Bridging of Platinacycles by *cis*-Azobenzenes: Synthesis and Photochemical Study. Structure of the Twisted Inorganic *Z*-1,1,2,2-Tetrasubstituted Diazaethene ((*Z*)-1,2-Diphenyldiazaethene)bis[chloro(((dimethylamino)methyl)phenyl-*C*,*N*)platinum(II)]

Alexander D. Ryabov,*[1a] Ludmila G. Kuz'mina,[1b] Natalia V. Dvortsova,[1b] Derk J. Stufkens,[1c] and Rudi van Eldik*[1d]

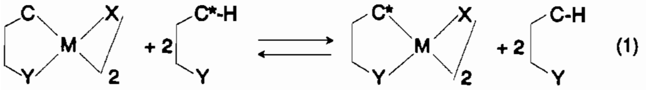
Division of Chemistry, G. V. Plekhanov Russian Economic Academy, Stremyanny per. 28, 113054, Moscow, Russia, N. S. Kurnakov Institute of General and Inorganic Chemistry, Leninsky pr. 31, 117907, Moscow, Russia, Anorganisch Chemisch Laboratorium, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands, and Institute for Inorganic Chemistry, University of Witten/Herdecke, Stockumer Strasse 10, 5810 Witten, Germany

Received February 11, 1993

The cycloplatinated chloro-bridged *N*,*N*-dimethylbenzylamine complexes **1**, $[Pt(C_6H_3RCH_2NMe_2)Cl]_2$ (R = H, 4-MeO), undergo addition to *cis*-azobenzenes **2** ($ZC_6H_4N{=}NC_6H_4Z$; Z = H, *p*-Me, *m*-Me, *p*-Cl) photoisomerized in situ from the *trans*-azobenzene precursors. The reaction is carried out in benzene or chloroform at room temperature to afford the unique intensively colored adducts **3** in which bridging *cis*-azobenzenes bind two platinum $[Pt(C_6H_3RCH_2NMe_2)Cl]$ fragments. The nitrogen atoms of the azobenzene are trans to the Pt–C bonds, and the chloro ligands are located at different sites with respect to the C–N=N–C plane of the *cis*-azobenzene moiety, as confirmed by X-ray crystallography. Compound **3a**: $C_{30}H_{34}N_4Cl_2Pt_2\cdot{}^1/_2C_6H_{14}$, triclinic, space group $P\bar{1}$, a = 10.644(3) Å, b = 11.932(6) Å, c = 13.874(4) Å, α = 72.22(3)°, β = 76.06(2)°, γ = 83.44(3)°, Z = 2. Adducts **3** possess the metal-to-ligand charge-transfer (MLCT) transitions involving the azobenzene π^*(N=N) orbital, as suggested by a resonance Raman spectroscopy study. The energy of the MLCT transitions depends on the substituents R and Z conforming to the Hammett law, when the latter are varied. Solutions of **3** show a thermochroic behavior due to reversible dissociation of the cycloplatinated moieties from *cis*-azobenzenes. The dissociation is a key process to account for the rate law of the thermal dissociation of **3** which is given by $k(\text{obsd}) = k_o + k[\text{Pt}]_t$, where $[\text{Pt}]_t$ is the total concentration of **3**. Interestingly, benzo[*c*]cinnoline, which may be considered as a mimetic of *cis*-azobenzene, binds only one such a fragment to form **4**. The latter reaction needs no irradiation, and the products are not as intensively colored as in the case of the azobenzenes.

Introduction

Complexation of azobenzenes to metal centers is a permanent subject of research for approximately 80 years,[2] and additional attention was brought about by showing that azobenzenes can easily be orthometalated by Pd(II) or Pt(II) salts via C(sp^2)–H bond cleavage.[3] Since this pioneering work of Cope, many orthometalation reactions of azobenzenes by transition metal complexes, as well as further transformations of the metallacycles, have been reported.[4] Our previous interest in azobenzenes was centered around the ligand-exchange reaction in the series of Pd(II) complexes in eq 1, i.e. a migration of the metal from one



(1)

metallacycle to a free ligand in acidic media to form a novel cyclopalladated derivative.[5] Azobenzenes proved to be excellent incoming ligands in reaction 1. In particular, orthopalladated *N*,*N*-dimethylbenzylamine, $[Pd(C_6H_4CH_2NMe_2)Cl]_2$, and azobenzene react readily at 55 °C providing orthometalated azobenzene, $[Pd(C_6H_4N{=}NPh)Cl]_2$, in a high yield.[6] An intriguing question was whether the same reaction under similar conditions will occur in the Pt(II) series; i.e., is it possible starting from chloro-bridged Pt(II) dimers **1** to arrive at orthoplatinated azobenzenes in acidic media? First experiments have, however, shown that the exchange in the Pt series is much more difficult to achieve. Orthoplatinated azobenzene was not formed under the conditions typical of reaction 1 (C_6H_6–HOAc, 70 °C, 5 days). Quite unexpectedly, by leaving the reaction mixture overnight in an illuminated hood, we noticed a photochemical process to form intensively colored products. This photochemical reaction was investigated in some detail, and in this paper we report on (i) photochemical synthesis and X-ray structural characterization of the new complexes **3** (Scheme I) from orthoplatinated *N*,*N*-dimethylbenzylamines **1** and azobenzenes **2**, in which the latter in the cis form serves as a bridging ligand that binds two platinum centers, (ii) spectral and thermochroic properties of complexes **3**, and (iii) kinetics of their thermal decomposition in solution.

---

(1) (a) Plekhanov Academy; Alexander von Humboldt Fellow 1991–1993 at the Institut für Anorganische Chemie, Universität Witten/Herdecke. (b) Kurnakov Institute. (c) University of Amsterdam. (d) Universität Witten/Herdecke.

(2) Vanstone, E. *J. Chem. Soc.* **1914**, *105*, 1491. For review, see: Laing, I. G. In *Rodd's Chemistry of Carbon Compounds. Vol. 3. Aromatic Compounds. Part C*, 2nd ed.; Coffey, S., Ed.; Elsevier: Amsterdam, 1973; p 164.

(3) Cope, A. C.; Siekman, R. W. *J. Am. Chem. Soc.* **1965**, *87*, 3272.

