, 526.

(12) Tanase, T.; Horiuchi, T.; Yamamoto, Y.; Kobayashi, K. *J. Organomet. Chem.* **1992**, *440*, 1.

(13) Tanase, T.; Nomura, T.; Yamamoto, Y.; Kobayashi, K. *J. Organomet. Chem.* **1991**, *410*, C25.

(14) Tanase, T.; Nomura, T.; Fukushima, T.; Kobayashi, K.; Yamamoto, Y. *Inorg. Chem.* **1993**, *32*, 4578.

(15) (a) Walborsky, H. M.; Nizwk, G. E. *J. Org. Chem.* **1972**, *37*, 187. (b) Yamamoto, Y.; Aoki, K.; Yamazaki, H. *Inorg. Chem.* **1979**, *18*, 1681.

(16) Bonati, F.; Minghett, G. J. *J. Organomet. Chem.* **1970**, *24*, 251.

(17) Cava, M. P.; Narasimhan, K. *J. Org. Chem.* **1969**, *34*, 3641.

(18) Hirsch, S. S.; Bailey, W. J. *J. Org. Chem.* **1978**, *43*, 4090.

Table 1. Crystallographic and Experimental Data for **3**, **4b**, **6b**, and **8**

	3	**4b**	**6b**	**8**
formula	$C_{97}H_{77}N_2Pd_2$	$C_{79}H_{66}N_2Pd_2Cl_2$	$C_{72}H_{62}N_2Pd_2$	$C_{36}H_{42}N_{14}Pd_2B_2$
fw	1483.49	1327.15	1168.14	929.26
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
lattice consts				
a, Å	13.391(8)	14.907(3)	11.511(4)	11.243(3)
b, Å	23.793(9)	18.794(3)	12.768(3)	15.871(6)
c, Å	13.681(6)	11.769(2)	10.157(2)	12.035(2)
α, deg	90.24(4)	101.88(2)	103.23(2)	
β, deg	118.13(4)	97.33(2)	91.71(2)	91.99(2)
γ, deg	90.30(4)	89.40(2)	96.83(2)	
V, Å^3	3844	3200	1441	2146
Z	2	2	1	2
T, °C	23	23	23	23
D_{calcd}, g cm^{-3}	1.282	1.378	1.347	1.438
μ, mm^{-1}	0.51	0.68	0.66	0.87
R	0.085	0.047	0.034	0.062
R_w	0.088	0.038	0.033	0.073

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

$Pd_2\{HB(pz)_3\}_2(\mu\text{-}2,4,6\text{-}Me_3C_6H_2NC)_2$ (8). Crystal data and experimental conditions for 3, 4b, 6b, and 8 are listed in Table 1. Violet crystals of **3** and **4b**, a dark red crystal of **6b**, and a yellow crystal of **8** sealed into a 0.7-mm-o.d. glass-tube capillary were used in the intensity data collection on Rigaku four-circle AFC4 (**4b**, **6b**) and AFC5S (**3**, **8**) automated diffractometers equipped with Mo Kα radiation. Three standard reflections were monitored every 150 reflections for each compound and showed no systematic decrease in intensity. Since the crystals of **3** and **8** were very unstable in air, each was sealed into a capillary with a small droplet of the mother liquor. Totals of 5628 reflections (**3**), 8008 reflections (**4b**), 6403 reflections (**6a**), and 1813 reflections (**8**) were measured and the intensities were corrected for Lorentz–polarization effects. Absorption corrections with the ψ scan method were applied.

Structure Solution and Refinement. Compound 3. The coordinates of the two palladium atoms were determined by the Patterson techniques, and subsequent Fourier syntheses gave the positions of other non-hydrogen atoms. Hydrogen atoms except for those of the solvated molecule were calculated at the ideal positions with a C–H distance of 0.95 Å, and were not refined. The structure was refined with full-matrix least-squares techniques. Final refinement with anisotropic thermal parameters for palladium atoms and isotropic temperature factors for the other non-hydrogen atoms converged to R = 0.085 and R_w = 0.088, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ ($w = 1/\sigma^2$(Fo)). A final difference Fourier synthesis showed peaks at heights up to 1.3 e Å^{-3} around the Pd(1) atom. Atomic scattering factors and values of f' and f'' for Pd, Cl, P, F, N, and C were taken from refs 19 and 20. All calculations were carried out on a Digital VAX Station 3100 M38 with the TEXSAN-TEXRAY program system.[21] The perspective views were drawn by using the programs ORTEP[22] and PLUTO.[23]

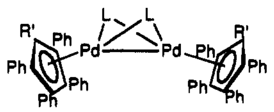
Compound 4b. The structure was solved by direct methods with MULTAN78.[24] The two palladium atoms were located in the initial E map, and subsequent Fourier syntheses gave the positions of other non-hydrogen atoms. Disordered models for the three phenyl rings (C(141)–(146), C(151)–C(156), and C(251)–C(256)) and the dichloromethane molecules were introduced in the structure refinement. The coordinates of all hydrogen atoms except for those of the solvate molecules were determined by difference Fourier syntheses. The structure was refined with block-diagonal least-squares techniques. Final refinement with anisotropic thermal parameters for non-hydrogen atoms and isotropic temperature factors for hydrogen atoms converged to R = 0.047 and R_w = 0.038 ($w = 1/\sigma^2(F_o)$). A final difference Fourier synthesis showed peaks at heights up to 0.69 e Å^{-3} around the Cl(1)′ atom. All calculations were carried out on a FACOM M-780 computer at the Computer Center of the Institute of Physical and Chemical Research with the universal crystallographic computing program system UNICS III.[25]

Compound 6b. The structure was solved by the similar method described in the compound **4b**. The palladium atom was located in the initial E map, and subsequent Fourier syntheses gave the positions of other non-hydrogen atoms. The coordinates of all hydrogen atoms except for those of the solvated molecules were determined by difference Fourier syntheses. The structure was refined with the full-matrix least-squares techniques. Final refinement with anisotropic thermal parameters for non-hydrogen atoms and isotropic temperature factors for hydrogen atoms converged to R = 0.034 and R_w = 0.033 ($w = 1/\sigma^2(F_o)$). A final difference Fourier synthesis showed peaks at heights up to 1.02 e Å^{-3} around the Pd atom.

