It is noteworthy that a different heterocumulene, namely diphenylketene, was anodically oxidized in acetonitrile and afforded benzophenone as the sole product (eq 5). Clearly, no molecular

$$\mathrm{Ph_2C{=}C{=}O} \xrightarrow[n\,=\,2.3]{2.3\ \mathrm{V}} \mathrm{PhCOPh}\ (60\%) \qquad (5)$$

oxygen is involved in the formation of the product since the same result was obtained when the reaction was carried out under nitrogen atmosphere.

Further mechanistic studies as well as MO calcualtions on various heteroallenes and their corresponding radical cations are in progress in our laboratory.

Registry No. 1, 538-75-0; **2**, 691-24-7; **3**, 3173-53-3; **4**, 1122-82-3; **1a**, 108-94-1; **1b**, 1124-53-4; **1c**, 2387-23-7; **2a**, 762-84-5; **2b**, 5336-24-3; diphenyl ketene, 525-06-4; benzophenone, 119-61-9.

Mixed-Metal Cluster of Isocyanide Containing a Mercury Atom in the Center of a Trigonal-Prismatic Platinum Framework. Hg[Pt$_3$(2,6-Me$_2$C$_6$H$_3$NC)$_6$]$_2$

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Metal clusters are of interest as plausible models of the surface of heterogeneous catalysts.[1] Carbonyl clusters with various kind of nuclearity are well-known, whereas there are few examples of metal clusters containing isocyanides as a sole ligand. Muetterties et al. have reported the synthesis and properties of a four-metal-atom cluster, Ni$_4$[(CH$_3$)$_3$CCN]$_7$.[2] Recently we established the crystal structure of an isocyanide cluster containing seven platinum atoms, Pt$_7$(2,6-Me$_2$C$_6$H$_3$NC)$_{12}$.[3] We here describe the synthesis and characterization of a unique mixed-metal cluster having platinum and mercury atoms.

A mixture of dichlorobis(2,6-xylyl isocyanide)platinum(II) (0.6 g, 1.14 mmol) and 2,6-xylyl isocyanide (0.05 g, 0.38 mmol) was treated with Na–Hg in THF at room temperature under a nitrogen atmosphere. After 4 h, the resulting dark green solution was chromatographed on deactivated alumina under nitrogen atmosphere, and two bands were observed. The first elution with benzene gave dark green solution. After removal of the solvent, the green crystals (0.157 g) resulting from crystallization of the residue from benzene–hexane were formulated as HgPt$_6$(2,6-Me$_2$C$_6$H$_3$NC)$_{12}$, **1**.[4] The mother liquor changed from dark green to reddish brown after removal of **1**. Further crystallization from the mother liquor gave known brown crystals **2** (0.07 g) formulated as Pt$_7$(2,6-Me$_2$C$_6$H$_3$NC)$_{12}$.[3] The second elution from benzene–CH$_2$Cl$_2$ eluted a pale yellow solution, from which a pale yellow crystalline solid having the formula Pt(2,6-Me$_2$C$_6$H$_3$NC)$_5$ **3** (0.01 g),[5] was obtained.

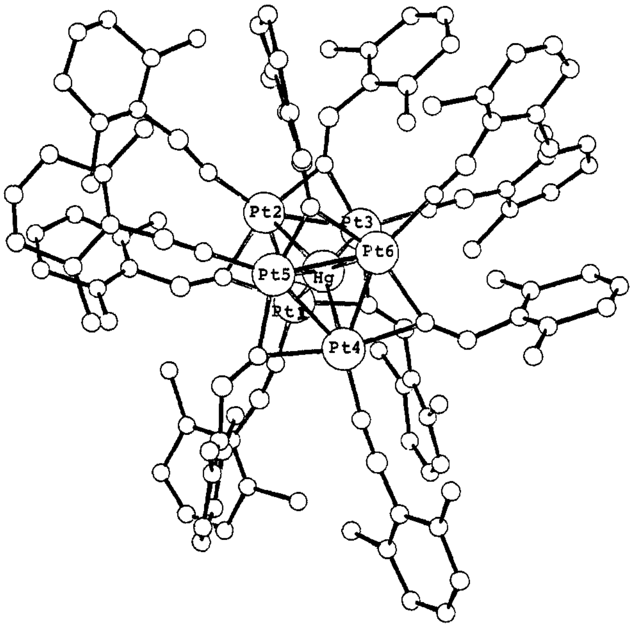

Figure 1. Crystal structure of Hg[Pt$_3$(2,6-Me$_2$C$_6$H$_3$NC)$_6$]$_2$.