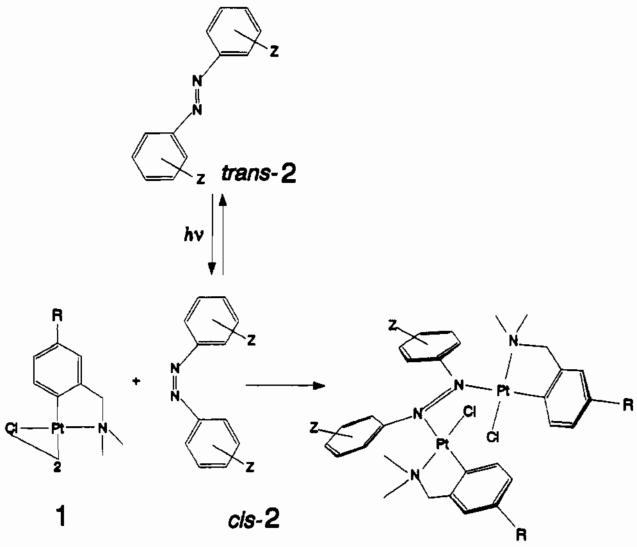
(4) Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 327. Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73. Omae, I. *Chem. Rev.* **1979**, *79*, 287; *Coord. Chem. Rev.* **1979**, *28*, 97; **1980**, *32*, 235; **1982**, *42*, 245; **1988**, *83*, 137. *Organometallic Intramolecular-Coordination Compounds*; Elsevier Science Publishers: Amsterdam, New York, 1986. Abicht, H.-P.; Issleib, P. *Z. Chem.* **1977**, *17*, 1. Constable, E. C. *Polyhedron* **1984**, *3*, 1037. Rothwell, I. P. *Polyhedron* **1985**, *4*, 177; *Acc. Chem. Res.* **1988**, *21*, 153. Newkome, G. R.; Puckett, W. E.; Gupta, V. K.; Kiefer, G. *Chem. Rev.* **1986**, *86*, 451. Evans, D. W.; Baker, G. R.; Newkome, G. R. *Coord. Chem. Rev.* **1989**, *93*, 155. Dunina, V. V.; Zalevskaya, O. A.; Potapov, V. M. *Usp. Khim.* **1988**, *57*, 434. Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* **1989**, *22*, 91. Ryabov, A. D. *Synthesis* **1985**, 233. *Chem. Rev.* **1990**, *90*, 403. Pfeffer, M. *Recl. Trav. Chim. Pays-Bas* **1990**, *109*, 567.

(5) For review see: Ryabov, A. D. In *Perspectives in Coordination Chemistry*; Williams, A. F., Floriani, C., Merbach, A. E., Eds.; Verlag Helvetica Chimica Acta: Basel, VCH Weinheim, New York, Basel, Cambridge, 1992; pp 271–292.

(6) Ryabov, A. D.; Yatsimirsky, A. K. *Inorg. Chem.* **1984**, *23*, 789.

0020-1669/93/1332-3166$04.00/0

Scheme I



R = H (a), OMe (b)   Z = H (a), *p*-Me (b), *m*-Me (c), *p*-Cl (d)

3	R	Z
a	H	H
b	H	*p*-Me
c	MeO	H
d	MeO	*p*-Me
e	MeO	*m*-Me
f	MeO	*p*-Cl

Experimental Section

General Methods. Spectrophotometric measurements were made on Hitachi U-3200, Shimadzu UV-250, and Cary 1 (Varian) spectrophotometers. ^{1}H and ^{2}H NMR spectra were run on a AM 400 WB Bruker instrument. Chemical shifts are in δ scale and J are in Hz throughout. FT-IR spectra of solid compounds were recorded in KBr disks by using a Nicolet 5SX spectrophotometer. Resonance Raman spectra were measured for complexes **3a,c** incorporated into a KNO$_3$ pellet with a Dilor XY Raman spectrophotometer. The spectra were excited by the lines of a SP 2016 Ar$^+$ laser or by a CR-590 dye laser employing Rhodamine 6G as a dye, pumped by the Ar$^+$ laser. The 1051-cm^{-1} Raman line of NO$_3^-$ was used as internal standard to establish the resonance Raman effects. Kinetics of the thermal decomposition of **3** were run on a Shimadzu spectrophotometer equipped with a temperature-controlled (±0.1 °C) cell compartment, providing three independent measurements. The kinetic traces were analyzed by using a homemade computer program designed by A. Neubrand. Analytical data were obtained from Beller Analytisches Laboratorium (Göttingen, Germany). Melting points were determined with the help of a Digital Melting Point Apparatus and are all uncorrected.

Materials. Ligands and Solvents. *trans*-Azobenzene was purchased from Aldrich and purified by recrystallization from ethanol. *trans*-4,4′- and *trans*-3,3′-Azotoluenes were obtained from ICN and used as received. *trans*-d_{10}-azobenzene and *trans*-[^{15}N]$_2$-azobenzene were synthesized in three steps starting from the corresponding benzene (C$_6$D$_6$ in the former case) and nitric acid [H^{15}NO$_3$ (52%, enrichment 95.9%, Predpiyatie P/Ya A-3521) in the latter case]. Nitration gave the corresponding nitrobenzene;[7] the latter was reduced by metallic Sn in the presence of HCl into d_5- or ^{15}N-aniline,[8] which was then oxidized by freshly prepared MnO$_2$[9] in benzene to yield the final products. 4,4′-Dichloroazobenzene was obtained by oxidation of 4-chloroaniline by MnO$_2$.[9] ^{1}H NMR (CDCl$_3$): 7.08, 7.65 (AA′BB′, J = 9). Benzo[*c*]cinnoline, a Janssen Chimica product, was used without additional purification. Commercially available solvents were usually employed. Benzene used for kinetic measurements was distilled under a Na–K alloy.