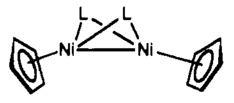
Compound 8. The structure was solved by direct methods with MITHRIL.[26] The palladium atom was located in the initial E map, and subsequent Fourier syntheses gave the positions of other non-hydrogen atoms. Hydrogen atoms were calculated at the ideal positions with C–H distance of 0.95 Å, and were not refined. The structure was refined with the full-matrix least-squares techniques. Final refinement with anisotropic thermal parameters for non-hydrogen atoms converged to R = 0.062 and R_w = 0.073 ($w = 1/\sigma^2(F_o)$). A final difference Fourier synthesis showed peaks at heights up to 0.72 e Å^{-3} around the Pd atom.

Results and Discussion

Preparation and Characterization of $Pd_2(\eta^5\text{-}C_5H_{5-n}Ph_n)_2(\mu\text{-}RNC)_2$ (3, n = 5; 4, n = 4). The IR spectrum of **3** showed an intense peak around 1956 cm^{-1}, indicating the presence of bridging isocyanides having a C–N–C linear form as observed in $Pd_2Cl_2(\mu\text{-}2,6\text{-}Me_2C_6H_3NC)_2(py)_2$ (py = pyridine) (**9**)[5] and $Pd_4(\mu\text{-}OAc)_4(\mu\text{-}{}^tBuNC)_4$ (**10**).[14] The ^{13}C NMR spectrum showed one environment of isocyanide and the C_5Ph_5 group; resonances at δ 20.33, 116.86, and 145.46 are assigned respectively to the 2,6-methyl carbons of RNC, the cyclopentadienyl carbons, and the N≡C carbons. In the electronic spectrum, an absorption band was observed around 581 nm characteristic of the $\eta^5\text{-}C_5Ph_5$ palladium complexes.[1,2]



3 R' = Ph
4 R' = H
L = RNC



11 L = MeNC

A perspective drawing of **3** with the atomic numbering scheme is given in Figure 1, and some selected bond lengths and angles are listed in Table 2. The unit cell is composed of two discrete complex molecules and three solvated benzene molecules, with no abnormally short intermolecular contacts. The complex consists of two palladium atoms bridged by two linear isocyanide ligands and terminally capped by the $\eta^5\text{-}C_5Ph_5$ groups. The structure is analogous to that of $Ni_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CH_3NC)_2$ (**11**).[27] The two isocyanide ligands symmetrically interact with the two Pd atoms (the average Pd–C_t bond length is 2.05 Å, and the average Pd–C_t–Pd angle is 80°; C_t = terminal N≡C carbon of isocyanide), and the isocyanide groups deviate slightly from linearity (the average C–N–C_t angle is 162°, and the average N–C_t bond length is 1.19 Å). This nearly linear bridging system presumably results from the repulsive interaction between the bulky C_5Ph_5 groups and isocyanides, and indicates a weak bockbonding interaction from the occupied d orbital of the Pd_2 unit to the π^* orbitals of isocyanides. A similar structure has been already observed in **9** and **10**. The Pd_2C_2 core is folded as

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(19) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol IV.
(20) Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17.
(21) *TEXSAN-TEXRAY Structure Analysis Package*; Molecular Structure Corp.: The Woodlands, TX, 1985.
(22) Johnson, C. K. *ORTEPII*; Oak Ridge National Laboratory: Oak Ridge, TN, 1976.
(23) Motherwell, S.; Clegg, W. PLUTO. University of Cambridge, England, 1978.
(24) Main, P.; Lessinger, L.; Woolfson, M. M.; Germain, G.; Declerq, J. P. MULTAN78. Universities of York, England, and Louvain, Belgium, 1978.
(25) Sakurai, T.; Kobayashi, K. *Rikagaku Kenkyusho Hokoku* **1979**, *55*, 69.
(26) Gilmore, G. J. *J. Appl. Crystallogr.* **1984**, *17*, 42.
(27) Byers, L. R.; Dahl, L. F. *Inorg. Chem.* **1980**, *19*, 680.

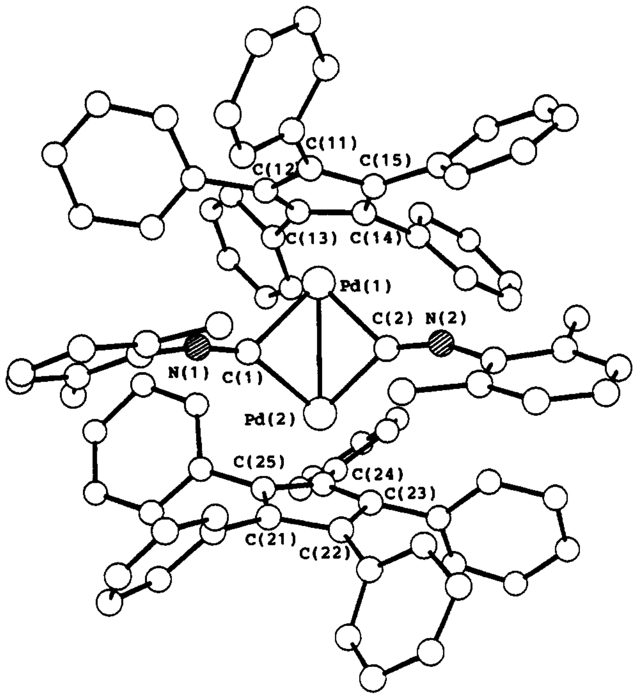


Figure 1. Perspective drawing of the complex $Pd_2(\eta^5\text{-}C_5Ph_5)_2(\mu\text{-}2,6\text{-}Me_2C_6H_3NC)_2$ (**3**).

