When the infrared spectra of **1**, poly(bisphenol A hexamethyleneurethane) (PBAU), and **3** are compared, the IR spectrum of **3** is essentially superimposable with that of PBAU. Since the band intensities of the C_{61} moiety are very weak, they are overwhelmed by the absorptions of the aliphatic hydrocarbon and urethane vibrations of the polymer.

Comparative thermogravimetric analysis (TGA) results for **1**, PBAU, and **3** shows that PBAU exhibits a rapid weight loss (90%) from 180 to 300 °C. The weight loss observed in almost all polyurethanes is attributed to "unzipping" to its original monomers. Similar to PBAU, the TGA of **3** also reveals a weight loss between 180 and 340 °C. The latter is consistent with the urethane structure of **3**. The nonquantitative weight loss of about 9.5–10% (calculated for 100% loss of diisocyanate = 15.5%) for the unzipping of **3** is unexplained at this time.[11]

While PBAU displays an endothermal peak at about 88 °C, which is believed to be the glass transition temperature, the differential scanning calorigram of **3** shows no transitions.[12]

We have shown above that polymers containing fulleroid units[3] can be prepared and characterized. While the polyurethane is insoluble, the polyester is much more tractable. The remarkable retention of the electronic structure of the C_{60} moieties as witnessed by UV–vis spectroscopy and cyclic voltammetry is a very encouraging result which augurs well for observation of unusual fullerene-type properties of products fabricated from these polymers.

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Supplementary Material Available: UV–vis and IR spectra, comparative thermogravimetric analysis, and cyclic voltammetry (5 pages). Ordering information is given on any current masthead page.

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(10) Anal. Calcd for $(C_{81}H_{22}N_2O_4)_n$: C, 89.50; H, 2.03; N, 2.58. Found: C, 88.23; H, 2.91; N, 2.47. Other analytical data are in accord with the proposed structure. M_w could not be determined due to insolubility.

(11) It could be attributable to the thermal stability of the fulleroid moieties and their trapping of "nascent" diisocyanate.

(12) This observation and the insolubility of the polymer could imply cross-linking during urethane formation, but a control experiment (dimethoxyphenyl fulleroid + hexamethylene diisocyanate) showed no reaction, indicating no cross-linking reaction between C_{61} and the isocyanate function.

Synthesis and Structural Characterization of a Layer-Segregated Platinum–Ruthenium Cluster Complex That Exhibits Selective Coordination and a High Activity for the Catalytic Hydrogenation of Diphenylacetylene

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The unique reactivity observed for certain metal alloy catalysts may be produced by preferential interactions of the substances at selected metal sites.[2] In recent studies we have observed a tendency of the metal atoms in high-nuclearity platinum–ruthenium and platinum–osmium carbonyl cluster complexes to segregate into layers of the pure elements.[3] We have now prepared a new member of this family and found that the alkyne PhC_2Ph exhibits a coordination preference for a triruthenium site in the monoalkyne derivative and also displays a high activity for the catalytic hydrogenation of PhC_2Ph to (*Z*)-stilbene, Ph(H)C=C(H)Ph.