Platinum(II) Complexes 1a,b. The starting complexes [Pt(C$_6$H$_3$-XCH$_2$NMe$_2$)Cl]$_2$ (X = H, 3-MeO) were prepared using essentially the same procedure as described in the literature.[10] A solution of *freshly* distilled *N*,*N*-dimethylbenzylamine (1.30 g, 9.64 mmol, Aldrich) in 10 mL of MeOH was added to 23 mL of an aqueous solution of K$_2$PtCl$_4$ (2.00 g, 4.82 mmol). The mixture was gently stirred for 48 h at 20 °C. A brown precipitate formed, which was filtered out, washed with water, air dried, and dissolved in ca. 15 mL of CHCl$_3$, and then the mixture was brought on a short (ca. 8-cm height, 4-cm diameter) silica gel column. Product **1a** was eluted with CHCl$_3$, and the solvent was removed by using a rotary evaporator to afford 0.47 g (27%) of sufficiently pure material which could be additionally purified by recrystallization from benzene–hexane. UV–vis (EtOH): λ(max) 260 (ϵ 17 600 M^{-1} cm^{-1}) nm. ^{1}H NMR: CDCl$_3$, 2.93 (s, N–CH$_3$), 2.96 (s, N–CH$_3$), 3.84 (s, N–CH$_2$), 3.83 (s, N–CH$_2$), 6.76–6.88 (m, H3–5), 6.76–6.88 (m, H3–5), 7.01 (d, J = 7.9, H6), 6.96 (d, J = 7.9, H6); C$_6$D$_6$, 2.25 (s, N–CH$_3$), 2.34 (s, N–CH$_3$), 3.01 (s, N–CH$_2$), 3.04 (s, N–CH$_2$), 6.73 (d, J = 7.3, H3), 6.73 (d, J = 7.3, H3), 6.9–7.1 (m, H4,5), 6.9–7.1 (m, H4,5), 7.78 (d, J = 7.3, H6), 7.66 (d, J = 7.3, H6) (a mixture of *ab–hg* and *ab–gh* isomers). In the case of *N*,*N*-dimethyl-3-methoxybenzylamine (Aldrich), the product (**1b**) was eluted with CH$_2$Cl$_2$; longer elution time was needed as compared to the above case. The speed of elution can be increased by addition of 20% EtOAc to CH$_2$Cl$_2$. However, this also results in the elution of another yellow-brown material, the nature of which has not been identified. Yield of **1b**: 14%. UV–vis (EtOH): λ(max) 392 (ϵ 6000), 265 (ϵ 29 000 M^{-1} cm^{-1}) nm. ^{1}H NMR: CDCl$_3$, 2.96 (s, N–CH$_3$), 2.98 (s, N–CH$_3$), 3.84 (s, N–CH$_2$), 3.83 (s, N–CH$_2$), 3.72 (s, O–CH$_3$), 3.72 (s, O–CH$_3$), 6.51–6.57 (m, H3–5), 6.51–6.57 (m, H3–5), 6.99 (d, J = 8.7, H6), 6.94 (d, J = 8.7, H6); C$_6$D$_6$, 2.29 (s, N–CH$_3$), 2.37 (s, N–CH$_3$), 3.00 (s, N–CH$_2$), 3.02 (s, N–CH$_2$), 3.41 (s, O–CH$_3$), 3.40 (s, O–CH$_3$), 6.55 (d, J = 2, H3), 6.55 (d, J = 2, H3), 6.73 (dd, J = 8.5, 2, H5), 6.59 (dd, J = 8.5, 2, H5), 7.66 (d, J = 8.5, H6), 7.54 (d, J = 8.5, H6) (a mixture of *ab-hg* and *ab-gh* isomers).

Preparation of the Photochemical Adduct from 1a and *trans*-Azobenzene 3a. The complex (0.105 g, 0.144 mmol) and *trans*-azobenzene (0.131 g, 0.720 mmol) were dissolved in 22 mL of benzene, and the solution was placed in a quartz cell (10-mm width) and irradiated by a 150-W Hg lamp for 2 h. The solution changed color from light-orange to brownish-red. It was then concentrated ca. 2–3-fold on a rotary evaporator keeping the bath temperature not higher than 25 °C and hexane (30 mL) added. The mixture was kept overnight at ca. –5 °C. Brownish-red crystals formed were filtered out, washed with hexane, and dried in the air. Yield: 0.103 g (79%). Anal. Found: C, 42.22; H, 3.95; N, 5.75; Cl, 7.45; Pt, 41.38. Calcd for C$_{30}$H$_{34}$N$_4$Cl$_2$Pt$_2$·$^1/_2$C$_6$H$_6$: C, 41.69; H, 3.92; N, 5.89; Cl, 7.45; Pt, 41.03%. Mp: 133.5 °C. ^{1}H NMR: CDCl$_3$, 3.03 (s, N–CH$_3$),[11] 3.51 (d, J = 13, N–C*H*H), 3.55 (s, N–CH$_3$),[11] 4.40 (d, J = 13, N–CH*H*), 6.8–7.3 (m, Ar), 7.48 (d, J = 8, H6), 7.96 (br, H2′,6′); C$_6$D$_6$, 2.72 (d, J = 13, N–C*H*H), 2.78 (s, N–CH$_3$),[11] 3.39 (s, N–CH$_3$),[11] 3.78 (d, J = 13, N–CH*H*), 6.63 (t, J = 8, H4′), 6.75 (t, J = 8, H3′,5′), 6.80 (d, J = 8, H3), 7.06 (td, J = 8; 2, H4), 8.20 (br, H2′,6′), 8.21 (dd, J = 8; 2, H6).

Preparation of 3b. Complex **1a** (0.0544 g, 0.075 mmol) and *trans*-**2b** (0.047 g, 0.223 mmol) were dissolved in 8 mL of CHCl$_3$ and irradiated as above. The solvent was removed, the residue was dissolved in 2 mL of C$_6$H$_6$, and ca. 12 mL of hexane was added. Further procedure was as above. Yield: 0.048 g (65%). Anal. Found: C, 43.40; H, 4.75. Calcd for C$_{32}$H$_{38}$N$_4$Cl$_2$Pt$_2$·$^1/_2$C$_6$H$_6$: C, 42.94; H, 4.22. Mp: dec >130 °C. ^{1}H NMR (C$_6$D$_6$): 1.69 (s, CH$_3$), 2.74 (d, J = 13, N–C*H*H), 2.85 (s, N–CH$_3$),[11] 3.43 (s, N–CH$_3$),[11] 3.84 (d, J = 13, N–CH*H*), 6.63 (d, J = 7, H3′,5′), 6.81 (d, J = 8, H3), 6.98–7.08 (m, H4,5), 8.20 (br, H2′,6′), 8.22 (d, J = 8, H6).