Table 2. Selected Bone Lenghts (Å) and Angles (deg) for **3**[a]

	Bond Lengths		
Pd(1)–Pd(2)	2.632(5)		
Pd(1)–C(1)	2.13(3)	Pd(2)–C(1)	2.05(3)
Pd(1)–C(2)	2.03(3)	Pd(2)–C(2)	1.99(3)
Pd(1)–C(11)	2.31(3)	Pd(2)–C(21)	2.33(3)
Pd(1)–C(12)	2.34(3)	Pd(2)–C(22)	2.37(3)
Pd(1)–C(13)	2.47(3)	Pd(2)–C(23)	2.32(3)
Pd(1)–C(14)	2.40(3)	Pd(2)–C(24)	2.47(3)
Pd(1)–C(15)	2.29(3)	Pd(2)–C(25)	2.40(3)
N(1)–C(1)	1.16(3)	N(2)–C(2)	1.21(3)
N(1)–C(101)	1.35(3)	N(2)–C(201)	1.39(4)
C(11)–C(12)	1.44(4)	C(21)–C(22)	1.49(4)
C(12)–C(13)	1.33(3)	C(22)–C(23)	1.35(4)
C(13)–C(14)	1.40(3)	C(23)–C(24)	1.42(4)
C(14)–C(15)	1.36(3)	C(24)–C(25)	1.36(4)
C(15)–C(11)	1.45(4)	C(25)–C(21)	1.43(4)
	Bond Angles		
Pd(2)–Pd(1)–C(1)	49.5(7)	Pd(1)–Pd(2)–C(1)	52.4(7)
Pd(2)–Pd(1)–C(2)	48.3(9)	Pd(1)–Pd(2)–C(2)	49.8(9)
C(1)–Pd(1)–C(2)	82(1)	C(1)–Pd(2)–C(2)	86(1)
Pd(1)–C(1)–Pd(2)	78(1)	Pd(1)–C(2)–Pd(2)	82(1)
Pd(1)–C(1)–N(1)	135(2)	Pd(1)–C(2)–N(2)	135(3)
Pd(2)–C(1)–N(1)	147(2)	Pd(2)–C(2)–N(2)	143(3)
C(1)–N(1)–C(101)	167(3)	C(2)–N(2)–C(201)	157(3)

[a] Estimated standard deviations in parentheses.

a butterfly form with a dihedral angle of 121.6° between the two Pd_2C planes and one of 119.7° between the two PdC_2 planes (θ) (Table 3). The Pd–Pd bond distance of 2.632(5) Å is within the range for the Pd–Pd σ bond, and is comparable to that of $Pd_2(\eta^5\text{-}C_5Ph_5)_2(\mu\text{-}PhC{\equiv}CPh)$ (**1**) (2.639(1) Å).[1] The palladium–cyclopentadienyl carbon distance shows a large deviation from 2.29 to 2.47 Å, due to the steric repulsion of the phenyl groups between the two C_5Ph_5 groups. The tilting angle (τ) between the two cyclopentadienyl planes is 40.4°, and the cyclopentadienyl rings are staggered in order to minimize the steric repulsions involving the phenyl substituents (Figure 2).

When potassium tetraphenylcyclopentadienide ($K\{C_5HPh_4\}$) was used instead of $K\{C_5Ph_5\}$, similar violet crystals formulated as $Pd_2(\eta^5\text{-}C_5HPh_4)_2(\mu\text{-}RNC)_2$ (**4a**, R = $2,6\text{-}Me_2C_6H_3$, 21%; **4b**, R = $2,4,6\text{-}Me_3C_6H_2$, 69%) were obtained. The IR spectra indicated an intense peak around 1960 cm^{-1} just as observed for complex **3**, and the UV–vis spectra showed a characteristic absorption at about 550 nm. The ^1H NMR spectra showed the presence of one kind of isocyanide and C_5HPh_4 group; a singlet for the cyclopentadienyl proton (Cp–H) was observed at δ 6.42. In the ^{13}C NMR spectrum of **4b**, resonances at δ 19.36, 21.40, and 146.85 were assigned to the 2,6-methyl, 4-methyl, and the terminal N≡C carbons of isocyanide, respectively, and three peaks for the cyclopentadienyl carbons were observed at δ 95.10, 115.75, and 118.57.

Table 3. Structural Parameters of **3**, **4b**, and **8**

	3	**4b**	**8**	**9**[d]
Pd–Pd, Å	2.632(5)	2.673(1)	2.757(4)	2.662(1)
$[PdC_{t2}]$ vs $[Pd'C_{t2}]$ (θ),[a] deg	119.7	135.0	180.0	129.8
$[Pd_2C_t]$ vs $[Pd_2C'_t]$,[b] deg	121.6	137.6	180.0	131.3
[Cp] vs [Cp] (τ),[c] deg	40.4	20.5		
av $Pd\text{–}C_t$, Å	2.05	2.03	1.95	2.01
av $C_t\text{–}Pd\text{–}C'_t$, deg	84	89.1	90(1)	86.4
av $Pd\text{–}C_t\text{–}Pd'$, deg	80	82.4	90(1)	82.9
av $C_t\text{–}N$, Å	1.19	1.17	1.24(3)	1.18
av $C_t\text{–}N\text{–}C$, deg	162	167.3	174(2)	166.4

[a] The dihedral angle (θ) between the two PdC_{t2} planes. C_t is the terminal carbon of isocyanide. [b] The dihedral angle between the two Pd_2C_t planes. [c] The dihedral angle (τ) between the two mean planes of the Cp rings. [d] Reference 5.

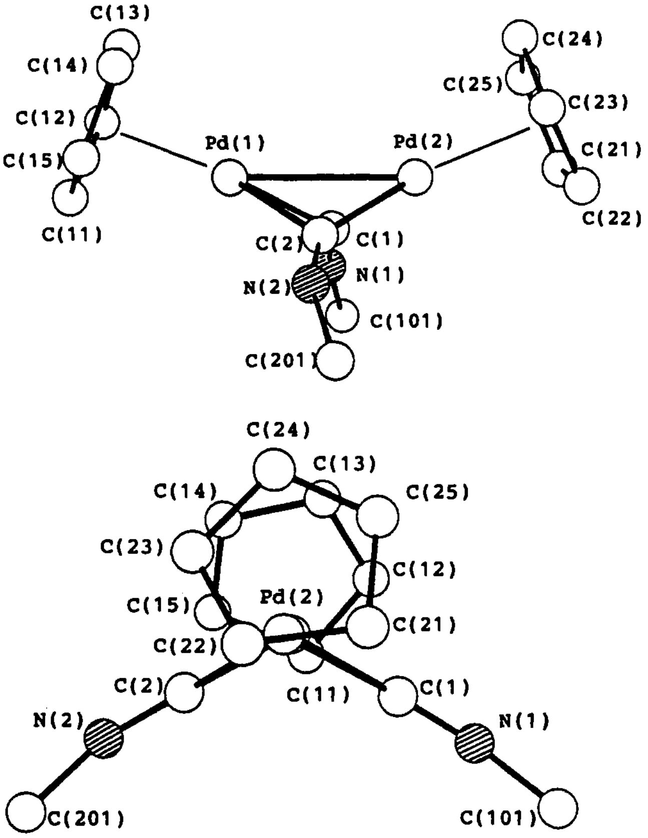


Figure 2. Perspective drawings of complex **3**, showing the folded structure. Phenyl rings are omitted for clarity.

