

electronegativities (EN), which are too small between Cu and As or Te for a discrete separation into Cu^{1+} and $\text{As}^{3-}/\text{Te}^{2-}$ ions; IP: 745.4(Cu), 946.5(As), 869.2(Te); EA: 118.5(Cu), 78.2(As), 190.2(Te); EN(Pauling): 1.9(Cu), 2.0(As), 2.1(Te). In other words, the formal charge assignment to give Cu^{1+} and $\text{As}^{3-}/\text{Te}^{2-}$ centers produces an “additional” electron pair which is described by an MO that is embedded in the valence band formed by the arsenic 4p orbitals or the tellurium 5p orbitals, and the 4s orbitals of copper.

Experimental Section

$\text{LiAs}(\text{SiMe}_3)_2 \cdot 1.2\text{THF}$ (0.77 g, 2.4 mmol) was added to a suspension of CuCl (0.2 g, 2 mmol) and dppm (0.5 g, 1.3 mmol) in DME (50 mL) at -20°C . A clear yellow solution was formed which as the temperature increased towards room temperature gradually turned a brilliant red, and was nearly black at room temperature. After reducing the volume of the solution by about half, black needlelike crystals of **1** were obtained in under two weeks (yield, based on CuCl , 0.12 g, 30%). The C and H analyses of **1** fit the given formula.

Received: June 21, 2000 [Z15307]

- [1] D. Fenske, J. Ohmer, J. Hachgenei, K. Merzweiler, *Angew. Chem.* **1988**, 100, 1300–1320; *Angew. Chem. Int. Ed. Engl.* **1988**, 27, 1277–1296.
- [2] H. Krautscheid, D. Fenske, G. Baum, M. Semmelmann, *Angew. Chem.* **1993**, 105, 1364–1367; *Angew. Chem. Int. Ed. Engl.* **1993**, 32, 1303–1305.
- [3] D. Fenske, N. Zhu, T. Langetepe, *Angew. Chem.* **1998**, 110, 2784–2788; *Angew. Chem. Int. Ed.* **1998**, 37, 2640–2644.
- [4] D. Fenske, W. Holstein, *Angew. Chem.* **1994**, 106, 1311–1312; *Angew. Chem. Int. Ed. Engl.* **1994**, 33, 1290–1292.
- [5] D. Fenske, F. Simon, *Angew. Chem.* **1997**, 109, 240–243; *Angew. Chem. Int. Ed. Engl.* **1997**, 36, 230–233.
- [6] D. Fenske, F. Simon, *Z. Anorg. Allg. Chem.* **1996**, 622, 45–52.
- [7] D. Fenske, J. Besinger, unpublished results.
- [8] X-ray structural analysis of **1**: STOE-IPDS (MoK_α irradiation), data collection and refinement (SHELXS-86, SHELXL-93). Monoclinic, space group $P2_1/c$ (no. 14), $Z=4$, cell (203 K): $a=3088.0(6)$, $b=2261.0(5)$, $c=3303.0(7)$ pm, $\beta=105.83(3)^\circ$, $V=22187(8) \cdot 10^6$ pm³, $\mu(\text{MoK}_\alpha)=46.43$ cm⁻¹; $2\theta_{\text{max}}=48^\circ$; 105 964 reflections, of which 33 395 are independent ($R_{\text{int}}=0.1163$), 24 809 reflections with $I>2\sigma(I)$, 2443 parameters; maximum / minimum electron density = 1.19 / -1.12 e⁻ · (10⁶ pm)⁻³; $R_1=0.05$; $wR_2=0.131$. The positions of the H atoms were calculated, all other atoms were refined anisotropically except those of the DME molecules. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-145570. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
- [9] A. F. Holleman, E. Wiberg, *Lehrbuch der Anorganischen Chemie*, 91st–100th ed., de Gruyter, Berlin, **1985**, p. 1032.
- [10] C. Elschenbroich, A. Salzer, *Organometallchemie*, 3rd ed., Teubner, Stuttgart, **1993**, p. 87.
- [11] *Gmelins Handbuch der Anorganischen Chemie, Kupfer Teil B, Lieferung 2*, 8th ed., Verlag Chemie, Weinheim, **1961**, p. 934.
- [12] S. Dehnen, D. Fenske, *Chem. Eur. J.* **1996**, 2, 1407–1416; A. Eichhöfer, D. Fenske, *J. Chem. Soc. Dalton Trans.* **1998**, 2969–2972.
- [13] A. Eichhöfer, J. F. Corrigan, D. Fenske, E. Tröster, *Z. Anorg. Allg. Chem.* **2000**, 626, 338–348.
- [14] P. Reis, F. Weigend, R. Ahlrichs, D. Fenske, *Angew. Chem.* **2000**, 112, 4085–4089; *Angew. Chem. Int. Ed.* **2000**, 39, 3925–3929.
- [15] W. Beesk, P. G. Jones, H. Rumpel, E. Schwarzmann, G. M. Sheldrick, *J. Chem. Soc. Chem. Commun.* **1981**, 664; C. Linke, M. Jansen, *Angew. Chem.* **1992**, 104, 618–619; *Angew. Chem. Int. Ed. Engl.* **1992**, 31, 653–654; C. Linke, M. Jansen, *Inorg. Chem.* **1994**, 33, 2614–2616;