Preparation of 3c. Complex **1b** (0.029 g, 0.037 mmol) and *trans*-**2c** (0.068 g, 0.371 mmol) were dissolved in 10 mL of CHCl$_3$, and the solution was irradiated for 3 h as above. Hexane (30 mL) was added, and the mixture was kept overnight at ca. –5 °C. Dark crystals formed, which were filtered out, washed with hexane, and dried in the air. Yield: 0.025 g (70%). Anal. Found: C, 39.64; H, 4.16. Calcd for C$_{32}$H$_{38}$N$_4$O$_2$Cl$_2$Pt$_2$: C, 39.55; H, 3.94. Mp: 186 °C. ^{1}H NMR: CDCl$_3$, 2.98 (s, N–CH$_3$),[11] 3.45 (d, J = 13, N–C*H*H), 3.52 (s, N–CH$_3$),[11] 3.71 (s, O–CH$_3$), 4.36 (d, J = 13, N–CH*H*), 6.56 (d, J = 8, H5), 6.59 (d, J = 2, H3), 7.34 (d, J = 8, H6), 7.12–7.28 (m, H3′–5′), 7.91 (br, H2′,6′); C$_6$D$_6$, 2.67 (d, J = 13, N–C*H*H), 2.79 (s, N–CH$_3$),[11] 3.45 (s, O–CH$_3$), 3.46 (s, N–CH$_3$),[11] 3.79 (d, J = 13, N–CH*H*), 6.59–6.65 (m, H3, H4′), 6.73 (t, J = 8, H3′,5′), 6.81 (dd, J = 8; 2, H5), 8.10 (d, J = 8, H6), 8.15 (br, H2′,6′).

Preparation of 3d. This was accomplished as described above for the azobenzene analog. Yield: 53%. Anal. Found: C, 39.89; H, 4.29. Calcd

---

(7) *Vogel's Textbook of Practical Organic Chemistry*, 5th ed.; Furniss, B. S., Hannaford, A. J., Smith, P. W. G., Tatchell, A. R., Eds.; Longman Scientific & Technical: Essex, U.K., 1989; p 854.

(8) Reference 7, p 892.

(9) Sandler, S. R.; Karo, W. *Organic Functional Group Preparation*, 2nd ed.; Academic Press: Orlando, San Diego, New York, Austin, Boston, London, Sydney, Tokyo, Toronto, 1986; Vol. 2, p 391.

(10) Cope, A. C.; Friedrich, E. C *J. Am. Chem. Soc.* **1968**, *90*, 909.

(11) Pt satellites are observed as shoulders.

for $C_{34}H_{42}N_4O_2Cl_2Pt_2$: C, 40.85; H, 4.23. Mp: 195 °C. ^{1}H NMR: C_6D_6,1.70 (s, CH_3), 2.71 (d, *J* = 13, N–C*H*H), 2.87 (s, N–CH_3),[11] 3.46 (s, O–CH_3), 3.51 (s, N–CH_3),[11] 3.84 (d, *J* = 13, N–CH*H*), 6.63 (d, *J* = 2, H3), 6.63 (d, *J* = 8, H3′,5′), 6.72 (dd, *J* = 8; 2, H5), 8.11 (d, *J* = 8, H6), 8.20 (br, H2′,6′).

Preparation of 3e. This was prepared as described above for **3c**, although the isolation procedure was slightly modified because of better solubility of the product in organic solvents. After the irradiation, $CHCl_3$ was removed under vacuum, the residue was dissolved in 3 mL of C_6H_6, ca. 30 mL of hexane was added, and the mixture was kept overnight at −20 °C. Black crystals formed were filtered out, washed with cold hexane, and air dried. Yield: 54%. Anal. Found: C, 42.44; H, 4.57; Pt, 37.20. Calcd for $C_{34}H_{42}N_4O_2Cl_2Pt_2\cdot{}^1/_2C_6H_6$: C, 42.77; H, 4.37; Pt, 37.56%. Mp: dec >195 °C. ^{1}H NMR: C_6D_6, 1.83 (s, CH_3), 2.70 (d, *J* = 13, N–C*H*H), 2.88 (s, N–CH_3),[11] 3.45 (s, O–CH_3), 3.49 (s, N–CH_3),[11] 3.83 (d, *J* = 13, N–CH*H*), 6.53 (d, *J* = 8, H4′), 6.61 (d, *J* = 2, H3), 6.72 (t, *J* = 8, H5′), 6.80 (dd, *J* = 8; 2, H5), 7.95 (br, H2′), 8.09 (d, *J* = 8, H6′), 8.30 (br, H6′).

Preparation of 3f. Ligand **2d** is less soluble in organic solvents and in some cases was crystallized together with **3f**. Therefore, one should avoid taking a large excess of the ligand. Complex **1b** (0.065 g, 0.082 mmol) and **2d** (0.028 g, 0.11 mmol) were dissolved in 20 mL of $CHCl_3$, and the solution was irradiated for 4 h as above. The volume was then reduced to ca. 5 mL under vacuum and 15 mL of hexane added. The mixture was kept for 2 h at −5 °C, and the next portion of hexane (8 mL) was added. The mixture was kept overnight at −20 °C. Dark-green crystals formed, which were filtered out, washed with hexane, and dried in the air. Yield: 0.048 g (56%). Anal. Found: C, 37.87; H, 3.49; Pt, 37.49. Calcd for $C_{32}H_{36}N_4O_2Cl_4Pt_2$: C, 36.93; H, 3.49; Pt, 35.87. Mp: dec >200 °C. ^{1}H NMR: C_6D_6, 2.71 (d, *J* = 13, N–C*H*H), 2.74 (s, N–CH_3),[11] 3.42 (s, N–CH_3),[11] 3.45 (s, O–CH_3), 3.84 (d, *J* = 13, N–CH*H*), 6.64 (d, *J* = 2, H3), 6.73 (d, *J* = 9, H3′,5′), 8.02 (br, H2′,6′), 8.03 (d, *J* = 8, H6).