A perspective drawing of **4b** with the atomic numbering scheme is given in Figure 3, and some selected bond lengths and angles are listed in Table 4. The phenyl groups on the C(14), C(15), and C(25) atoms were disordered with a population ratio of 55:45, rotating around the ipso–apex carbon axis of the phenyl ring. The major population set of the phenyl rings are illustrated in Figure 3. The unit cell contains two complex molecules and two solvate dichloromethane molecules. The molecular structure of **4b** is essentially identical to that of **3**. The binuclear Pd(I) unit was bridged by two isocyanides adopting the linear C–N–C structure (average $Pd\text{–}C_t$ = 2.03 Å, average $N\text{–}C_t$ = 1.17 Å, average $Pd\text{–}C_t\text{–}Pd$ = 82.4°, and average $C\text{–}N\text{–}C_t$ = 167.3°). The Pd_2C_2 core is folded with a dihedral angle (θ) of 137.6° (PdC_2 vs

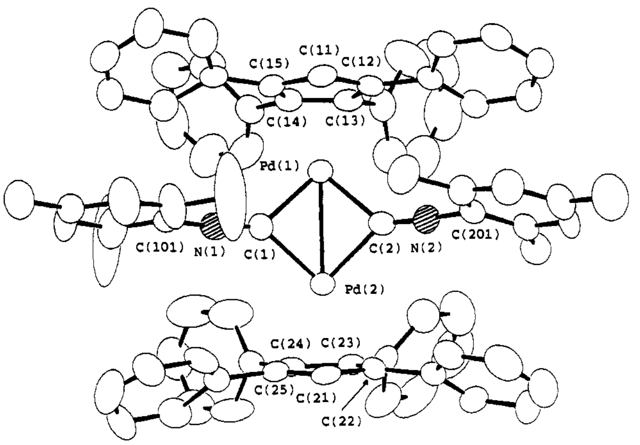


Figure 3. Perspective drawing of the complex $Pd_2(\eta^5\text{-}C_5HPh_4)_2(\mu\text{-}2,4,6\text{-}Me_3C_6H_2NC)_2$ (**4b**).

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **4b**[a]

	Bond Lengths		
Pd(1)–Pd(2)	2.673(1)		
Pd(1)–C(1)	2.022(7)	Pd(2)–C(1)	2.021(8)
Pd(1)–C(2)	2.035(8)	Pd(2)–C(2)	2.045(7)
Pd(1)–C(11)	2.317(8)	Pd(2)–C(21)	2.307(8)
Pd(1)–C(12)	2.375(7)	Pd(2)–C(22)	2.350(8)
Pd(1)–C(13)	2.471(8)	Pd(2)–C(23)	2.484(8)
Pd(1)–C(14)	2.470(8)	Pd(2)–C(24)	2.501(8)
Pd(1)–C(15)	2.347(9)	Pd(2)–C(25)	2.354(7)
N(1)–C(1)	1.172(10)	N(2)–C(2)	1.161(9)
N(1)–C(101)	1.407(10)	N(2)–C(201)	1.385(9)
C(11)–C(12)	1.44(1)	C(21)–C(22)	1.44(1)
C(12)–C(13)	1.43(1)	C(22)–C(23)	1.44(1)
C(13)–C(14)	1.39(1)	C(23)–C(24)	1.41(1)
C(14)–C(15)	1.45(1)	C(24)–C(25)	1.44(1)
C(15)–C(11)	1.41(1)	C(25)–C(21)	1.41(1)
	Bond Angles		
Pd(2)–Pd(1)–C(1)	48.6(2)	Pd(1)–Pd(2)–C(1)	48.6(2)
Pd(2)–Pd(1)–C(2)	49.2(2)	Pd(1)–Pd(2)–C(2)	48.9(2)
C(1)–Pd(1)–C(2)	89.2(3)	C(1)–Pd(2)–C(2)	89.0(3)
Pd(1)–C(1)–Pd(2)	82.8(3)	Pd(1)–C(2)–Pd(2)	81.9(3)
Pd(1)–C(1)–N(1)	139.0(7)	Pd(1)–C(2)–N(2)	138.4(6)
Pd(2)–C(1)–N(1)	138.1(7)	Pd(2)–C(2)–N(2)	139.5(7)
C(1)–N(1)–C(101)	167.5(8)	C(2)–N(2)–C(201)	167.0(8)

[a] Estimated standard deviations in parentheses.

Pd′C$_2$), which is smaller by 16° than that found in **3** (Table 3). The great bending structure of the pentaphenylcyclopentadienyl dimer is attributable to steric repulsion between the phenyl groups on the C(11) and C(21) carbons and the bridging isocyanides. The Pd–Pd bond length of 2.673(1) Å is longer by 0.041 Å than that of **3**. The C_5HPh_4 anions terminally coordinate to the palladium atoms in η^5-fashion. The palladium–cyclopentadienyl carbon distances are divided into two groups; the C(11), C(12), C(15), C(21), C(22), and C(25) atoms are bound to the Pd center within a range of 2.307–2.375 Å and the C(13), C(14), C(23), and C(24) atoms, within 2.470–2.501 Å, indicating a slight slippage toward the C(11) and C(21) apex carbon atoms which have no phenyl substituent. The two Cp rings adopt an eclipsed conformation with a tilting angle (τ) of 20.5° (Figure 4).

The reaction of the palladium(I) dimer, $Pd_2Cl_2(RNC)_4$, with $K\{C_5HPh_4\}$ resulted in a trace amount of **4** owing to the deposit of elemental palladium. The direct reaction of palladium(II) complex, $PdCl_2(RNC)_2$, with $K\{C_5HPh_4\}$ is an effective synthetic route to the dipalladium(I) complex **4**.