- H. G. von Schnering, K. G. Häusler, *Rev. Chim. Miner.* **1976**, 13, 71; M. Jansen, *Angew. Chem.* **1987**, 99, 1136–1138; *Angew. Chem. Int. Ed. Engl.* **1987**, 26, 1098–1110.
- [16] All calculations were carried out with the program package TURBOMOLE. a) R. Ahlrichs, M. Bär, M. Häser, H. Horn, C. Kölmel, *Chem. Phys. Lett.* **1989**, 162, 165–169. The DFT calculations were made with the Becke–Perdew 86 functional (BP) within the RI approximation (RI = resolution of the identity). b) A. D. Becke, *Phys. Rev. A* **1988**, 38, 3098–3100; c) S. J. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, 58, 1200–1211; d) J. P. Perdew, *Phys. Rev. B* **1986**, 33, 8822–8824; erratum: J. P. Perdew, *Phys. Rev. B* **1986**, 34, 7406; e) K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, *Chem. Phys. Lett.* **1995**, 242, 652. The basis sets used in the DFT calculations were SV(P) (split-valence plus polarization for all non-hydrogen atoms) and TZVP (triple zeta valence plus one polarization function); f) A. Schäfer, H. Horn, R. Ahlrichs, *J. Chem. Phys.* **1992**, 97, 2571–2577; g) A. Schäfer, C. Huber, R. Ahlrichs, *J. Chem. Phys.* **1994**, 100, 5829–5835. The core electrons of Te atoms were described by an effective core potential (ECP); h) A. Bergner, M. Dolg, W. Kuechle, H. Stoll, H. Preuss, *Mol. Phys.* **1993**, 80, 1431. The basis set dependency within population analyses was checked for HF calculations with a modified SV(P) basis set for the Cu atoms which was developed by an optimization of valence s functions for a small model cluster (Cu_4Cl_2).
- [17] If the symmetry threshold is lowered, S_6 , a subgroup of T_h is found. Therefore, a geometry optimization in S_6 symmetry was performed in which the energy as well as in the calculated structure converged to the results of T_h symmetry.
- [18] The combination of all basis functions would give for doubly occupied MOs $n_i=2$; for the population n_i , however, only those basis functions are combined which are centered at the cluster core, that is, the Cu atoms of the octahedra in **1b** and **2b**. Thus, the closer the value of n_i is to 2, the more this orbital is localized at the cluster core.

