Volume 30
Number 24
November 27, 1991

Inorganic Chemistry

Communications

Synthesis and X-ray Diffraction Crystal Structure of $[Ba(tmhd)_2\cdot 2NH_3]_2$ (tmhd = 2,2,6,6-Tetramethylheptane-3,5-dionate). A Novel Low-Molecularity Barium Compound

Discovery of superconducting metal oxides (SMO) spurred scientific researchers around the world in new directions.[1] One active arena in the first 5 years of SMO has been the quest for production of high-quality thin films[2] demanded for Josephson-based electronic devices, integrated circuit interconnects, and microwave cavity coatings.[3] One attractive method for preparation of these films is organometallic chemical vapor deposition (OMCVD).[4] A significant advantage of OMCVD over competing physical deposition methods (e.g., molecular beam epitaxy, laser ablation, sputtering, or evaporation) is its potential to combine high rates of deposition on variously shaped large-area substrates at low temperature with adaptability to compositional control over a broad range for multiple sources.[5] Although progress has been made in this technique, currently the future development of OMCVD of SMO is hampered by the lack of suitable group 2 precursors, particularly those of Ba.[6]

Precursor development for OMCVD of group 2 containing materials has focused primarily on substituted acac complexes.[7] Although sufficiently volatile, BaL_2 (L = tfac, hfac, fod) compounds[8] are unsuited for preparing high-quality SMO thin films due to BaF_2 formation during deposition and its subsequent removal by aqueous washing.[9] One alternative precursor is $Ba(tmhd)_2$ (tmhd = 2,2,6,6-tetramethylheptane-3,5-dionato, $(CH_3)_3CCOCHCOC(CH_3)_3^-$) (**1**); however, its thermal instability at use temperature is well documented,[10] it is difficult to obtain anhydrous material by available synthetic routes,[11] and the temperature demanded for attainment of sufficient vapor pressure to allow productive film growth is outside the practical operating limits of commercial OMCVD systems. Thus, the most critical *chemical* issue in OMCVD of Ba-containing SMO[12,13] is the need for thermally stable source compounds with enhanced volatility. In efforts to augment the modest volatility of **1**, previous workers added a variety of Lewis bases (Htmhd,[14] linear oligioethers,[15] H_2O,[16] THF,[17] or NH_3[18]) to carrier gases. No new Ba-containing species were identified in any of these cases. We now report the preparation and characterization of $[Ba(tmhd)_2\cdot 2NH_3]_2$ (**2**), a new, volatile, low-molecularity barium compound.

As a portion of a study aimed at preparing volatile group 2 (Mg-Ba) compounds,[19] we examined the reactivity of **1** with Lewis bases. Although the structural database on Ba compounds is increasing rapidly, the available information still is scarce;[20]

---

(1) Bednorz, J. G.; Mueller, K. A. *Z. Phys. B* **1986**, *64*, 189–193.

(2) *Thin Film Processing and Characterization of High Temperature Superconductors*; Harper, J. M. E., Colton, R. J., Feldman, L. C., Eds.; American Vacuum Society Series No. 3; American Institute of Physics Conference Proceedings No. 165; American Institute of Physics: New York, 1988.

(3) Venkatesan, T.; Wu, X. D.; Inam, A.; Hegde, M. S.; Chase, E. W.; Chang, C. C.; England, P.; Hwang, D. M.; Krchnavek, R.; Wachman, J. B.; McLean, W. L.; Levi-Setti, R.; Chabala, J.; Wang, Y. L. In *Chemistry of High-Temperature Superconductors II*; Nelson, D. L., George, T. F., Eds.; ACS Symposium Series 377; American Chemical Society: Washington, DC, 1988; pp 234–264.

(4) OMCVD sometimes also is referred to as MOCVD or OMVPE (metal organic chemical vapor deposition or organometallic vapor-phase epitaxy, respectively). For an excellent review on the early work in the area of OMCVD of SMO, see: Tonge, L. M.; Richeson, D. S.; Marks, T. J.; Zhao, J.; Zhang, J.; Wessels, B. W.; Marcy, H. O.; Kannewurf, C. R. In *Electron Transfer in Biology and the Solid State: Inorganic Compounds With Unusual Properties, Part III*; Johnson, M. K., King, R. B., Kurtz, D. M., Jr.; Kutal, C.; Norton, M. L., Scott, R. A., Eds.; ACS Advances in Chemistry Series 226; American Chemical Society: Washington, DC, 1990; pp 351–368.