After an isolation of the compound **4**, the mother liquor was chromatographed on silica gel eluted with hexane afforded a yellow organic compound **5** in 22–32% yields based on palladium. The mass spectra indicated that the compound **5** was composed of one cyclopentadienylidene unit (C_5Ph_4) and one isocyanide molecule, accompanied by a loss of one hydrogen atom. In the IR spectra, a sharp absorption band was observed at 2069–2094 cm^{-1}, which is consistent with a ketenimine unit (C=C=N). In the ^{1}H NMR spectra, a singlet for the 2,6-methyl protons of isocyanide appeared at about δ 1.80, and that for the cyclopentadienyl proton (Cp-H) was not observed. These spectral data suggested that the compound **5** is a ketenimine compound as shown in Scheme 1. Compound **5a** was also prepared by refluxing of **4a** and $2,6\text{-}Me_2C_6H_3NC$ in benzene in a yield of 51%. A possible mechanism for the formation of **5** is given in Scheme 1; an initial $\eta^5 \rightarrow \eta^1$ rearrangement of C_5HPh_4 ligand was presumably followed by an insertion of isocyanide into a Pd–C σ-bond, and subsequently an elimination of a β-hydrogen atom gave the ketenimine compound **5**. Otsuka et al. reported the ketenimine formation by the reaction of $Ni({}^tBuNC)_4$ with diazodicyanomethane, which involved a metal-assisted carbene addition to a coordinated isocyanide.[28] Recently, similar ketenimine formation has been observed in the reaction of $Co(\eta\text{-}C_5H_5)(RNC)(PMe_3)$ with diazoalkanes.[29] In these reactions, intermediate

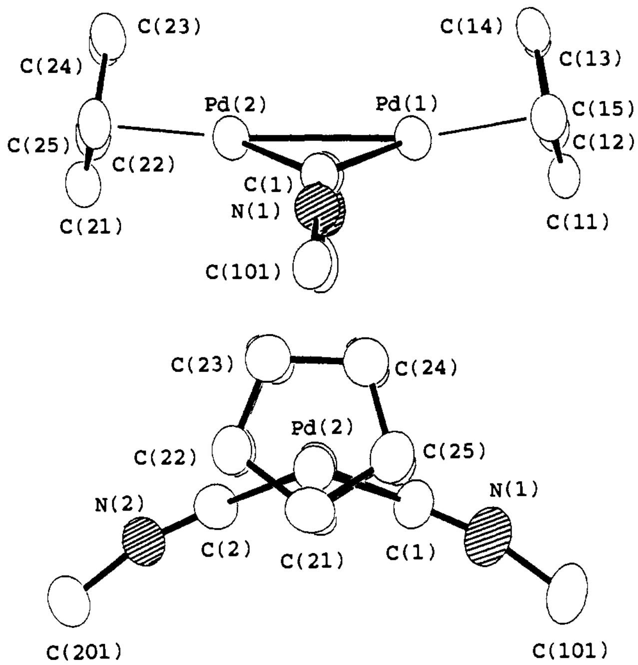
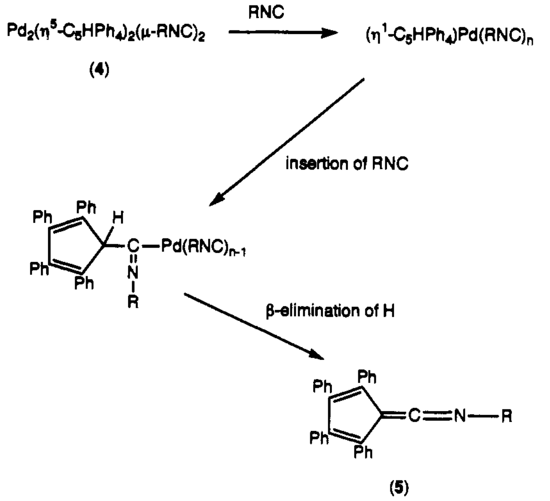


Figure 4. Perspective drawings of complex **4b**, showing the folded structure. Phenyl rings are omitted for clarity.

Scheme 1



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(28) Yarrow, D. J.; Ibers, J. A.; Tatsuno, Y.; Otsuka, S. *J. Am. Chem. Soc.* **1973**, *95*, 8590.

(29) (a) Strecker, B.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 275. (b) Strecker, B.; Horlin, G.; Schulz, M.; Werner, H. *Chem. Ber.* **1991**, *124*, 285.

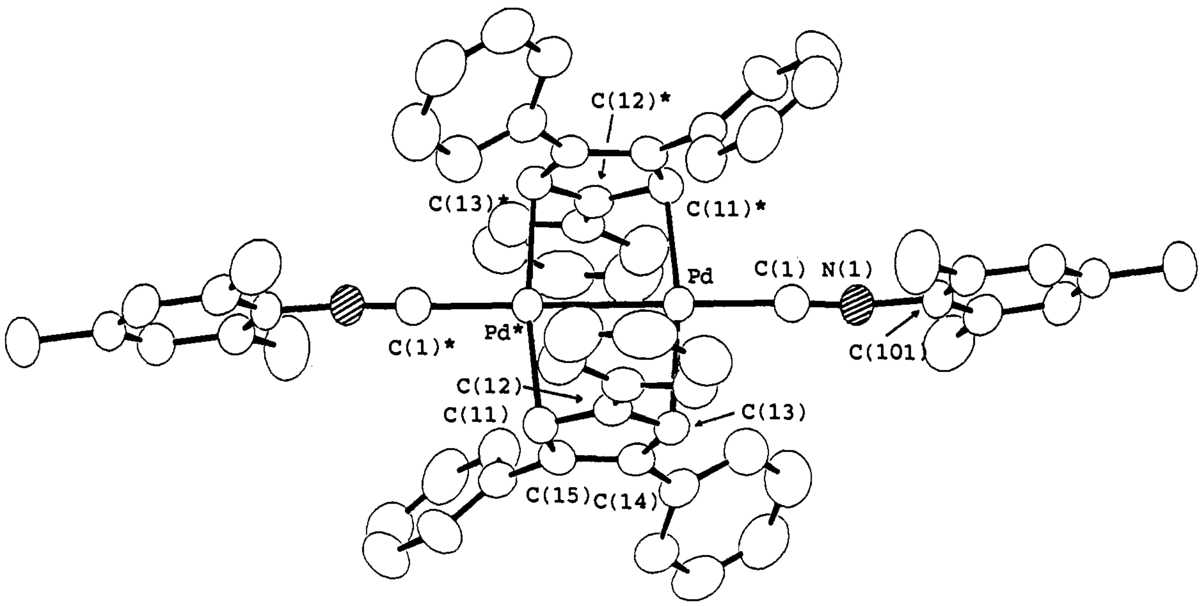
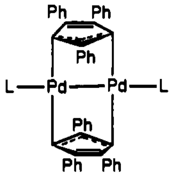


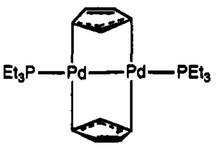
Figure 5. Perspective drawing of the complex $Pd_2(\mu\text{-}\eta^3\text{-}C_5H_2Ph_3)_2(2,4,6\text{-}Me_3C_6H_2NC)_2$ (**6b**).

complexes of ketenimine were isolated and characterized. In the present case, an intermediate cyclopentadienylidene palladium complex can not be thoroughly ruled out, but the $\eta^5 \rightleftharpoons \eta^1$ interconversion of cyclopentadienyl group is the more usual behavior in palladium complexes,[30,31] and is thus a plausible initial step.