Preparation of the Benzo[*c*]cinnoline Adducts. 4a. Complex **1a** (0.100 g, 0.137 mmol) was dissolved in 5 mL of $CHCl_3$, and bcc (0.0543 g, 0.302 mmol) was added on stirring. The pale-yellow solution immediately turned orange. After 10 min, hexane (15 mL) was slowly added to induce the precipitation of light-orange microcrystals. These were filtered out, washed with hexane, and air dried. Yield: 0.152 g (84%). Anal. Found: C, 42.14; H, 3.65; Pt, 31.56. Calcd for $C_{21}H_{20}N_3ClPt\cdot{}^1/_2CHCl_3$: C, 42.71; H, 3.42, Pt, 31.56%. Mp: dec > 205 °C. ^{1}H NMR: $CDCl_3$, 2.61 (br s, N–CH_3), 3.04 (br s, N–CH_3), 3.91 (br, N–C*H*H), 4.21 (br, N–CH*H*), 6.91–7.18 (m, H3–5), 7.83 (dd, *J* = 8; 2, H6), 7.89–8.05 (m, H5′–8′), 8.60–8.62 (m, H4′,9′), 8.75–8.77 (m, H10′), 10.38 (br, H3′).

4b. Complex **1b** (0.044 g, 0.056 mmol) was dissolved in 15 mL of $CHCl_3$ at 55 °C. The solution was cooled to 30 °C, and bcc (0.022 g, 0.122 mmol) was added on stirring. A 60-mL volume of hexane was needed to induce the precipitation. The product was isolated as in the above case. Yield: 0.051 g (80%). Anal. Found: C, 45.93; H, 4.10; Pt, 33.62. Calcd for $C_{22}H_{22}N_3OClPt$: C, 45.95; H, 3.86, Pt, 33.93%. Mp: dec >202 °C. ^{1}H NMR: $CDCl_3$, 2.61 (br s, N–CH_3), 3.04 (br s, N–CH_3), 3.79 (s, O–CH_3), 3.89 (br, N–C*H*H), 4.20 (br, N–CH*H*), 6.67 (d, *J* = 2, H3), 6.69 (dd, *J* = 8; 2, H5), 7.70 (d, *J* = 8, H6), 7.91–7.98 (m, H5′–8′), 8.59–8.63 (m, H4′,9′), 8.75–8.78 (m, H10′), 10.40 (br, H3′).

X-ray Structural Determination. Crystal data and details of the data-collection procedure, structure solution, and refinement are given in Table I. The structure was solved by the heavy-atom method and refined in an anisotropic least-squares approximation. At this step, the absorption of X-rays by the crystal was taken into account on the basis of the DIFABS (μ = 48.7 cm^{-1}) routine.[12] The subsequent refinement of the structure was performed by using the full-matrix anisotropic approximation. All hydrogen atoms and the solvate hexane molecule, which occupies a fractional position in the center of symmetry, were evaluated in the difference synthesis of the electronic density. The calculated coordinates of hydrogen atoms were, however, used in further calculations. The final refinement of the structure was made by the least squares in the anisotropic approximation for all non-hydrogen atoms of the molecule and in the isotropic approximation for carbon atoms of the solvate molecule taking into account the contribution from H atoms (positional and temperature parameters of which are fixed, B_{iso} = 6.32 Å^2). All calculations were performed on a IBM PC-AT computer with the SHELXC system of programs.

Table I. Crystallographic Data for Compound **3a**

chem formula	$C_{30}H_{34}N_4Cl_2Pt_2\cdot{}^1/_2C_6H_{14}$
fw	954.78
lattice	triclinic
space group	$P\bar{1}$ (No. 2)
a, Å	10.644(3)
b, Å	11.932(6)
c, Å	13.874(4)
α, deg	72.22(3)
β, deg	76.06(2)
γ, deg	83.44(3)
V, Å^3	1679.1
Z	2
T, °C	20
λ, Å	0.710 73
ρ_{calcd}, g cm^{-3}	1.88
μ(Mo Kα), cm^{-1}	48.7
R^a	0.037
$R_w{}^b$	0.049

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

Results

Photochemical Addition of Platinacycles 1 to Azobenzenes 2. General Procedure. In the absence of light, complexes **1** do not react with *trans*-azobenzenes in C_6H_6 or $CHCl_3$ solutions at ambient temperatures. The color of the mixtures remains yellow-orange due to the presence of *trans*-**2**, and the ^{1}H NMR spectrum of the mixture in $CDCl_3$ shows separate resonances arising from **1a** and *trans*-**2a**. On irradiation of the mixture by a 150-W Hg lamp the color changes in a few minutes turning brownish-red (**1a** and **2a** cases), and the ^{1}H NMR spectrum shows a reaction. The product is easy to isolate, and in the majority of cases it is only required to add *n*-hexane and to cool the mixture to 5 °C. This induces crystallization of deeply colored complexes which are stable enough as solids and do not show noticeable decomposition if they are kept in a desiccator for 6 months at room temperature.

Only the dimeric platinacycles **1** yield colored products on irradiation. Monomeric Pt(II) species derived from **1** were unreactive under the same conditions. For example, irradiation of $[Pt(C_6H_4CH_2NMe_2)Cl(4\text{-}Mepy)]$ in the presence of azobenzene for 3.5 h in $CHCl_3$ did not induce the reaction. Palladium analogs of **1** also do not undergo photoaddition: no colored products were observed on 5 h of photolysis of a solution of $[Pd(C_6H_4CH_2NMe_2)Cl]_2$ and azobenzene in $CHCl_3$.

The complexes isolated are 1:1 azobenzene to dimer adducts and may be formulated as **3**; see Scheme I. Azobenzene, which is now cis, binds two mononuclear Pt centers and is thus a bridging bidentate ligand. Evidence for such a formulation comes from analytical and various spectral data and an X-ray structural determination for **3a**.

Description of the Crystal Structure of 3a. The structure of dinuclear complex **3a** is presented in Figure 1, while the main bond distances and bond angles are given in Table II. Both Pt atoms have a square planar coordinative polyhedron with a slight tetrahedral distortion. *cis*-azobenzene bridges two metal centers, and its nitrogens are trans to carbons of orthoplatinated *N*,*N*-dimethylbenzylamines. Correspondingly, nitrogens of the latter and chloro ligands are also trans. The Pt–C bond distances in **3a** are typical of related cycloplatinated complexes.[13,14] The Pt–N(sp^3) bond distances are also normal when either Cl[15–17] or

---

(12) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *39A*, 158.