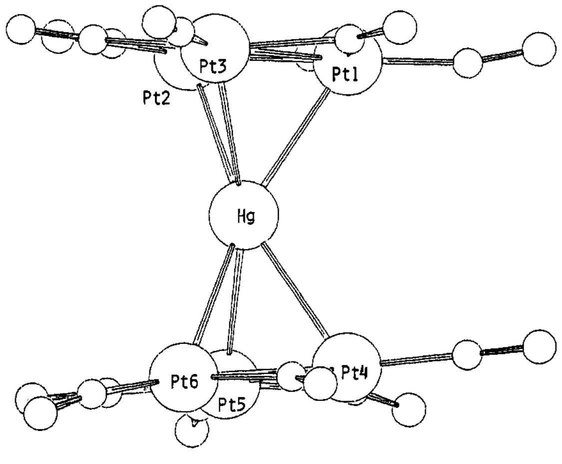

Figure 2. Crystal structure of Hg[Pt$_3$(2,6-Me$_2$C$_6$H$_3$NC)$_6$]$_2$. 2,6-Xylyl groups are omitted for clarity.

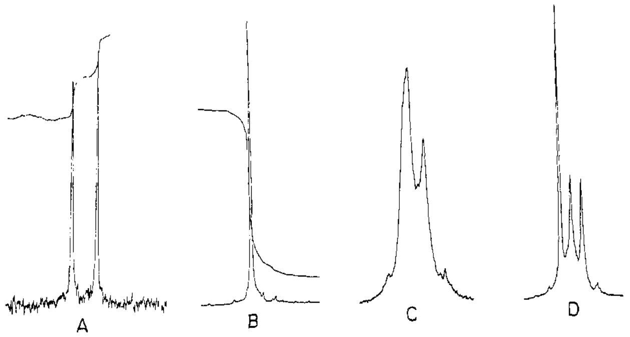

Figure 3. ^{1}H NMR spectra of Hg[Pt$_3$(2,6-Me$_2$C$_6$H$_3$NC)$_6$]$_2$ in C$_6$D$_6$ (A, 23 °C) and of a mixture of Hg[Pt$_3$(2,6-Me$_2$C$_6$H$_3$NC)$_6$]$_2$ and 2,6-Me$_2$C$_6$H$_3$NC [B (23 °C), C (−20 °C), D (−74 °C)] in CD$_2$Cl$_2$ (Hg-[Pt$_3$(2,6-Me$_2$C$_6$H$_3$NC)$_6$]$_2$ (40 mg) and 2,6-Me$_2$C$_6$H$_3$NC (8 mg)).

Crystals of **1** belong to the monoclinic space group *Cc*. Unit cell data are a = 27.2961 (0) Å, b = 15.8173 (1) Å, c = 24.5133 (0) Å, β = 102.37 (2)°, and Z = 4. The 4252 reflections having $I \geq 3\sigma(I)$ and $2\theta < 45°$ were collected on a Rigaku four-circle diffractometer by the ω–2θ scan technique, with Mo Kα radiation. The positions of the Hg and Pt atoms were located through a direct method (MULTAN) and the remaining atoms by standard difference Fourier syntheses. The final R value was 0.0481 (the Hg and Pt atoms were refined with anisotropic thermal parameters and

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(1) (a) Muetterties, E. L. *Bull. Soc. Chim. Belg.* **1976**, *85*, 451–470. (b) Muetterties, E. L.; Rhodin, T. N.; Band, E.; Brucker, C. F.; Pretzer, W. R. *Chem. Rev.* **1979**, *79*, 91–137.

(2) Thomas, M. G.; Pretzer, W. R.; Beier, B. F.; Hirsekorn, F. J.; Muetterties, E. L. *J. Am. Chem. Soc.* **1977**, *99*, 743–748.