(5) Stringfellow, G. B. *Organometallic Vapor Phase Epitaxy: Theory and Practice*; Academic Press: New York, 1989.

(6) Barron, A. R. *Strem Chem.* **1990**, *12* (Oct), 1–9.

(7) The barium complex of the unsubstituted acetylacetonate (pentane-2,4-dionato) ligand, $CH_3COCHCOCH_3^-$, is too involatile to be of practical use as an OMCVD precursor. See refs 16–24 in ref 4.

(8) tfac (1,1,1-trifluoropentane-2,4-dionato) = $CF_3COCHCOCH_3^-$; hfac (1,1,1,5,5,5-hexafluoropentane-2,4-dionato) = $CF_3COCHCOCF_3^-$; fod (7,7-dimethyl-1,1,1,2,2,3,3-heptafluorooctane-4,6-dionato) = $(CH_3)_3C$-$COCHCOCF_2CF_2CF_3^-$. See ref 4 and references therein.

(9) Although SMO lattices appear to be forgiving enough to permit observation of acceptable T_c and J_c values on BaF_2-contaminated films, goals of electronic device fabrication demand epitaxial material. Thus, obviously postdeposition washes removing contaminating material are to be avoided.

(10) See refs 16 and 17 in ref 4.

(11) Rees, W. S., Jr.; Carris, M. W. To be submitted for publication. See supplementary material.

(12) $YBa_2Cu_3O_{7-\delta}$: Chu, C. W.; Hor, P. H.; Meng, R. L.; Gao, L.; Huang, Z. J.; Wang, Y. Q.; Bechtold, J.; Campbell, D.; Wu, M. K.; Ashburn, J.; Huang, C. Y. *Phys. Rev. Lett.* **1987**, *58*, 405–407.

(13) $(TlO)_mBa_2Ca_{n-1}Cu_nO_x$ ($m = 1, 2$; $n = 1, 2, 3$): Sheng, Z. Z.; Hermann, A. M. *Nature* **1988**, *27*, 138–139.

(14) Dickinson, P. H.; Geballe, T. H.; Sanjurjo, A.; Hildenbrand, D.; Craig, G.; Zisk, M.; Collman, J.; Banning, S. A.; Sievers, R. E. *J. Appl. Phys.* **1989**, *66*, 444–447.

(15) Spee, C. I. M. A.; Mackor, A. In *Science and Technology of Thin Film Superconductors*; McConnell, R. D., Wolf, S. A., Eds.; Plenum: New York, 1989; pp 281–294.

(16) See refs 16 and 22 in ref 4.

(17) Matsuno, S.; Uchikawa, F.; Yoshizaki, K. *Jpn. J. Appl. Phys.* **1990**, *29*, L947–L948.

(18) Barron, A. R.; Buriak, J. M.; Chetham, L.; Gordon, R. Abstract 943 HTS, 177th Meeting of the Electrochemical Society, Montreal, Canada, 1990.

(19) (a) Rees, W. S., Jr.; Dippel, K. A. *Proceedings of the Fifth International Conference on Ultrastructure Processing of Ceramics, Glasses, Composites, Ordered Polymers, and Advanced Optical Materials*; Wiley: New York, in press. (b) Rees, W. S., Jr.; Caballero, C. R. To be submitted for publication. (c) Rees, W. S., Jr.; Moreno, D. A. *J. Chem. Soc., Chem. Commun.*, in press.

(20) (a) Caulton, K. G.; Chisholm, M. H.; Drake, S. R.; Streib, W. E. *Angew. Chem.* **1990**, *102*, 1492–1493. (b) Caulton, K. G.; Chisholm, M. H.; Drake, S. R.; Huffman, J. C. *J. Chem. Soc., Chem. Commun.* **1990**, 1498–1499. (c) Caulton, K. G.; Chisholm, M. H.; Drake, S. R.; Folting, K. *J. Chem. Soc., Chem. Commun.* **1990**, 1349–1351.