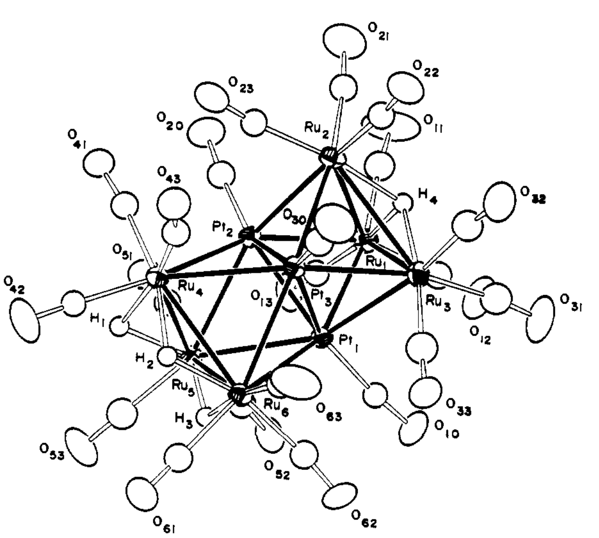

Figure 1. An ORTEP diagram of $Pt_3Ru_6(CO)_{20}(\mu\text{-}H)_3(\mu_3\text{-}H)$, **1**. Selected interatomic distances (Å) are Pt(1)–Pt(2) = 2.629 (1), Pt(1)–Pt(3) = 2.635 (1), Pt(2)–Pt(3) = 2.646 (1), Ru(1)–Ru(2) = 3.084 (2), Ru(1)–Ru(3) = 3.043 (2), Ru(2)–Ru(3) = 3.054 (3), Ru(4)–Ru(5) = 3.002 (2), Ru(4)–Ru(6) = 3.024 (2), Ru(5)–Ru(6) = 3.033 (2), Ru(1)–H(4) = 2.0 (1), Ru(2)–H(4) = 1.9 (2), Ru(3)–H(4) = 1.9 (1).

The new complex $Pt_3Ru_6(CO)_{21}(\mu\text{-}H)_3(\mu_3\text{-}H)$, **1**, was obtained in 83% yield from the reaction of $Ru_4Pt_2(CO)_{18}$ with hydrogen (1 atm) in a refluxing heptane solution. Compound **1** was characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses,[4] and an ORTEP diagram of its molecular structure is shown in Figure 1.[5] The structure consists of three triangular layers of nine metal atoms arranged in the form of a face-shared bioctahedron. The central layer consists of three platinum atoms while the outer layers are pure ruthenium. Three hydride ligands bridge each edge of the Ru(4)–Ru(5)–Ru(6) triangle while the fourth hydride is a triple bridging ligand across the Ru(1)–Ru(2)–Ru(3) triangle, δ (at −88 °C) −15.84 (s, 3 H), −19.26 (s, 1 H). The platinum–platinum distances are similar to those found in other layered mixed metal clusters,[3] but with ruthenium–ruthenium distances are unusually long due to the presence of the hydride ligands.[6] The molecule also contains 21 carbonyl ligands and obeys the conventional electron counting theories for condensed polyhedra.[7]

When allowed to react with PhC_2Ph in a refluxing hexane solution, **1** was converted to the derivative $Pt_3Ru_6(CO)_{20}(\mu_3\text{-}$

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(1) (a) University of South Carolina. (b) Molecular Structure Corp.

(2) (a) Sinfelt, J. H. *Bimetallic Catalysts.* Discoveries, Concepts and Applications; Wiley: New York, 1983. (b) Sinfelt, J. H. *Sci. Am.* **1985**, *253*, 90. (c) Sinfelt, J. H. *Acc. Chem. Res.* **1977**, *10*, 15. (d) Sachtler, W. M. H. *J. Mol. Catal.* **1984**, *25*, 1. (e) Ponec, V. *Adv. Catal.* **1983**, *32*, 149. (f) Biswas, J.; Bickle, G. M.; Gray, P. G.; Do, D. D.; Barbier, J. *Catal. Rev.—Sci. Eng.* **1988**, *30*, 161. (g) Goodman, D. W.; Houston, J. E. *Science* **1987**, *236*, 403. (h) Braunstein, P.; Rose, J. In *Stereochemistry of Organometallic and Inorganic Compounds*; Bernal, I., Ed.; Elsevier: Amsterdam, 1989; Vol. 3.

(3) (a) Adams, R. D.; Lii, J. C.; Wu, W. *Inorg. Chem.* **1991**, *30*, 3613. (b) Adams, R. D.; Lii, J. C.; Wu, W. *Inorg. Chem.* **1992**, *31*, 2556. (c) Adams, R. D.; Lii, J. C.; Wu, W. *Inorg. Chem.* **1991**, *30*, 2257. (d) Adams, R. D.; Li, Z.; Lii, J. C.; Wu, W. *Organometallics*, in press.