(3) Yamamoto, Y.; Aoki, K.; Yamazaki, H. *Chem. Lett.* **1979**, 391–392.

(4) Mp 207–209 °C(dec). Anal. Calcd for C$_{108}$H$_{108}$N$_{12}$Pt$_6$Hg: C, 44.04; H, 3.70, N, 5.71; Pt, 39.74; Hg, 6.81. Found: C, 44.14; H, 3.72; N, 5.76; Pt, 39.62; Hg, 7.04.

(5) Mp 254–256 °C(dec); IR (Nujol) 2168, 2176 (N≡C), 1614, 1584 (C=N) cm^{-1}, NMR (CDCl$_3$) δ 2.26 (b s, 6, CH$_3$), 2.59 (s, 2, CH$_3$), 2.65 (s, 2, CH$_3$), 2.84 (s, CH$_3$), 5.8–7.5 (aromatic protons); UV (CH$_2$Cl$_2$) 307 (sh), 280 (sh) nm. The structure was tentatively assigned to *cis*-bis(2,6-xylyl isocyanide)tris(2,6-xylylimino)platinacyclobutane. Single crystals of **3** belong to the orthorhombic system, a = 22.702 (5) Å, b = 22.197 (5) Å, c = 18.543 (10) Å, and V = 9343 (6) Å^3. The data revealed systematic extinctions consistent with P$_{\mathrm{nam}}$ and P$_{\mathrm{na2_1}}$. However, the intensity is going down rapidly with increasing angles and also shows pseudo C center position. The resultant Fourier map using the Pt atom shows C center distribution. Because of the low quality of data and the pseudosymmetry, the analysis was unsuccessful.

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others with isotropic ones). The six platinum atoms, shown in Figures 1 and 2, define a trigonal prism whose edges are associated with bridging isocyanide groups; the remaining six isocyanide ligands are terminally bonded one per each platinum atom. The mercury atom occupies the pseudocenter of the prism. The molecule shows a small but significant rotational distortion of the two related Pt_3 fragments from an eclipsed pseudo-D_{3h} conformation by ca. 11° along one of the triangular Pt–Pt edges. The mean Hg–Pt and intratriangular Pt–Pt distances are 2.943 and 2.643 Å, respectively. The former distance is slightly longer than the sum (2.88 Å) of each of the covalent radii, suggesting relatively weak bond strength. The Pt–Pt distance is comparable to those found in $Pt_3(t\text{-BuNC})_6$[6] and $Pt_7(2,6\text{-}Me_2C_6H_3NC)_{12}$.[3] The closest intertriangular Pt–Pt distance, Pt(1)–Pt(4), is 4.954 Å, suggesting the absence of interaction between both platinum triangles. The dihedral angle between two triangles is ca. 7.4°, lying in the nearly parallel plane. The Hg atom is nearly equiv distant (ca. 2.51 Å) from each of two Pt_3 planes. The average distances for Pt–C(terminal) and Pt–C(bridge) bonds are 1.914 and 2.096 Å and resemble closely those found in other platinum isocyanide complexes.[3,6]

The infrared spectrum of **1** showed the presence of terminal and bridging isocyanide groups at 2095 and 1720 cm^{-1}, respectively. The ^1H NMR spectrum in C_6D_6 at ambient temperature showed two kinds of resonances due to *o*-methyl groups at δ 2.16 and 2.52 in a 1:1 ratio, assignable to the bridging and terminal isocyanide ligands. Intermolecular exchange between [1] and added 2,6-xylyl isocyanide was observed. The ^1H NMR spectrum at −77 °C in CD_2Cl_2 showed three resonances, at δ 2.06, 2.23, and 2.37, due to the bridging, terminal, and free isocyanide ligands, respectively.[7] The signals broaden on warming, and the latter two signals coalesce at ca. −30 °C, sugesting the presence of intermolecular ligand exchange between the terminal and free isocyanides. The spectrum at ca. −19 °C leads to coalescence of two broad resonances to a broad singlet, due to the intramolecular ligand exchange between the terminal and bridging isocyanide ligands. Further warming gives a sharp singlet at δ 2.24 (25 °C), suggesting the presence of a rapid intra- and intermolecular ligand exchanges. The activation free energies at coalescence temperatures are ca. 12.7 kcal/mol (T_c = −30 °C) for the intermolecular ligand-exchange process and ca. 12.9 kcal/mol (T_c = −19 °C) for the intramolecular process.[8] Although we have no detailed information for the mechanism of exchange processes, the exchange observed is probably an intermolecular process, catalyzed by free isocyanide ligand. A similar phenomenon has been observed in the $Pt_3(t\text{-BuNC})_6$–*t*-BuNC system.[6]