0020-1669/91/1330-4479$02.50/0

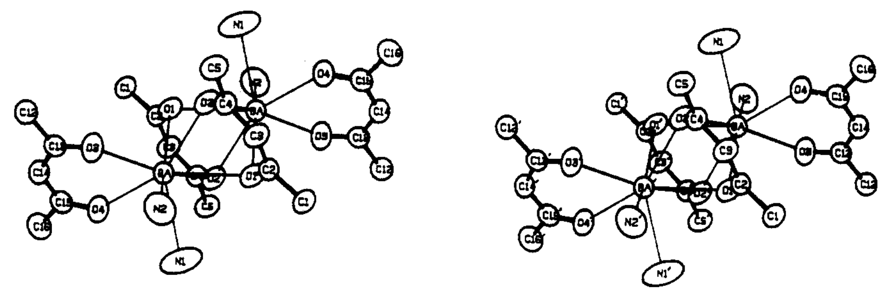

Figure 1. ORTEP plot of **2** (50% probability). Hydrogen atoms and methyl groups are omitted for clarity. Pertinent interatomic distances [Å (esd)]: Ba(01)–O(01) = 2.765 (3), Ba(01)–O(02) = 2.776 (4), Ba(01)–O(03) = 2.595 (4), Ba(01)–O(04) = 2.603 (3), Ba(01)–N(01) = 2.888 (6), Ba(01)–N(02) = 2.923 (5), Ba(01)–O(01′) = 2.834 (4), Ba(01)–O(02′) = 2.874 (4).

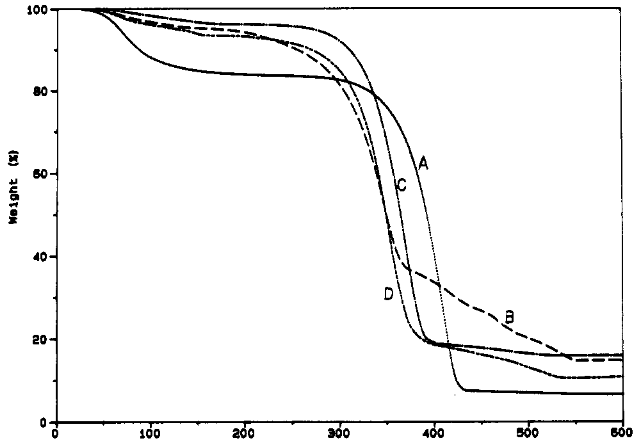

Figure 2. TGA plots (10 °C/min, N_2 atmosphere, 50–600 °C): (A) **3**; (B) **1**; (C) **2**; (D) **2** after sublimation. Note that weight loss is not always 100%. This may imply that some minor component other than simple sublimation is present in this process.

however, the emerging trend is that coordination numbers of 8–10 are preferred. The coordination number of Ba in **1** nominally is only 4. Thus, the motive for the present investigation was to secure coordinative saturation of the metal, thereby decreasing solid-state cross-catenation and concomitantly increasing vapor pressure. During this exploration, we discovered the solution reaction between ammonia and **1** yielded a compound having the desired coordinative saturation.[21] As the nature of this species could not be elucidated fully from spectroscopic investigation alone,[22] an X-ray diffraction crystal structure determination was carried out.[23]

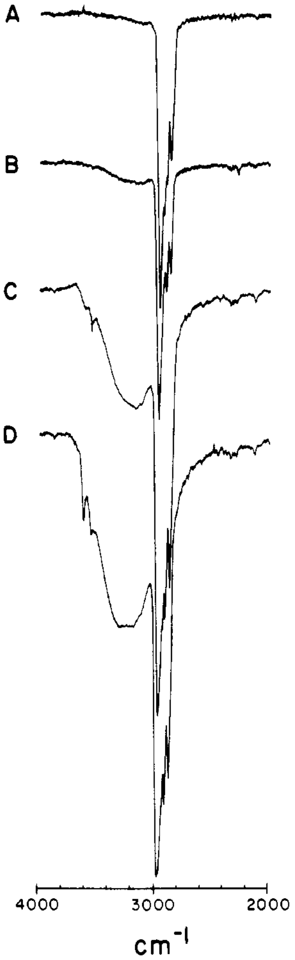

Figure 3. Infrared spectra (4000–2000 cm^{-1}): (A) **2** after sublimation; (B) **1**; (C) **2**; (D) **3**.

This new compound, **2**, is a novel, highly symmetric dimer of $Ba(tmhd)_2{\cdot}2NH_3$ possessing an inversion center (ORTEP representation, Figure 1).

---

(21) Under dry, pure N_2, 0.417 g of **1** (0.83 mmol) was dissolved in 3 mL of C_6H_{14} in a dried flask equipped with a septum, the solution was cooled to 0 °C, and a 5:1 N_2:dry NH_3 mixture was passed through the solution (~2–3 bubbles/s); after 0.5 h, a white precipitate formed, the flow was continued for 0.3 h, and the cold C_6H_{14} was removed by cannulation, leaving 0.103 g (0.096 mmol, 23%) of **2** as a white powder. Sublimation (2 h, 5×10^{-4} mmHg, 213–224 °C) yielded 43% **1** (sublimate) and 14% **2** (residue).