Preparation and Characterization of $Pd_2(\mu\text{-}\eta^3\text{-}C_5H_2Ph_3)_2(RNC)_2$ (6). The IR spectra of **6** showed a sharp peak around 2100 cm^{-1}, corresponding to the terminal isocyanides coordinated to a monovalent palladium center. In the UV–vis spectra, the characteristic absorption at 550–580 nm was not observed, suggesting the absence of a η^5-cyclopentadienyl mode. The ^1H NMR spectra indicated the presence of one kind of isocyanide and $C_5H_2Ph_3$ groups; a singlet for the cyclopentadienyl protons was observed at δ 6.47.



6 L = RNC



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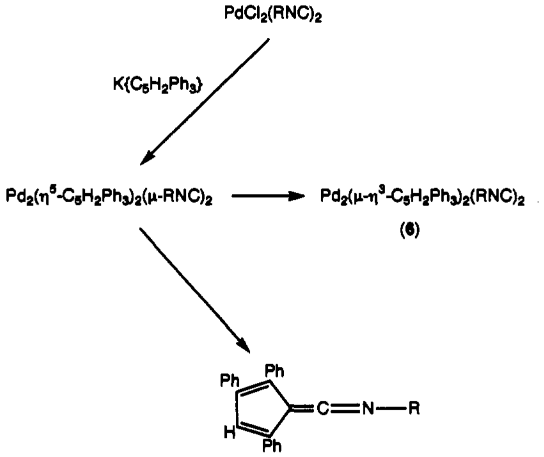
A perspective drawing of 6b with the atomic numbering scheme is given in Figure 5, and some selected bond lengths and angles are listed in Table 5. The complex molecule has a crystallographically imposed inversion center in the middle of the Pd–Pd bond. The molecule of **6b** consists of two palladium atoms bridged by two $C_5H_2Ph_3$ groups and terminally coordinated by two isocyanide ligands. The two cyclopentadienyl planes are parallel in an *anti* arrangement. Similar binuclear structure was observed in $Pd_2(\mu\text{-}\eta^3\text{-}C_5H_5)_2(PEt_3)_2$ (**12**).[32] The palladium–palladium bond length of 2.6309(9) Å is shorter than that of **12** (2.673(1) Å). The bond distances of Pd–C(13) and Pd*–C(11) are 2.168(3) and 2.162(3) Å, and those of Pd–C(12) and Pd*–C(12) are 2.509(3) and 2.644(3) Å. The distances of Pd–C(14) and Pd*–C(15) are 2.902(4) and 2.766(3) Å, which are out of the normal bonding range. Further, the C(14)–C(15) bond length of 1.385(5) Å is shorter than those of other C-C bonds in the cyclopentadienyl ring (1.432–1.450 Å). These structure indicated the η^3-allylene bonding mode of the $C_5H_2Ph_3$ anions. The $Pd_2(RNC)_2$ core adopts an almost linear structure; the bond angles of Pd*–Pd–C(1), Pd–C(1)–N(1), and C(1)–N(1)–C(101) are 176.62(9), 177.0(3), and 174.8(4)°, respectively.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **6b**[a]

	Bond Lengths		
Pd–Pd*	2.6309(9)		
Pd–C(1)	1.974(3)	Pd–C(11)*	2.162(4)
Pd–C(13)	2.168(4)	Pd–C(12)	2.509(3)
Pd–C(12)*	2.644(3)	Pd–C(14)	2.902(4)
Pd–C(15)*	2.766(3)		
N(1)–C(1)	1.153(4)	N(1)–C(101)	1.407(4)
C(11)–C(12)	1.433(5)	C(12)–C(13)	1.432(4)
C(13)–C(14)	1.450(5)	C(14)–C(15)	1.387(4)
C(15)–C(11)	1.441(5)		
	Bond Angles		
Pd*–Pd–C(1)	176.62(9)	Pd*–Pd–C(11)*	84.30(9)
Pd*–Pd–C(13)	86.27(9)	C(1)–Pd–C(11)*	96.7(1)
C(1)–Pd–C(13)	93.1(1)	C(11)*–Pd–C(13)	168.4(1)
Pd–C(1)–N(1)	177.0(3)	C(1)–N(1)–C(101)	174.8(4)
Pd*–C(11)–C(12)	92.5(2)	Pd*–C(11)–C(15)	98.3(2)
Pd–C(13)–C(12)	85.8(2)	Pd–C(13)–C(14)	104.9(2)

[a] Estimated standard deviations in parentheses.

Scheme 2



In the reaction of $PdCl_2(RNC)_2$ with $K\{C_5H_2Ph_3\}$, the color of the reaction mixture changed from violet reminiscent of the formation of η^5-cyclopentadienyl complex to dark red; the

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(30) O'Connor, J. M.; Casey, C. P. *Chem. Rev.* **1987**, *87*, 307.
(31) Powell, J.; Dowling, N. I. *Organometallics* **1983**, *2*, 1742.
(32) Werner, H.; Kraus, H. J.; Schubert, U.; Ackermann, K. *Chem. Ber.* **1982**, *115*, 2905.