(13) (a) Chassot, L.; Müller, E.; von Zelewsky, A. *Inorg. Chem.* **1984**, *23*, 4249. (b) Deuschel-Cornioley, C.; Stoeckli-Evans, H.; von Zelewsky, A. *J. Chem. Soc., Chem. Commun.* **1990**, 121.

(14) Pregosin, P. S.; Wombacher, F.; Albinati A.; Lianza, F. *J. Organomet. Chem.* **1991**, *418*, 249.

(15) Palenik, G. J.; Giordano, T. J. *J. Chem. Soc., Dalton Trans.* **1987**, 1175.

(16) Tsubomura, T.; Yano, S.; Kobayashi, K.; Sakurai, Y.; Yoshikawa, S. *J. Chem. Soc., Chem. Commun.* **1986**, 459.

(17) Rochon, F. D.; Melanson, R. *Acta Crystallogr.* **1986**, *C42*, 1291.

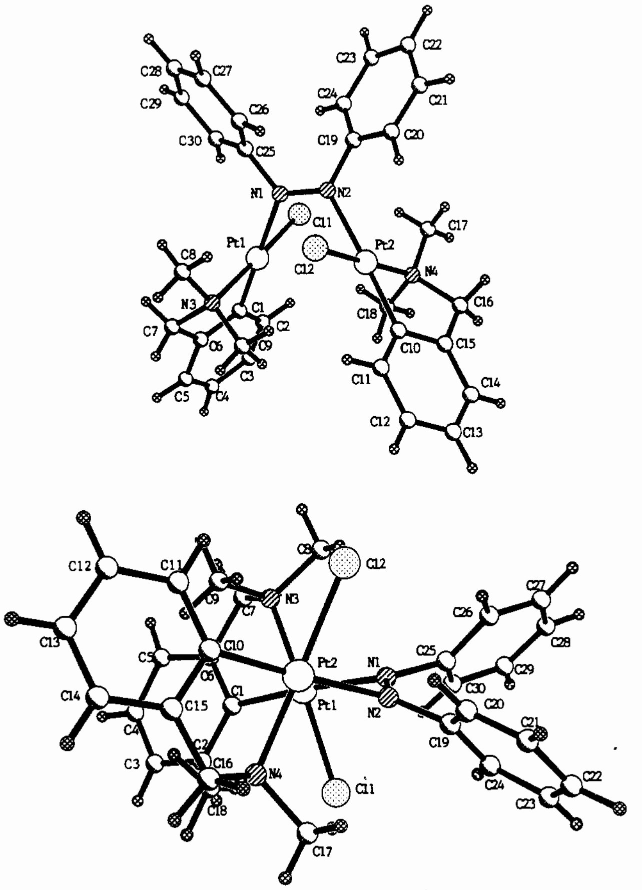


Figure 1. Two perspective views of complex **3a**.

Table II. Selected Bond Lengths (Å) and Bond Angles (deg) in Complex **3a**

	Bond Lengths		
Pt(1)–Cl(1)	2.295(4)	Pt(1)–N(1)	2.14(1)
Pt(1)–N(3)	2.06(1)	Pt(1)–C(1)	1.99(1)
Pt(2)–Cl(2)	2.312(4)	Pt(2)–N(2)	2.14(1)
Pt(2)–N(4)	2.03(1)	Pt(2)–C(10)	1.95(2)
N(1)–N(2)	1.27(2)	N(2)–C(19)	1.44(2)
N(1)–C(25)	1.47(2)		
	Bond Angles		
Cl(1)–Pt(1)–N(1)	82.5(3)	Cl(1)–Pt(1)–N(3)	173.5(4)
Cl(1)–Pt(1)–C(1)	93.2(4)	N(1)–Pt(1)–N(3)	102.9(5)
N(1)–Pt(1)–C(1)	175.6(5)	N(3)–Pt(1)–C(1)	81.3(5)
Cl(2)–Pt(2)–N(2)	82.9(4)	Cl(2)–Pt(2)–N(4)	173.4(4)
Cl(2)–Pt(2)–C(10)	95.2(5)	N(2)–Pt(2)–N(4)	101.6(5)
N(2)–Pt(2)–C(10)	177.7(6)	N(4)–Pt(2)–C(10)	80.5(6)
Pt(1)–N(1)–N(2)	119.8(9)	Pt(2)–N(2)–N(1)	116.7(9)
Pt(1)–N(1)–C(25)	119.3(8)	Pt(2)–N(2)–C(19)	120.1(9)
N(1)–N(2)–C(19)	122(1)	N(2)–N(1)–C(25)	120(1)

N[18,19] is positioned trans to it. The strong σ-donor, phenyl group manifests itself in elongation of the Pt–N(sp^2) bonds between platinacycles and *cis*-**2**, as was observed in the related complexes[13,14] in which carbon atoms were trans to the pyridine nitrogen. The Pt–Cl bond distances seem also to be normal for the cases when Cl and N(sp^3) are mutually trans.[15] The five-membered platinacycles have an envelope conformation, the nitrogens being out of the planes Pt(1)C(1)C(6)C(7) and Pt(2)C(10)C(15)C(16) by 0.66 and –0.63 Å, respectively. To this end, there is nothing unusual in the "platinum" part of the molecule. The geometry of *cis*-azobenzene is moderately affected by the coordination of two Pt(II) centers. The N=N bond length in *trans*- and *cis*-azobenzenes is equal to 1.23 Å.[20] In complex **3a** it is slightly longer, 1.27(2) Å. There is, however, a twist of 32.3° around this bond. The angles between the planes at the nitrogens comprising the double N=N bond and the phenyl rings are 41.0 and 32.3°, and these are between that of *trans*- and *cis*-azobenzenes, viz. 15 and 50°, respectively.[20] Remarkably, the platinum planes are practically perpendicular to the azobenzene nitrogen planes; the corresponding dihedral angles are equal to 98.9 and 101.8°. The Pt–Pt distance is equal to 3.568 Å, but there is practically no interaction between the two metal centers, as it was suggested for other systems,[13a] since, in addition to the large PtNN angles, the torsion angle Pt(1)N(1)N(2)Pt(2) is equal to 42.5°.