(22) (a) Spectroscopic data for **2** are as follows. ^1H NMR (300 MHz, positive δ downfield referenced to $Si(CH_3)_4$ = 0 utilizing residual $CHCl_3$ = 7.24 ppm in solvent $CDCl_3$): 5.51 (s, 1, CH), 0.97 (s, 21, CH_3). $^{13}C\{^1H\}$ NMR (75 MHz, positive δ downfield referenced to $Si(CH_3)_4$ = 0 utilizing solvent $CDCl_3$ = 77.0 ppm): 199.5 (CO), 90.3 (CH), 41.0 (ipso C), 28.4 (CH_3). Solid-state IR (cm^{-1}, Nujol mull, NaCl plates): 2966 (m, sh) (C–H), 1580 (s), 1570 (s), 1560 (s) (CO), 1500 (s, sh) (BaOC), 1445 (m), 1410 (vs), 1385 (m), 1355 (s) (CH), 1240 (w), 1220 (w), 1180 (w) (CCOC), 860 (m, sh) (OCC), 560 (vw) (BaO).[22b] Solution IR (see Figure 3 for 4000–2000 cm^{-1} (cm^{-1}, CCl_4 vs CCl_4 reference, NaCl plates)): 1590 (vs) (CO), 1500 (vs, sh) (BaOC), 1445 (vs, sh), 1410 (vs, br), 1355 (vs, sh) (CH), 1240 (m, sh), 1220 (s, sh), 1180 (m, sh) (CCOC), 1130 (s, sh) (BaOC), 865 (s, sh) (OCC), 590 (w, sh), 480 (m, sh) (BaO). TGA: see Figure 2. Mp: 153.3 °C, partial melting (yellow solid/solution); 170.3–173.1 °C, complete melting (yellow solution). (b) For assignment of the IR data for **1**, see: Harima, Hiroshi; Ohnishi, Hiroshi; Hanaoka, Ken-ichi; Tachibana, Kunihide; Kobayashi, Minoru; Hoshinouchi, Susumu. *Jpn. J. Appl. Phys.* **1990**, *29*, 1932–1938.

(23) (a) Crystals of **2** were obtained by passing the described N_2–NH_3 mixture through a 0 °C C_6H_{14} solution of **1** at ~1 bubble/3 s (10 min), followed by standing at −20 °C (12 h). (b) Complete details of the collection and refinement of diffraction data and the structure solution will be published elsewhere. Crystallographic data: Crystals of **2** were sealed in 0.5-mm capillary tubes under N_2. Data collection was carried out in the range $2° < 2\theta < 60°$ in the $\omega/2\theta$ scan mode at ambient temperature, using an Enraf-Nonius CAD4 diffractometer with Mo Kα(0.71073 Å) radiation. The space group was $P\bar{1}$ (No. 2), with a = 10.450 (3) Å, b = 10.567 (2) Å, c = 13.794 (4) Å, α = 93.58 (2)°, β = 110.54 (3)°, γ = 91.17 (2)°, V = 1422.1 Å^3, Z = 2, and ρ_c = 1.256 g cm^{-3}. Two standard reflections, measured every hour, gave <2% intensity deviation over the data collection of 4 days. Of 8712 measured reflections, 5485 were observed and 4380 reflections with $I > 2\sigma(I)$ were used for structure solution and refinement employing the SDP computer programs by Enraf-Nonius. The final cycle of least-squares refinement of 270 parameters gave residuals of R = 5.6% and R_w = 6.6% and greatest unassigned electron density of 1.248 e Å^{-3}.

As evident upon examination of the data (Figure 2), **2** is comparable to **1** in volatility. The onset of weight loss (1 atm) for **1** is ~275 °C, changing slightly to ~300 °C for **2**. Data for **2** after sublimation and for commercially available[24] $Ba_5(tmhd)_9(OH)\cdot 3H_2O$ (**3**) also are presented for comparison. The reproducible shift to higher volatility (lower temperature weight loss) evidenced by **2** after sublimation is understood best by comparison of the IR data for it to those for **1**. Significant changes between 4000 and 2000 cm^{-1} in the IR spectra for **1**–**3** (Figure 3) are symptomatic of structural differences in these compounds. A broad absorption at ~3300–3200 cm^{-1} for **3** indicates the presence of O–H[25] in the compound. This absorption is not seen for **1**. For **2**, the N–H diagnostic absorption is evident at ~3200 cm^{-1}. The IR spectrum of **2** after sublimation is virtually identical to that of **1**. This indicates loss of coordinated ammonia upon sublimation of **2** (eq 1). However, other than the volatility and