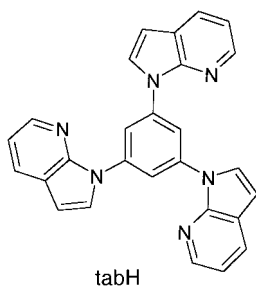
A Blue Luminescent Starburst Molecule and Its Orange Luminescent Trinuclear Pd^{II} Complex: 1,3,5-tris(7-azaindol-1-yl)benzene (tabH) and $[\text{Pd}^{\text{II}}(\text{tab})_2\text{Cl}_4]**$

Qingguo Wu, Andrea Hook, and Suning Wang*

Luminescent organic and organometallic compounds have attracted much attention recently, mostly because of their potential applications in organic light-emitting devices (OLEDs).^[1,2] We have demonstrated previously that Al^{III} and B^{III} complexes of 7-azaindolyl (deprotonated 7-azaindole) are bright blue emitters^[3] and capable of producing a bright blue light when in OLEDs.^[4] Our recent efforts have focused on the modification of the 7-azaindolyl ligand to improve the stability and performance of compounds based on 7-azaindole. One of the modifications we carried out was to replace the proton on the indole nitrogen atom by an

[*] Prof. Dr. S. Wang, Q. Wu, A. Hook
Department of Chemistry
Queen's University
Kingston, Ontario, K7L 3N6 (Canada)
Fax: (+1) 613-533-6669
E-mail: wangs@chem.queensu.ca

[**] This work was financially supported by the Natural Sciences and Engineering Research Council of Canada and the Xerox Research Foundation.



aromatic group so that the new ligand can bind to a metal ion as a neutral chelate ligand.^[5] An example of the modified 7-azaindolyl ligands obtained by our group is the novel starburst molecule, 1,3,5-tris(7-azaindol-1-yl)benzene (tabH).

tabH was synthesized by the reaction of 1,3,5-tribromobenzene with 7-azaindole using Ullmann condensation methods,^[6] in which Cu^{II} and K₂CO₃ were used as the catalyst and bromide scavenger. tabH has a melting point of 220 °C and emits a bright blue color in solution and in the solid state when irradiated by UV light. The emission maxima of tabH in solution (5 mg mL⁻¹, CH₂Cl₂) and the solid state are at 409 nm and 413 nm, respectively (Figure 1). The luminescence of tabH is believed

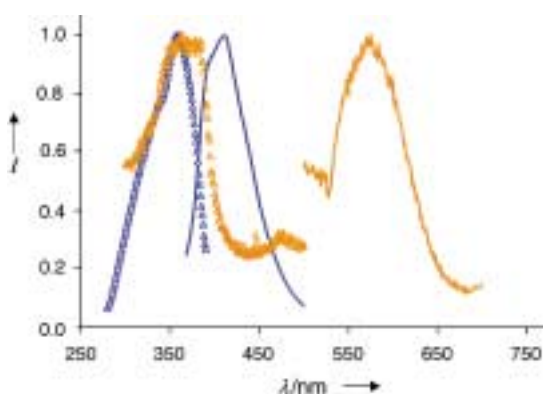


Figure 1. Excitation and emission spectra of solid tabH (blue) at ambient temperature and **1** (orange) at 77 K. Excitation = triangles, emission = solid line.

to be of fluorescent origin, based upon our previous studies on related molecules.^[3, 4] The blue luminescence of tabH is in sharp contrast to 7-azaindole, which has an emission band in the $\lambda_{\text{max}} < 400$ nm region. The attachment of the benzene moiety to 7-azaindole is clearly responsible for the red shift of emission energy by tabH. A similar red shift in the emission energy, on account of the replacement of the indole proton in 7-azaindole by an aromatic group, has been observed previously.^[5] The photoluminescent efficiency of tabH in solution was determined to be ~0.40 relative to that of 9,10-diphenylanthracene, which indicates that it is a bright blue emitter. Examples of luminescent and electroluminescent starburst organic molecules are previously known.^[7] However, stable and blue luminescent starburst molecules are still rare. Our preliminary investigation showed that tabH is promising as a blue emitter in OLEDs. Further details will be published in due course.