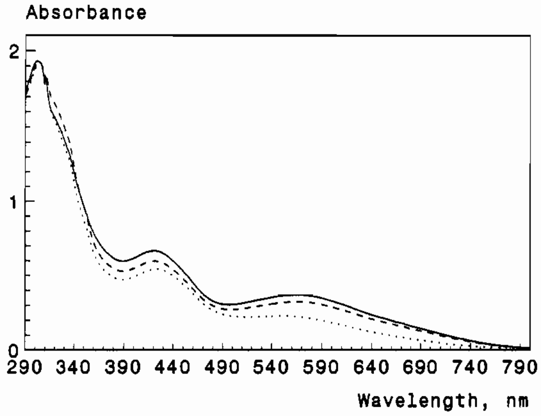


Figure 2. Electronic spectra of **3c** in benzene recorded under different conditions: Solid line, freshly prepared solution; dotted line, after thermostating at 70 °C for 1 min; broken line, after cooling at 5 °C ([**3c**] = 2.06 × 10^{-4} M, temperature of the cell compartment 25 °C, scan rate 300 nm min^{-1}).

Table III. Parameters for the Visible and Near-UV Spectra of Azobenzenes, Benzo[*c*]cinnoline, and Their Complexes with Platinacycles in Benzene at 23 ± 2 °C[a]

compd (R/Z)	color	λ_1, nm (ϵ, M^{-1} cm^{-1})	λ_2, nm (ϵ, M^{-1} cm^{-1})
trans-azobenzene	orange	321 (21 000)	448 (600)
cis-asobenzene	orange	278 (5200)	431 (1470)[b]
trans-p-azotoluene	orange	336 (27 000)	440 (800)
trans-m-azotoluene	orange	326 (23 500)	450 (640)
trans-p,p′-Cl$_2$azobenzene	orange	336 (31 000)	447 (1600)
3a (H/H)	brownish-red	414 (2600)	507[c] (1500)
3b (H/*p*-Me)	gray-purple	403 (4500)	507[c] (2900)
3c (MeO/H)	brownish-red	429 (4900)	563 (3000)
		428 (1300)[d]	*d*
3d (MeO/*p*-Me)	gray-purple	422 (4700)	554 (2600)
3e (MeO/*m*-Me)	black	405[c] (4700)	560 (2230)
3f (MeO/*p*-Cl)	dark-green	432 (4000)	592 (1900)
benzo[*c*]cinnoline	lemon	335 (1220)	399 (460)
		349 (1570)	
		364 (1280)	
4a (H)	yellow	364 (2100)	456 (690)
		391 (1570)	
4b (MeO)	orange-yellow	366 (3000)	469 (800)
		390[c] (2500)	

[a] The solutions of 3 were prepared right before measurements from the weighted amount of complexes. [b] Reference 21. [c] Shoulder. [d] CHCl$_3$ as solvent, additional band at 271 nm (29 700).

UV–Vis and Resonance Raman Spectra. A typical electronic spectrum of complex **3c** in the near-UV and visible regions recorded in benzene as solvent is shown in Figure 2, while the corresponding data for the related complexes **3** are collected in Table III. It should be first pointed out that in all the cases the spectra are time-dependent (see below). Therefore the spectral data were obtained by using freshly prepared solutions of **3** in a corresponding solvent. The spectrum in Figure 2 indicates two important features. There are two new well-defined bands at 429 and 563 nm. Although the position of the former band is

---

(18) Hazell, A.; Simonsen, O.; Wernberg, O. *Acta Crystallogr.* **1986**, *C42*, 1707.

(19) Schollhorn, H.; Thewalt, U.; Raudaschl-Sieber, G.; Lippert, B. *Inorg. Chim. Acta* **1986**, *124*, 207.

(20) Robertson, J. M. *J. Chem. Soc.* **1939**, 232.

(21) Rau, H.; Kortürn, G. *Ber. Bunsen-Ges Phys. Chem.* **1967**, *71*, 664.

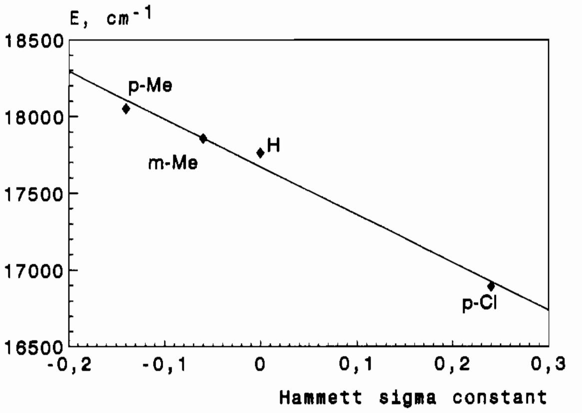


Figure 3. Energy of the low-energy MLCT band for **3c-f** plotted versus the Hammett σ constants of the substituents in the azobenzene part of the complexes.

close to that of the n → π^* transition of free *trans*- and *cis*-azobenzene, its intensity is appreciably higher, suggesting a metal-to-ligand charge-transfer (MLCT) transition. Moreover, the n → π^* is expected to shift to higher energy upon complexation due to stabilization of the nitrogen lone pairs. There is more evidence that the two lowest energy transitions are MLCT in character, since their positions depend on the electronic properties of azobenzenes **2a–d** and shift to lower energies on going to ligands with electron-withdrawing substituents. This red shift is especially clear for the adducts derived from the methoxy-substituted dimer **1b**, since the maximum of the band can easily be localized as opposed to derivatives of **1a** where only a shoulder is observed. The energy of the band is correlated with the Hammett σ constants of the substituents in the phenyl ring of azobenzenes in Figure 3. A straightforward correlation, the analytical form of which is given by

$$E\,(\mathrm{cm}^{-1}) = (1.767 \pm 0.004) \times 10^4 - (3.11 \pm 0.28) \times 10^3\sigma \quad (2)$$

and a strong dependence of the spectra on the nature of solvent (Table III) both provide evidence for a MLCT band.