$$\underset{\mathbf{1}}{4[\mathrm{Ba(tmhd)_2}]_{3,4}} \underset{-28\mathrm{NH_3}}{\overset{+28\mathrm{NH_3}}{\rightleftharpoons}} \underset{\mathbf{2}}{7[\mathrm{Ba(tmhd)_2\cdot 2NH_3}]_2} \tag{1}$$

these differences in the IR spectra, **1**–**3** were spectroscopically remarkably similar (^1H and ^{13}C NMR). Therefore, to clearly differentiate between these compounds, we examined the solid-state structure of **2** by single-crystal X-ray diffraction.

Each Ba atom in **2** has local square-antiprismatic coordination. This results in a molecular symmetry of an axially enlongated cuboctahedron. The μ_2-oxygen atoms of the bridging tmhd ligands form the inside corners of this cube. The 45° skewed outside corners of the two cubes (vs the inside) are formed by two oxygen atoms of one terminal tmhd ligand and the nitrogen atoms of two ammonia ligands. One interesting feature of **2** is the somewhat shortened intramolecular Ba–Ba distance of 3.83 Å. To our knowledge, this is the lowest molecularity $Ba(acac)_2$-derived compound structurally characterized to date, and thus there are no other data available with which to directly compare the observed metal–metal distance in this dimeric species. We, and others, recently have observed interatomic distances between 4.03 and 4.12 Å for trimeric,[20a] pentameric,[24b] and hexameric[26] structures. The plane defined by a barium atom and its two ammonia ligands intersects the plane of the same barium atom and its two terminal oxygen atoms with an angle of 89.2°. The terminal tmhd ligands deviate by 15.5° from their normal planar configuration.[27] The bridging tmhd ligands intersect the $Ba(\mu_2\text{-}O)_2$ planes with an angle of 130.4°.[28]

Compound **2** currently is undergoing evaluation as an OMCVD precursor in the fabrication of $YBa_2Cu_3O_{7-\delta}$ thin films on large-area (>2-in. diameter) substrates at low (<700 °C) deposition temperatures.[29] Initial results have been encouraging and will be reported in due course.

Acknowledgments. We gratefully acknowledge the generous financial support provided for this project from DARPA Contract No. MDA 972-88-J-1006 and the Deutsche Forschungsgemeinschaft (postdoctoral fellowship to W.H.). We also thank Professor Sievers for willingly sharing a preprint of ref 24b with us.

Supplementary Material Available: Tables of positional and thermal parameters and interatomic distances and angles for compound **2** and a textural presentation of the preparation and characterization data for compound **1** (10 pages); a listing of observed and calculated structure factors for compound **2** (19 pages). Ordering information is given on any current masthead page.

Department of Chemistry and Materials
Research and Technology Center
The Florida State University
Tallahassee, Florida 32306-3006

William S. Rees, Jr.*
Michael W. Carris
Werner Hesse

Received June 19, 1991

---

(24) (a) Although supplied commercially as "anhydrous $Ba(tmhd)_2$", this frequently used OMCVD source material recently has been identified as $Ba_5(tmhd)_9(OH)\cdot 3H_2O$. (b) Turnipseed, S. B.; Barkley, R. M.; Sievers, R. E. *Inorg. Chem.* **1991**, *30*, 1164–1170. (c) The thermal instability of **3** at use temperatures (230–300 °C) is well documented. See ref 4 and references contained therein.

(25) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 3rd ed.; Wiley: New York, 1974.

(26) Rees, W. S., Jr.; Carris, M. W.; Hesse, W.; Goedken, V. To be submitted for publication.

(27) (a) This angle is defined by the intersection of the plane containing Ba(01), O(03), and O(04) with the plane containing O(03), C(13), C(14), C(15), and O(04). (b) For a thorough compilation of structural data on metal acac complexes, see: Mehrotra, R. C.; Bohra, R.; Gaur, D. P. *Metal β-Diketonates and Allied Derivatives*; Academic: New York, 1978; pp 58–194.

(28) This angle is defined by the intersection of the plane containing Ba(01), O(01), and O(02) with the plane containing O(01), C(02), C(03), C(04), and O(02).

(29) Rees, W. S., Jr.; Stuckey, D.; Zhao, J.; Norris, P. E. To be submitted for publication.