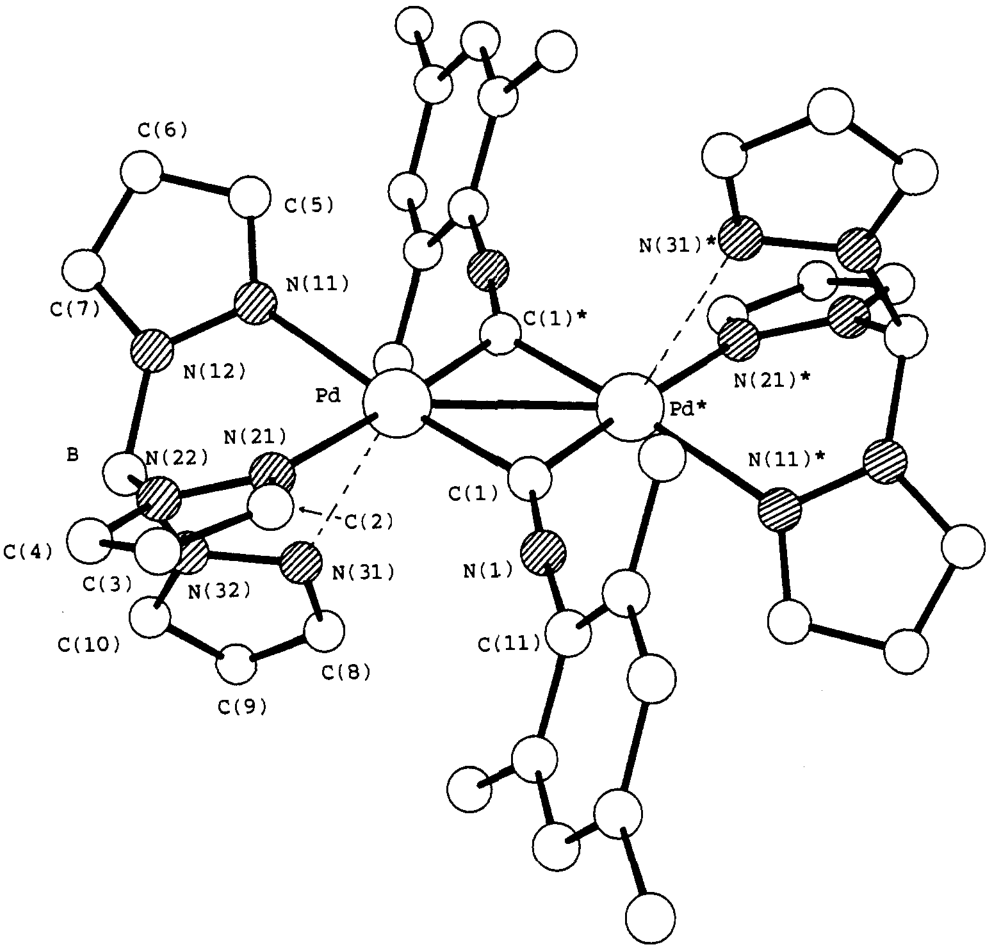


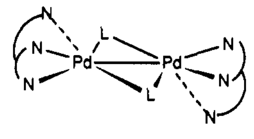
Figure 6. Perspective drawing of the complex $Pd_2(\mu\text{-}2,4,6\text{-}Me_3C_6H_2NC)_2\{HB(pz)_3\}_2$ (**8**).

transition from a η^5- to a η^3-mode would take place in solution. Presumably, the electron-rich dimer of $Pd_2(\eta^5\text{-}C_5H_2Ph_3)_2(\mu\text{-}RNC)_2$ (34 valence electrons) was not sufficiently stabilized by the triphenyl cyclopentadienyl ligands and was alternatively transformed to the dimer of $Pd_2(\mu\text{-}\eta^3\text{-}C_5H_2Ph_3)_2(RNC)_2$ (30 valence electrons). By chromatography of the reaction mixture on silica gel, the ketenimine compound, $Ph_3HC_4C{=}C{=}N{-}R$ (**7a**, R = $2,6\text{-}Me_2C_6H_3$; **7b**, R = $2,4,6\text{-}Me_3C_6H_2$), was obtained in low yields (10–12% based on Pd). Unlike the dimer **4**, the reaction of **6** with RNC did not afford the ketenimine **7**. Thus, compound **7** was seemingly formed via the isocyanide-bridged dimer of $Pd_2(\eta^5\text{-}C_5H_2Ph_3)_2(\mu\text{-}RNC)_2$ generated at an early stage of the reaction (Scheme 2).

When $PdCl_2(RNC)_2$ was treated with an excess of NaC_5H_5, the trinuclear palladium cluster of isocyanide, $Pd_3(\mu\text{-}RNC)_3(RNC)_3$,[33] was obtained in 50–55% yields instead of palladium dimers with cyclopentadienyl ligands. The electron-withdrawing effect as well as the steric bulkness of phenyl substituents in Cp is very important in stabilizing the binuclear palladium structures.

Preparation and Characterization of $Pd_2\{HB(pz)_3\}_2(\mu\text{-}RNC)_2$ (8). An attempt to introduce the tris(pyrazol-1-yl)borate ligand ($HB(pz)_3$) into the Pd_2 center was made to compare with the reaction of phenyl-substituted cyclopentadienyl groups. The $HB(pz)_3$ ligand usually is tridentate in octahedral complexes and is often compared with cyclopentadienyl analogues. Contrasted with studies on a number of octahedral complexes, studies on square planar complexes with $HB(pz)_3$ were limited to some mononuclear species.[34-36]

The IR spectrum indicated the presence of $HB(pz)_3$ groups (ν_{BH} 2452 cm^{-1}) and the bridging isocyanides having the C–N–C$_t$ linear form ($\nu_{C{=}N}$ 1997 cm^{-1}). In the ^1H NMR spectrum, only one environment of pyrazolyl rings was observed at room temperature (δ 6.02 for H_4, and 7.57, 7.58 for H_3 and/or H_5 protons of $HB(pz)_3$), indicating a fluxional behavior of three pyrazolyl rings.



8 L = RNC

A perspective drawing of complex **8** with the atomic numbering scheme is illustrated in Figure 6, and some selected bond lengths and angles are listed in Table 6. The complex consists of two palladium atoms bridged by two isocyanides, and the Pd_2C_2 core is crystallographically planar (an inversion center is on the middle of the Pd–Pd bond), with an average Pd–C distance of 1.95 Å. The bridging isocyanide takes a linear form as observed in **3** and **4b** (C(1)–N(1)–C(11) = 174(2)°). The C(1)–N(1) distance of 1.24(3) Å is longer than those found in **3** (average 1.19 Å), **4b** (average 1.17 Å), and **9** (average 1.18 Å). The $HB(pz)_3$ ligand coordinates to the metal in an asymmetrical tridentate manner. The N(11) and N(21) atoms bound to the palladium atom with an average distance of 2.16 Å, and the N(31) atom weakly

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(33) Stone, F. G. A.; et al. *J. Chem. Soc., Chem. Commun.* **1983**, 3.