(4) $Ru_4Pt_2(CO)_{18}$, 25.0 mg, dissolved in 140 mL of heptane was heated to reflux for 12 min in the presence of a slow purge with hydrogen. After cooling, a small amount of dark precipitate was removed by filtration and discarded. The solvent was removed from the filtrate, and the residue was washed with pentane several times to yield pure **1**, 16.1 mg. An additional 3.0 mg of **1** was subsequently obtained from the washings by TLC using 3/1 hexane/CH_2Cl_2 solvent. Total yield: 19.1 mg (83%). IR for **1** (ν_{CO} in CH_2Cl_2): 2081 (w, sh), 2066 (vs), 2052 (m, sh), 2026 (w). ^1H NMR (δ in acetone at −88 °C): −15.84 (s, 3 H), −19.26 (s, 1 H). Anal. Calcd (found): for C, 14.14 (14.49); for H, 0.23 (0.26).

(5) Crystal data for **1**: space group = $P2_1/c$, a = 18.157 (3) Å, b = 11.701 (4) Å, c = 17.580 (4) Å, Z = 4, 2657 reflections, R = 0.033. Diffraction data at 20 °C were collected on a Rigaku AFC6S diffractometer using Mo Kα radiation.

(6) Bau, R. *Struct. Bonding (Berlin)* **1981**, *44*, 1.

0002-7863/92/1514-10657$03.00/0

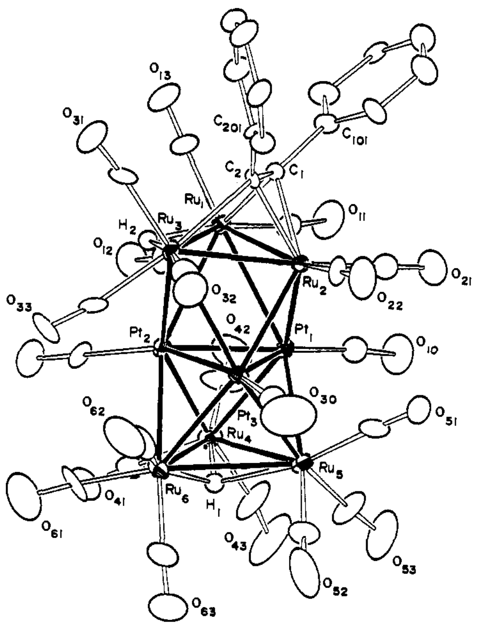
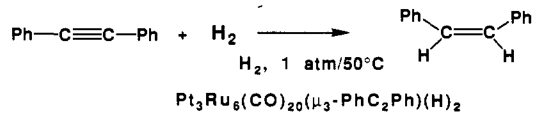


Figure 2. An ORTEP diagram of $Pt_3Ru_6(CO)_{20}(\mu_3\text{-}PhC_2Ph)(\mu_3\text{-}H)(\mu\text{-}H)$, **2**. Selected interatomic distances (Å) are Pt(1)–Pt(2) = 2.631 (1), Pt(1)–Pt(3) = 2.686 (1), Pt(2)–Pt(3) = 2.636 (1), Ru(1)–Ru(2) = 2.854 (2), Ru(1)–Ru(3) = 2.986 (2), Ru(2)–Ru(3) = 2.771 (2), Ru(4)–Ru(5) = 3.052 (2), Ru(4)–Ru(6) = 2.921 (2), Ru(5)–Ru(6) = 3.037 (2), C(1)–C(2) = 1.36 (2).

$PhC_2Ph)(\mu_3\text{-}H)(\mu\text{-}H)$, **2**, in 28% yield.[8] Compound **2** was characterized by IR, ^1H NMR, and single-crystal X-ray diffraction analyses, and an ORTEP diagram of its molecular structure is shown in Figure 2.[9] This molecule also consists of a layered structure of Pt_3 and Ru_3 triangles analogous to that of **1**, but in addition, there is a triply bridging PhC_2Ph ligand coordinated to the Ru(1)–Ru(2)–Ru(3) triangle. The alkyne has adopted the μ-$\|$ coordination mode that is commonly observed for these ligands in trimetallic cluster complexes.[9] Complex **2** contains only two hydride ligands, δ −17.97 (s, 1 H), −18.71 (s, 1 H) at −58 °C. These were observed crystallographically as an edge-bridging ligand across the Ru(1)–Ru(3) bond and a triply bridging ligand spanning the Ru(4)–Ru(5)–Ru(6) triangle.[10] Bridging alkyne ligands have been observed in ruthenium cluster complexes[9b] and in platinum cluster complexes.[11]