Recently, several examples of luminescent transition metal complexes have been reported to be promising emitters in light-emitting devices.^[8] However, luminescent transition metal complexes that are useful in OLEDs are still scarce. We therefore investigated the potential of the tabH molecule as a ligand to form luminescent transition metal complexes. We have found that the tabH molecule complexes readily with

Pd^{II} and Pt^{II} ions to form a variety of novel compounds, an example of which is [Pd₃(tab)₂Cl₄] (**1**), obtained from the treatment of K₂PdCl₄ with tabH in a 3:2 ratio using a procedure similar to that reported recently by Cadenas et al.^[9] The structure of **1** was determined by a single-crystal X-ray diffraction analysis.^[10] As shown in Figures 2 and 3, **1** has three Pd^{II} ions in two different environments: Pd(2) is situated at the crystallographically imposed inversion center and coordinated by two nitrogen and two chlorine atoms in a *trans* fashion while Pd(1) and Pd(1A) are related by the inversion

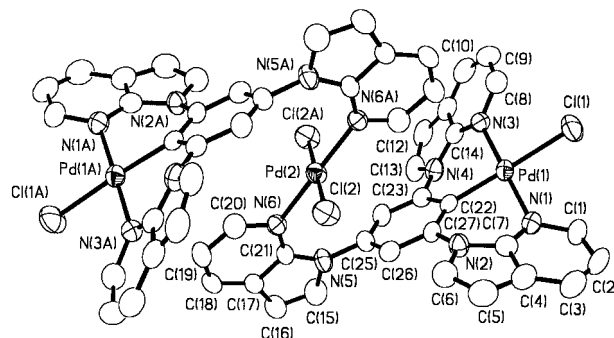


Figure 2. ORTEP representation of the molecular structure of **1** with labeling schemes and 50 % thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Pd(1)–C(22) 1.989(5), Pd(1)–N(1) 2.019(5), Pd(1)–N(3) 2.047(4), Pd(1)–Cl(1) 2.3946(15), Pd(2)–N(6) 2.045(4), Pd(2)–Cl(2) 2.3031(14); N(1)–Pd(1)–N(3) 176.22(18), C(22)–Pd(1)–Cl(1) 172.96(15), N(6)–Pd(2)–Cl(2) 89.07(12), N(6)–Pd(2)–Cl(2A) 90.93(12).

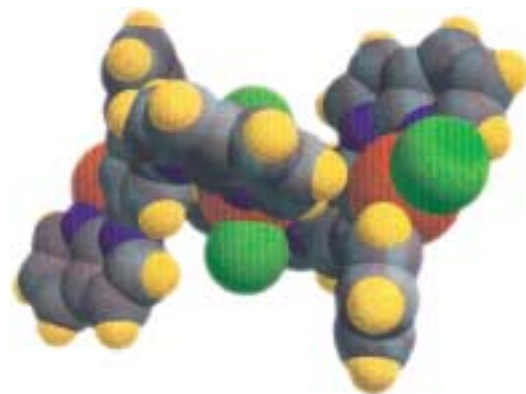


Figure 3. A space-filling diagram showing the orientation of the tab⁻ ligands in **1**.

center of symmetry and coordinated by two nitrogen, one chlorine and one carbon atom. Owing to the presence of the inversion center, the three Pd^{II} ions are in a rigorous linear arrangement with the Pd(1)–Pd(2) separation being 5.866(1) Å. The Pd(1) and Pd(2) centers have a square-planar geometry with a dihedral angle of 30.0° between the Pd(1) and Pd(2) square planes. The tab ligand acts both as a chelating and a bridging ligand. The formation of the Pd(1)–C(22) bond is a consequence of cyclometalation of tabH, favored by the geometry of the ligand and the chelating effect—a common phenomenon in organopalladium and organoplatinum compounds.^[9, 11] The palladium–ligand bonds in **1** are typical.^[9, 11] The three 7-azaindolyl groups of the tab ligand are not coplanar with the benzene moiety. The dihedral angles between the benzene ring and the N(2), N(4), and N(6) rings

are 23.4°, 35.1°, and 68.4°, respectively, attributable to steric interactions between hydrogen atoms and the geometric constraint of the ligand.