(34) (a) Canty, A. J.; Minchin, N. J.; Engelhardt, L. M.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1986**, 645. (b) Canty, A. J.; Minchin, N. J.; Patrick, J. M.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 1253.

(35) (a) Rush, P. E.; Oliver, J. D. *J. Chem. Soc., Chem. Commun.* **1974**, 996. (b) Reger, D. L.; Baxter, J. C.; Lebioda, L. *Inorg. Chim. Acta* **1989**, *165*, 201.

(36) Canty, A. J.; Minchin, N. J.; Healy, P.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 1795.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for **8**[a]

	Bond Lengths		
Pd–Pd*	2.757(4)		
Pd–C(1)	1.95(2)	Pd–C(1)*	1.94(3)
Pd–N(11)	2.19(2)	Pd–N(21)	2.12(3)
Pd–N(31)	2.69(2)		
N(1)–C(1)	1.24(3)	N(1)–C(11)	1.42(3)
N(12)–B	1.53(4)	N(22)–B	1.53(3)
N(32)–B	1.55(3)		
	Bond Angles		
Pd*-Pd-N(11)	136.2(6)	Pd*-Pd-N(21)	137.3(5)
Pd*-Pd-N(31)	110.0(5)	Pd*-Pd-C(1)	44.7(9)
Pd*-Pd-C(1)*	45.1(7)	C(1)-Pd-C(1)*	90(1)
Pd-C(1)-Pd*	90(1)	Pd-C(1)-N(1)	135(2)
N(11)-Pd-N(21)	85.8(8)	N(11)-Pd-C(1)	172.1(9)
N(11)-Pd-C(1)*	92(1)	N(21)-Pd-C(1)	93(1)
N(21)-Pd-C(1)*	177.1(8)	N(11)-Pd-N(31)	81.6(7)
N(21)-Pd-N(31)	78.5(8)	C(1)-N(1)-C(11)	174(2)

[a] Estimated standard deviations in parentheses.

interacts with the palladium atom (Pd···N(31) = 2.64(3) Å) in the axial site. The Pd, C(1), C(1)*, N(11), and N(21) atoms lie in a planar array, and the largest deviation from the mean plane is 0.21 Å (N(11)). The mean plane of the axial pyrazolyl ring forms a dihedral angle of 82° with the PdC_2N_2 mean plane. A similar axial interaction was observed in $Au\{HC(pz)_3\}(CH_3)_2$ (**13**) (the Au···N distance = 3.139(7) Å),[36] however, the Pd···N distance in **8** is somewhat shorter and the distortion from the planar geometry in **8** is much more significant than found in **13**. The isolated structure is regarded as a five-coordinated intermediate of the fluxional structure in solution. The Pd–Pd bond length of 2.757(4) Å is significantly longer than the normal value for Pd–Pd single bonds and is comparable to the Pd–Pd bond length in the metal (2.751 Å).[37]

The metal–metal interaction is estimated to be weak because the σ^* and π^* orbitals between the two metals are all occupied in the $Pd_2(\mu\text{-RNC})_2$ dimer.[38] Figure 7 has been constructed to show the definite change in the Pd–Pd distance as the core bends (θ) in the series of $Pd_2(\mu\text{-RNC})_2$ dimers (**3**, **4b**, **8**, and **9**). A linear correlation between the Pd–Pd distance and the dihedral angle of the PdC_2–$Pd'C_2$ fragment is observed with a correlation coefficient of 0.996. This indicated that the large deviation of the Pd–Pd distance (2.632–2.757 Å) in these compounds is primarily attributed to the bending deformation of the $Pd_2(\mu\text{-RNC})_2$ core, rather than to the metal–metal interaction, on the basis of the assumption that the perturbation of Pd_2C_2 core by the terminal ligands is not so significant.

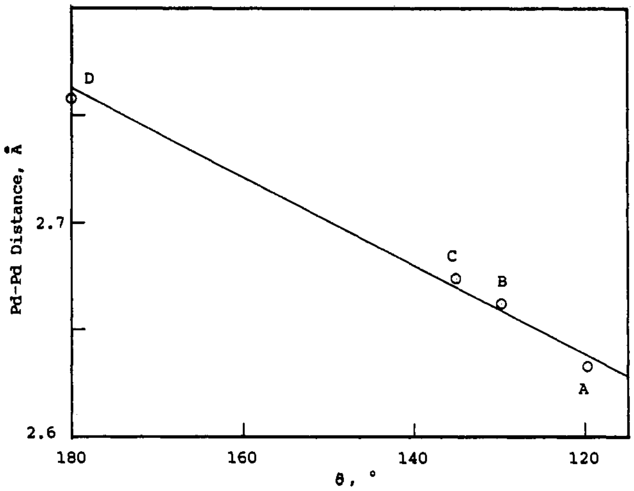

Figure 7. Plots of the Pd–Pd bond distance vs the dihedral angle (θ) between the two PdC_2 planes: (A) **3**; (B) **9**; (C) **4a**; (D) **8**.

The present work provides an efficient route to a new series of binuclear palladium(I) complexes containing cyclopentadienyl analogues and isocyanides. It is notable that the dipalladium compounds with the phenyl-substituted cyclopentadienyl anions can be treated even under aerobic atmosphere. Both the steric and electronic effects of the phenyl groups on the cyclopentadienyl anion might be responsible for the greater stability of the Pd_2 core compared with the previously reported cyclopentadienyl compounds **2** and **11**. Further studies including reactions of the dipalladium compound with $HB(pz)_3$ ligand as well as those with cyclopentadienyl derivatives are now in progress.

Supplementary Material Available: Listing of crystallographic data, positional and thermal parameters, atomic parameters of hydrogen atoms, and bond lengths and angles for **3**, **4b**, **6b**, and **8**, (38 pages). Ordering information is given on any current masthead page.

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(37) Donohue, J. *The Structure of Elements*; Wiley: New York, 1974; p 216.

(38) Pinhas, A. R.; Hoffmann, R. *Inorg. Chem.* **1979**, *18*, 654.