Preliminary experiments have indicated that compound **2** is also an unusually active catalyst for the selective hydrogenation of diphenylacetylene to (*Z*)-stilbene, eq 1.[12] When 8.0 mg of **2** was allowed to react with PhC_2Ph (present in a 100-fold excess) in hexane solution (65 mL) under 1 atm of H_2 at 50 °C for 1 h, 31% of the PhC_2Ph was converted to (*Z*)-stilbene with 100% selectivity, corresponding to a turnover frequency of 31 h^{-1}. The catalytic activity for **2** is both significantly higher and more selective than that observed for catalysts derived from cluster complexes of either pure ruthenium or pure platinum.[13]

1)



$Pt_3Ru_6(CO)_{20}(\mu_3\text{-}PhC_2Ph)(H)_2$

The reason for the preference of the alkyne for a triruthenium site in **2** is not clear at this time, but coordination preferences sometimes referred to as "metalloselectivity"[14] can be expected to lead to reactivity preferences and the potential for cooperative reactivity by involving the different types of metal atoms. This may provide an explanation for the high catalytic activity of **2**. It may also explain some aspects of the unique activity of certain metal alloy catalysts.[2g]

Acknowledgment. These studies were supported by the National Science Foundation under Grant No. CHE-8919786.

Supplementary Material Available: Complete listings of crystal data, atomic positional parameters, bond distances and angles, and anisotropic thermal parameters for **1** and **2** (23 pages); listing of structure factor amplitudes for **1** and **2** (49 pages). Ordering information is given on any current masthead page.

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(7) Mingos, D. M. P.; May, A. S. In *The Chemistry of Metal Cluster Complexes*; Shriver, D. F., Kaesz, H. D., Adams, R. D., Eds.; VCH Publishers: New York, 1990; Chapter 2.

(8) **1**, 15.0 mg (0.0084 mmol), and 3.3 mg (0.0185 mmol) of Ph_2C_2 were dissolved in 80 mL of hexane, and the solution was refluxed for 70 min. Separation by TLC using 3/1 hexane/CH_2Cl_2 solvent yielded gray-green $Ru_7Pt_3(CO)_{22}(\mu_3\text{-}H)_2$[2d] (1.2 mg, 10%), followed by gray-green $Ru_6Pt_3(CO)_{20}(Ph_2C_2)(\mu_3\text{-}H)(\mu\text{-}H)$, **2** (4.2 mg, 28%). IR for **2**: 2098 (w), 2065 (vs), 2033 (m), 2015 (w, sh), 2000 (w, sh), 1950 (vw, sh). ^1H NMR (δ in CD_2Cl_2 at −58 °C): 7.70–7.05 (m, 10 H), −17.97 (s, 1 H), −18.71 (s, 1 H). Crystal data for **2**: space group = *Pccn*, a = 10.852 (4) Å, b = 45.509 (2) Å, c = 17.172 (3) Å, Z = 8, 4441 reflections, R = 0.043. Diffraction data at 20 °C were collected on a Rigaku AFC5R diffractometer using Cu Kα radiation.

(9) (a) Raithby, P. R.; Rosales, M. J. *Adv. Inorg. Chem. Radiochem.* **1985**, *29*, 169. (b) Sappa, E.; Tiripicchio, A.; Braunstein, P. *Chem. Rev.* **1983**, *83*, 203.

(10) The two hydride ligands that were lost in the reaction were transferred to an equivalent of PhC_2Ph to yield (*Z*)-stilbene. This was confirmed by ^1H NMR spectroscopy by performing the reaction in C_6D_6 solvent.