The coordination of the tabH ligand to the Pd^{II} centers leads to a drastic change of luminescence. At ambient temperature, in contrast to the free tabH ligand, **1** has no luminescence. At 77 K, upon excitation at $\lambda = 370$ nm, an orange emission band at $\lambda_{\text{max}} = 575$ nm from **1** was observed, as shown in Figure 1. The excitation band of **1** is similar to that of tabH. The ~160 nm red shift of the emission energy cannot be attributed to the abstraction of one proton from the benzene ring of tabH, based on the fact that Li⁺tab[−] does not have an orange emission. Luminescence observed in previously reported Pd^{II} complexes has often been attributed to metal-to-ligand charge transfer (MLCT) or metal-metal-to-ligand charge transfer (MMLCT) bands.^[11] The Pd–Pd separation distance of 5.866 Å in **1** is too large to allow any significant Pd–Pd interactions or MMLCT. The participation of 4d orbitals from the Pd^{II} ion in the luminescent transition of **1** appears to be very likely, based on the results of our preliminary ab initio molecular orbital calculations. However, a complete understanding of the luminescence displayed by **1** awaits further theoretical and experimental study.

Although **1** is not suitable as an emitter for electroluminescent devices because of the absence of luminescence at ambient temperature, it demonstrates that the tab[−] ligand can bind readily to a transition metal center to form luminescent complexes, thus providing a new avenue for luminescent transition metal compounds. It is conceivable, that with the appropriate choice of the central metal ion and the non-emitting ligands (for example, chloride in **1**), bright luminescent transition metal complexes based on tab ligands could be obtained.

Experimental Section

tabH: 1,3,5-Tribromobenzene (4.00 mmol, 1.259 g), 7-azaindole (16.00 mmol, 1.890 g), K₂CO₃ (16.00 mmol, 2.211 g), and CuSO₄ (0.100 mmol, 0.025 g) were mixed and heated at 205°C for 9 h under N₂. After being cooled to ambient temperature, the reaction mixture was dissolved in CH₂Cl₂ (300 mL) and washed with water. The organic layer was separated, dried over sodium sulfate, and evaporated to dryness by vacuum. The residue was passed through a silica gel column using hexanes/ethyl acetate (3/1) as the eluent. The first fraction collected was 1-bromo-3,5-bis(7-azaindol-1-yl)benzene, the second was tabH. Recrystallization from CH₂Cl₂/hexanes yielded a colorless solid of tabH (0.92 g, 54% yield). M.p. 220°C. ¹H NMR (CDCl₃, 25°C): δ = 8.36 (d, ³J = 5.1 Hz, 3H; 7-azain), 8.34 (s, 3H; benzene), 7.97 (dd, ³J₁ = 7.5, ³J₂ = 1.8 Hz, 3H; 7-azain), 7.70 (d, ³J = 4.2 Hz, 3H; 7-azain), 7.14 (dd, ³J₁ = 7.5, ³J₂ = 4.5 Hz, 3H; 7-azain), 6.67 (d, ³J = 3.6 Hz, 3H; 7-azain); ¹³C NMR (CDCl₃, 25°C): δ = 143.72 (7-azain), 129.20 (7-azain), 127.77 (7-azain), 117.05 (benzene), 116.12 (7-azain), 102.36 (7-azain); elemental analysis for C₂₇H₁₈N₆ · 0.3 CH₂Cl₂: calcd: C 72.55, H 4.08, N 18.59; found: C 72.35, H 3.99, N 18.41; MS: *m/z*: 426.3 [*M*⁺].