When 1 was heated in toluene at reflux, elimination of a mercury atom occurred to give $Pt_3(2,6\text{-}Me_2C_6H_3NC)_6$. The reactions with fumaronitrile and methyl iodide led to fragmentation of Pt–Pt and Hg–Pt bonds to produce $Pt(2,6\text{-}Me_2C_6H_3NC)_2(NCHC{=}CHCN)$[9] and *cis*-$Pt(2,6\text{-}Me_2C_6H_3NC)_2(CH_3)I$,[10] respectively.

Supplementary Material Available: Table of atomic positional and thermal parameters (2 pages). Ordering information is given on any current masthead page.

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[6] Green, M.; Howard, J. A.; Murray, M.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1509–1514.

[7] Our assignment may be incompatible with the fact that the chemical shifts of the terminal isocyanide groups appear in a higher field than those of the bridging ones.[11] However, we assigned them on the basis of the general assessment that the intermolecular exchange is faster for the terminal than for the bridging ligands.[6]

[8] The temperatures were calibrated by using the chemical-shift separation obtained from a methanol solution. The activation energies were calculated by the following equations, and their uncertainties are within ca. 10%: $\Delta G^* = 2.3RT(10.3 + \log T - \log k)$ and $k = (\Delta h)\pi/\sqrt{2}$, where T represents the coalescence temperature, and Δh represents the chemical shift difference of the peaks in the absence of exchange, and k is the rate constant in the coalescence temperature.

[9] Mp 197–198 °C(dec). Anal. Calcd for $C_{22}H_{20}N_4Pt$: C, 49.34; H, 3.76; N, 10.46. Found: C, 49.21; H, 3.77; N, 10.56. IR (KBr) 2225 (C≡N), 2180, 2150 (N≡C) cm^{-1}; NMR ($CDCl_3$) δ 2.49 (s, 4, CH_3), 2.94 (s, $J_{Pt\text{-}H}$ = 32.4 Hz, 2, CH), ca. 7.20 (c, aromatic protons).

[10] Mp 180–182 °C(dec). Anal. Calcd for $C_{19}H_{21}N_2IPt$: C, 38.07; H, 3.53; N, 4.67. Found C, 38.08; H, 3.50; N, 4.28. IR (KBr) 2175, 2146 (N≡C) cm^{-1}; NMR ($CDCl_3$) δ 1.15 (t, $J_{Pt\text{-}H}$ = 39.6 Hz, Pt–CH_3), 2.51 (s, 4, CH_3), ca. 7.1 (c, aromatic protons).

[11] For example: Basset, J. M.; Barker, G. K.; Green, M.; Howard, J. A. k.; Stone, F. G. A.; Wolsey, W. C. *J. Chem. Soc., Dalton Trans.* **1981**, 219–227.

Enantioselective Allylborane Condensations

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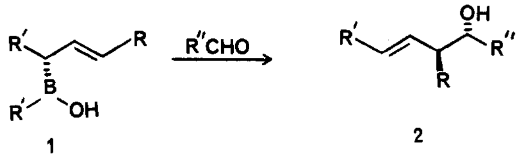
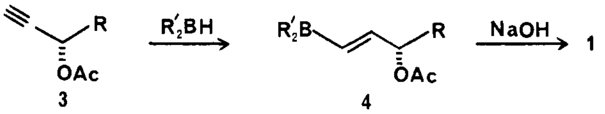
The control of stereochemistry during carbon–carbon bond formation is of great importance in synthesis. Recently a high degree of selectivity has been reached in aldol-type reactions.[2] We report that condensations of aldehydes with enantiomerically enriched allylboranes of type **1** provide homoallylic alcohols with a high degree of enantio- and diastereoselectivity. The enantiomeric purities obtained range from 50% to 85% ee. the diastereoselectivities are >95% of the less commonly produced[2] threo isomer **2** (eq 1). Results for representative aldehydes are illustrated in Table I.