(11) (a) Rashidi, M.; Puddephatt, R. J. *Organometallics* **1988**, *7*, 1636. (b) Manojlovic, L.-M.; Muir, K. W.; Rashidi, M.; Schoettel, G.; Puddephatt, R. J. *Organometallics* **1991**, *10*, 1719. (c) Stone, F. G. A. *Inorg. Chim. Acta* **1981**, *50*, 33.

(12) A solution of 8.0 mg of **2** (0.004 14 mmol) and 73.7 mg of PhC_2Ph (0.414 mmol) in 65 mL of hexane was heated to 50 °C and purged slowly with H_2 (1 atm) for 1 h. Workup by TLC yielded 22.6 mg of (*Z*)-stilbene (31%, 0.126 mmol), 36.9 mg of unreacted PhC_2Ph, and 1.8 mg of 1,2-diphenylethane (0.0099 mmol). **2**, 7.3 mg was recovered. The turnover number of formation of (*Z*)-stilbene is 31 at a rate of 31 h^{-1}. There was no evidence for the formation of (*E*)-stilbene.

(13) (a) Süss-Fink, G.; Neumann, G. *The Chemistry of the Metal–Carbon Bond*; Hartley, F. R., Ed.; Wiley: New York, 1989; Vol. 5, Chapter 7 and references therein. (b) Fusi, A.; Ugo, R.; Psaro, R.; Braunstein, P.; Dehand, J. *J. Mol. Catal.* **1982**, *16*, 217. (c) Castiglioni, M.; Sappa, E.; Valle, M.; Lanfranchi, M.; Tiripicchio, A. *J. Organomet. Chem.* **1983**, *241*, 99. (d) Castiglioni, M.; Giordano, R.; Sappa, E. *J. Organomet. Chem.* **1989**, *369*, 419.

(14) (a) Matsuzaka, H.; Kodama, T.; Uchida, Y.; Hidai, M. *Organometallics* **1988**, *7*, 1608. (b) Hidai, M.; Matsuzaka, H. *Polyhedron* **1988**, *7*, 2369. (c) Rossi, S.; Pursiainen, J.; Pakkanen, T. A. *J. Organomet. Chem.* **1990**, *397*, 81. (d) Braunstein, P.; Mourey, L.; Rosé, J.; Granger, P.; Richert, T.; Balegroune, F.; Grandjean, D. *Organometallics* **1992**, *11*, 2628.

Site-Specific Covalent Duocarmycin A—Intramolecular DNA Triplex Complex

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DNA triple helices[1] can be either of the pyrimidine•purine•pyrimidine type, where the third pyrimidine strand is positioned in the major groove and parallel to the purine strand,[2] or of the pyrimidine•purine•purine type where the third purine strand is positioned in the major groove and antiparallel to the purine

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(1) (a) Felsenfeld, G.; Davies, D.; Rich, A. *J. Am. Chem. Soc.* **1957**, *79*, 2023–2024. (b) Arnott, S.; Selsing, E. *J. Mol. Biol.* **1974**, *88*, 509–521. (c) Wells, R. D.; Collier, D. A.; Hanvey, J. C.; Shimizu, M.; Wohlraub, F. *FASEB J.* **1988**, *2*, 2939–2949.

(2) (a) Moser, H.; Dervan, P. B. *Science* **1987**, *238*, 645–650. (b) Le Doan, T.; Perronault, L.; Praseuth, D.; Habhoub, N.; Decoult, J. L.; Thuong, N. T.; Lhomme, J.; Helene, C. *Nucleic Acids Res.* **1987**, *15*, 7749–7760. (c) Plum, G. E.; Park, Y. W.; Singleton, S. F.; Dervan, P. B.; Breslauer, K. J. *Proc. Natl. Acad. Sci. U.S.A.* **1990**, *87*, 9436–9440. (d) Roberts, R. W.; Crothers, D. M. *Proc. Natl. Acad. Sci. U.S.A.* **1991**, *88*, 9397–9401.

0002-7863/92/1514-10658$03.00/0