[Pd₃(tab)₂Cl₄] (**1**): tabH (0.20 mmol, 0.0853 g) and K₂PdCl₄ (0.30 mmol, 0.0979 g) were added to acetate acid (10 mL). The mixture was heated at 110–120°C and refluxed for 6 h under N₂. After the reaction mixture was cooled to ambient temperature, the off-white solid was collected by filtration and washed by acetic acid, CH₃OH, and diethylether (each 5 mL). Recrystallization of the crude product from DMF and ethanol yielded light yellow crystals of **1** in a 76% yield. M.p. 196°C. ¹H NMR ([D₆]DMSO, 25°C): δ = 9.08 (d, ³J = 5.7 Hz, 2H; 7-azain), 8.58 (d, ³J = 3.9 Hz, 2H; 7-azain), 8.36–8.30 (m, 3H; 7-azain), 8.09 (d, ³J = 7.5 Hz, 1H; 7-azain), 8.03 (d, ³J = 3.6 Hz, 1H; 7-azain) 7.93(s, 2H; benzene), 7.33 (dd, ³J₁ = 7.2, ³J₂ =

6.3 Hz, 2H; 7-azain), 7.22 (dd, ³J₁ = 7.5, ³J₂ = 4.5 Hz, 1H; 7-azain), 7.02 (d, ³J = 3.6 Hz, 2H; 7-azain), 6.69 (d, ³J = 3.6 Hz, 1H; 7-azain); ¹³C NMR ([D₆]DMSO, 25°C): δ = 156.69 (benzene), 148.18 (7-azain), 146.96 (7-azain), 143.10 (7-azain), 141.35 (7-azain), 137.26 (benzene), 136.27 (benzene), 132.47 (7-azain), 129.39 (7-azain), 128.62 (7-azain), 128.09 (7-azain), 123.07 (benzene), 121.44 (7-azain), 116.94 (7-azain), 113.96 (7-azain), 109.99 (7-azain), 105.49 (7-azain), 101.64 (7-azain); elemental analysis for C₃₄H₃₄N₁₂Cl₄Pd₃ · 2(CH₃)₂NCHO · H₂O: calcd: C 48.77, H 3.38, N13.27; found: C 48.33, H 3.50, N 13.22.

Received: May 18, 2000 [Z15141]