(1)

The reactions are carried out by first generating the allylborane **1**.[3] Hydroboration of optically active propargylic acetate **3**[4] with 1.0 equiv of either dicyclohexyl- or diisopinocampheylborane[5] (1.0 M in THF) proceeds smoothly to form the vinylborane **4**. The intermediate **4** is not isolated but treated directly with 3.0 eq of 3.0 N sodium hydroxide (−15 °C for 15 min, room temperature for 5 min). Again the allylborane **1** is not isolated but treated with 2.0 eq of an aldehyde (−15 °C for 15 min, room temperature for 2 h). Oxidative workup (100% excess 30% hydrogen peroxide, 2 h, 40 °C) is followed by extraction with ether, washing with water, and drying over potassium carbonate. The solvents are removed under vacuum, and the alcohol **2** is isolated by bulb to bulb distillation.



(2)

The threo configuration for *trans*-allylborane condensations has been determined previously.[6] Nevertheless, for confirmation of

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[1] (a) Alfred P. Sloan Foundation Fellow, 1978–1982. (b) University of California Regents Fellow, 1979–1981.

[2] (a) Evans, D. A.; Bartroli, J.; Shih, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 2127. (b) Evans, D. A.; McGee, L. R. *Ibid.* **1981**, *103*, 2876. (c) Pirrung, M. C.; Heathcock, C. H. *J. Org. Chem.* **1980**, *45*, 1727. (d) Meyers, A. I.; Yamamoto, Y. *J. Am. Chem. Soc.* **1981**, *103*, 4278. (e) Nagaoka, H.; Rutsch, W.; Schmid, G.; Iio, H.; Johnson, M. R.; Kishi, Y. *Ibid.* **1980**, *102*, 7965. (f) Masamune, S.; Choy, W.; Kerdesky, F. A. J.; Imperiali, B. *Ibid.* **1981**, *103*, 1566. (g) Bartlett, P. A. *Tetrahedron* **1980**, *36*, 3 and references cited therein.

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[4] (a) Midland, M. M.; McDowell, D. C.; Hatch, R. L.; Tramontano, A. *J. Am. Chem. Soc.* **1980**, *102*, 867. The propargylic alcohols can be further purified to >99% ee by recrystallization: (b) Fried, J.; Lin, C. H.; Mehra, M. M.; Kao, W. L.; Daven, P. *Ann. N.Y. Acad. Sci.* **1971**, *180*, 38.

[5] Brown, H. C.; Mandal, A. K.; Kulkarni, S. V. *J. Org. Chem.* **1977**, *42*, 1391.

[6] (a) Hoffmann, R. W.; Kemper, B. *Tetrahedron Lett.* **1980**, *21*, 4883. (b) Hoffmann, R. W.; Zeiss, H. J. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 218. (c) Hoffmann, R. W.; Ladner, W. *Tetrahedron Lett.* **1979**, 4653. (d) Hoffmann, R. W.; Ladner, W.; Steinbach, K.; Massa, W.; Schmidt, R.; Snatzke, G. *Chem. Ber.* **1981**, *114*, 2786. (e) Hoffmann, R. W.; Helbig, W. *Ibid.* **1981**, 2802. (f) Hoffmann, R. W.; Weidemann, W. *J. Organomet. Chem.* **1980**, *195*, 137. (g) Tasai, D. J. S.; Matteson, D. S. *Tetrahedron Lett.* **1981**, *22*, 2751. (h) Yamaguchi, M.; Mukaiyama, T. *Chem. Lett.* **1980**, 993. (i) Yamamoto, Y.; Yatagai, H.; Maruyama, K. *J. Am. Chem. Soc.* **1981**, *103*, 3229.

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