An Interesting Low Barrier to Metal–Ligand Contrarotational Fluxionality in Closed 11-Vertex $[1,1\text{-}(PMe_2Ph)_2\text{-}1,2,3\text{-}PtC_2B_8H_9X]$ Compounds That Is Characterized by Arachno ⇌ Nido Geometric Changes within the 10-Vertex η^6-$\{C_2B_8H_9X\}$ Ligand[1]

There is a long and continuing fascination with the variations in the modes of interaction of transition-element centers with boron hydride and related clusters. This is exemplified classically by the ideas generated by the observation[2] in 12-vertex metalladicarbaborane compounds of the "slippage" from closed to open structures that arises from changes in the carbaborane-to-metal binding mode in the complexes of the 11-vertex η^5-{7,8-*nido*-$C_2B_9H_{11}$} ligand with platinum metals[3] and in the extension of these ideas to include a broader spectrum of metallic elements.[4] We here now report preliminary results of an interesting structural change in 11-vertex platinadicarbaborane chemistry.

The 11-vertex platinadicarbaborane $[1,1\text{-}(PPh_3)_2\text{-}1,2,3\text{-}PtC_2B_8H_{10}]$ (compound **1**) is known to exhibit a closed 11-vertex cluster structure with an η^6 cluster-to-metal interaction.[5,6] We have now found that its closely related PMe_2Ph congeners $[1,1\text{-}(PMe_2Ph)_2\text{-}1,2,3\text{-}PtC_2B_8H_9\text{-}2\text{-}X]$ (X = H, Me, Ph) also have a closely related closed cluster geometry, but in addition exhibit an interesting rotational fluxionality, *within the constraints of their closed η^6-carborane-to-metal bonding*, that is accompanied by a remarkable flexing of the 10-vertex η^6-$\{C_2B_8H_9X\}$ moiety between extreme nido and arachno 10-vertex geometries.

The solid-state molecular structures of $[1,1\text{-}(PPh_3)_2\text{-}1,2,3\text{-}PtC_2B_8H_{10}]$ (**1**)[5,6] and $[1,1\text{-}(PMe_2Ph)_2\text{-}2\text{-}Me\text{-}1,2,3\text{-}PtC_2B_8H_9]$ (**2**; upper diagram in Figure 1)[7] show orthogonally different rotational orientations of the $\{Pt(PR_3)_2\}$ moiety with respect to the $\{C_2B_8H_9X\}$

---

(1) Contribution No. 16 from the Leeds–Řež Anglo–Czech Polyhedral Collaboration (ACPC).

(2) Warren, L. F.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1968**, *90*, 4823–4828.

(3) Mingos, D. M. P.; Forsyth, M. I.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1977**, 605–607; *J. Chem. Soc., Dalton Trans.* **1978**, 1363–1374.

(4) Colquhoun, H. M.; Greenhough, T. J.; Wallbridge, M. G. H. *J. Chem. Soc., Chem. Commun.* **1977**, 737–738; *J. Chem. Soc., Dalton Trans.* **1979**, 619–628.

(5) Kukina, G. A.; Porai-Koshits, M. A.; Sergienko, V. C.; Štrouf, O.; Baše, K.; Zakharova, I. A.; Štíbr, B. *Izv. Akad. Nauk SSSR., Ser. Khim.* **1980**, 1686. Kukina, G. A.; Porai-Koshits, M. A.; Sergienko, V. C. *Koord. Khim.* **1986**, *12*, 561–570.

(6) Štíbr, B.; Janoušek, Z.; Baše, K.; Heřmánek, S.; Plešek, J.; Zakharova, I. A. *Collect. Czech. Chem. Commun.* **1984**, *46*, 1891–1894.

(7) Crystal Data for compound **2**:[9] $C_{19}H_{34}B_8P_2Pt$, $M = 605.99$, monoclinic, $a = 947.6$ (1) pm, $b = 1547.7$ (3) pm, $c = 1804.0$ (3) pm, $\beta = 104.78$ (1)°, $V = 2.5581$ (8) nm^3, $Z = 4$, space group $P2_1/n$, $D_c = 1.57$ Mg m^{-3}, $\mu = 53.82$ cm^{-1}, $F(000) = 1184$, R (R_w) = 0.0216 (0.0234) for refinement of 4200 unique absorption-corrected reflections with $I > 2.0\sigma(I)$ and $4.0 < 2\theta < 50.0°$.

0020-1669/91/1330-4481\$02.50/0