- [1] a) C. W. Tang, S. A. VanSlyke, *Appl. Phys. Lett.* **1987**, *51*, 913; b) C. W. Tang, S. A. VanSlyke, C. H. Chen, *J. Appl. Phys.* **1989**, *65*, 3611; c) Y. Shirota, Y. Kuwabara, H. Inada, T. Wakimoto, H. Nakada, Y. Yonemoto, S. Kawami, K. Imai, *Appl. Phys. Lett.* **1994**, *65*, 807; d) Y. Hamada, T. Sano, M. Fujita, T. Fujii, Y. Nishio, K. Shibata, *Jpn. J. Appl. Phys.* **1993**, *32*, L514; e) V. Bulovic, G. Gu, P. E. Burrows, S. R. Forrest, *Nature* **1996**, *380*, 29.
- [2] a) N.-X. Hu, M. Esteghamatian, S. Xie, Z. Popovic, B. Ong, A. M. Hor, S. Wang, *Adv. Mater.* **1999**, *11*, 1460; b) C. Adachi, T. Tsutsui, S. Saito, *Appl. Phys. Lett.* **1990**, *56*, 799; c) X. T. Tao, H. Suzuki, T. Wada, H. Sasabe, S. Miyata, *Appl. Phys. Lett.* **1999**, *75*, 1655; d) Z. Shen, P. E. Burrows, V. Bulovic, S. R. Forrest, M. E. Thompson, *Science* **1997**, *276*, 2009; e) H. Aziz, Z. Popovic, N. X. Hu, A. M. Hor, G. Xu, *Science* **1999**, *283*, 1900; f) Y. Hamada, T. Sano, H. Fujii, Y. Nishio, H. Takahashi, K. Shibata, *Appl. Phys. Lett.* **1997**, *71*, 3338; g) Q. Wu, M. Esteghamatian, N. X. Hu, Z. Popovic, G. Enright, Y. Tao, M. D'Iorio, S. Wang, *Chem. Mater.* **2000**, *12*, 79.
- [3] a) W. Liu, A. Hassan, S. Wang, Q. Wu, *Organometallics* **1997**, *16*, 4257; b) J. Ashenhurst, L. Brancaloni, A. Hassan, W. Liu, H. Schmitter, S. Wang, Q. G. Wu, *Organometallics* **1998**, *17*, 3186; c) J. Ashenhurst, G. Wu, S. Wang, *J. Am. Chem. Soc.* **2000**, *122*, 2541; d) S. Gao, Q. G. Wu, G. Wu, S. Wang, *Organometallics* **1998**, *17*, 4666; e) A. Hassan, S. Wang, *Commun. Chem.* **1998**, 211.
- [4] Q. Wu, M. Esteghamatian, N. X. Hu, Z. Popovic, G. Enright, S. R. Breeze, S. Wang, *Angew. Chem.* **1999**, *111*, 1039; *Angew. Chem. Int. Ed.* **1999**, *38*, 985.
- [5] a) S. F. Liu, Q. Wu, H. L. Schmitter, H. Aziz, N. X. Hu, Z. Popovic, S. Wang, *J. Am. Chem. Soc.* **2000**, *122*, 3671; b) Q. Wu, J. Lavigne, S. Wang, *Inorg. Chem.* **2000**, in press.
- [6] a) H. B. Goodbrand, N. X. Hu, *J. Org. Chem.* **1999**, *64*, 670; b) J. Lindley, *Tetrahedron* **1984**, *40*, 1433; c) P. E. Fanta, *Synthesis* **1974**, 1.
- [7] N. Tamoto, C. Adachi, K. Nagai, *Chem. Mater.* **1997**, *9*, 1077.
- [8] a) M. A. Baldo, S. Lamansky, P. Burrows, M. E. Thompson, S. R. Forrest, *Appl. Phys. Lett.* **1999**, *75*, 5; b) M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, S. R. Forrest, *Nature* **1998**, *395*, 151; c) X. Gong, P. K. Ng, W. K. Chan, *Adv. Mater.* **1998**, *10*, 1337; d) D. F. O'Brien, M. A. Baldo, M. E. Thompson, S. R. Forrest, *Appl. Phys. Lett.* **1999**, *74*, 442; e) R. C. Kwong, S. Sibley, T. Dubovoy, M. Baldo, S. R. Forrest, M. E. Thompson, *Chem. Mater.* **1999**, *11*, 3709.
- [9] D. J. Cárdenas, A. M. Echavarren, *Organometallics* **1999**, *18*, 3337.
- [10] The crystals of **1** were obtained from a DMF/ethanol solution. Crystal data for **1**: C₃₄H₃₄N₁₂Cl₄Pd₃ · 2(CH₃)₂NCHO, monoclinic, space group P2₁/c, *a* = 9.1343(6), *b* = 15.6271(10), *c* = 20.3907(15) Å, β = 102.1530(10)°, *V* = 2845.4(3) Å³, *Z* = 2, GOF(*F*²) = 0.881, *R*₁ = 0.0356 (*I* > 2 σ (*I*)), *wR*₂ = 0.0719; *R*₁ = 0.0621 (all data), *wR*₂ = 0.0779. Data were collected on a Siemens Smart CCD 1000 X-ray diffractometer operated at 50 kV and 35 mA at ambient temperature. The structural solution and refinement were performed on a PC using Bruker AXS SHELXTL software package (Version 5.10). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-144749. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
- [11] a) K. A. Van Houten, D. C. Heath, C. A. Barringer, A. L. Rheingold, R. S. Pilato, *Inorg. Chem.* **1998**, *37*, 4647; b) F. Neve, A. Crispini, S. Campagna, *Inorg. Chem.* **1997**, *36*, 6150; c) S. W. Lai, T. C. Cheung, M. C. W. Chan, K. K. Cheung, S. M. Peng, C. M. Che, *Inorg. Chem.* **2000**, *39*, 255.