The fact that the azobenzene ligand has lost its original trans configuration in complexes **3** is in accord with the absence of a strong band arising from a $\pi \rightarrow \pi^*$ transition at $\lambda \geq 320$ nm (λ_1 in Table III; see also Figure 7). Both the conjugated acid of *trans*-**2a**[22] and its complex $SbCl_5(PhNNPh)$[23] show this high-intensity transition ($\epsilon \approx 28\,000$ M^{-1} cm^{-1}) at about 410 nm, while it hardly shifts in energy with respect to the free ligand in the complexes $PtCl_2(PhNNPh)(AsEt_3)$ and $PdX_2(PhNNPh)_2$.[24] The absence of such transitions in **3** is due to the fact that azobenzenes are now cis, and the $\pi \rightarrow \pi^*$ transition of the cis isomer is much weaker and shifted to higher energy with respect to *trans*-azobenzene.[25] An azo group is still present in complexes **3**, and this was confirmed by the resonance Raman (rR) spectroscopy.

These rR spectra, obtained by excitation into both MLCT bands with laser wavelengths varying from 458 to 620 nm, showed a rather strong rR effect for a band at about 1400 cm^{-1} (Figure 4). The assignment of this band to ν(N=N) of a coordinated azobenzene ligand was confirmed by labeling both nitrogen atoms of the starting *trans*-**2a** with ^{15}N. The 1399-cm^{-1} Raman band of complex **3a** then shifted to 1356 cm^{-1} very close in frequency to the calculated value of an isolated $\nu(^{15}\mathrm{N}{=}^{15}\mathrm{N})$ vibration. The frequencies of ν(N=N) (1399 cm^{-1} for **3a** , 1416 cm^{-1} for **3c**) are much lower than for free *trans*- (1442 cm^{-1}) and *cis*- (1511 cm^{-1}) azobenzene and also for the complexes $PtCl_2(PhNNPh)L$ ($L = PEt_3, AsEt_3$) (1450, 1448 cm^{-1}) and *trans*-$PdX_2(PhNNPh)_2$ (X = Cl, Br) (1446 cm^{-1})[24] in which *trans*-**2a** coordinates to the metal as a monodentate ligand. The rR effect for azobenzene coordinated in a bidentate fashion is known for the complex $IrHCl(C_6H_4NNPh)(PPh_3)_2$.[26] However, *trans*-**2a** is orthometalated and the resulting ν(N=N) frequency is 1348 cm^{-1}. Although there is a close similarity between ν(N=N) frequencies of **3** and those of the conjugated acid of *trans*-**2a** (1407 cm^{-1}) in $(PhNNPhH^+)ClO_4^-$[27] and the *trans*-azobenzene ligand in $SbCl_5(PhNNPh)$ (1390 cm^{-1}),[23] the latter two compounds both possess an intense low-energy $\pi \rightarrow \pi^*$ transition at about 410 nm, which is not present in the spectra of complexes **3**.

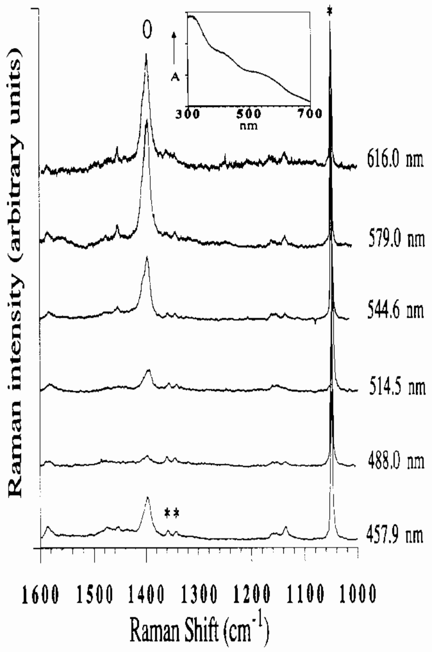


Figure 4. Resonance Raman spectrum of **3a** in a KNO_3 pellet (* = NO_3^-; 0 = ν(N=N)). Insert: absorption spectrum of **3a** in a KBr disk.

The Raman spectrum of **3** obtained by excitation with λ = 616.0 nm into the lowest energy absorption band only shows the resonance enhancement of intensity for ν(N=N) (Figure 4). This means that the first MLCT transition is directed to a π^* orbital of the bridging ligand localized at the azo group. Excitation with λ = 457.9 nm gives rise to a much weaker rR effect for ν(N=N). At the same time new ligand vibrations show up as weak bands in the wavenumber region 1100–1600 cm^{-1}. This indicates that the second absorption band belongs to one or more MLCT transitions to a more delocalized π^* orbital of the ligand.

Visualization of Trans to Cis Isomerization of Azobenzenes during Complexation. As mentioned above, no complex formation occurs without irradiation. Both reagents, platinacycles **1** and *trans*-**2**, could, in principle, be activated photochemically. Photochemical trans ⇄ cis interconversions of **2** is a subject of common knowledge.[9,28] The spectral properties of both the forms are known (Table III), and the quantum yields for the forward and reverse processes have been reported.[29] Some platinacycles are also involved in photochemical oxidative additions with alkyl halides.[30] The following experiment has demonstrated that the photo-

---

[22] Jaffe, H. H.; Si-Jung Yeh; Gardner, R. W. *J. Mol. Spectrosc.* **1958**, *2*, 120.

[23] Gutmann, V.; Steiniger, A. *Monatsh. Chem.* **1965**, *96*, 1173.

[24] Van Baar, J. F.; Vrieze, K.; Stufkens, D. J. *J. Organomet. Chem.* **1974**, *81*, 247.

[25] Beveridge, D. L.; Jaffe, H. H. *J. Am. Chem. Soc.* **1966**, *88*, 1948.

[26] Van Baar, J. F.; Vrieze, K.; Stufkens, D. J. *J. Organomet. Chem.* **1975**, *85*, 249.

[27] Denning, R. G.; Thatcher, J. *J. Am. Chem. Soc.* **1968**, *90*, 5917.

[28] Atkinson, R. S. In *Comprehensive Organic Chemistry. The Synthesis and Reactions of Organic Compounds*; Barton, D., Ollis, W. D., Eds.; Pergamon Press: Oxford, New York, Toronto, Sydney, Paris, Frankfurt, 1979; Vol. 2, p 237.

[29] Gegiou, A.; Muszkat, K. A.; Fischer, E. *J. Am. Chem. Soc.* **1968**, *90*, 3907.

[30] Maestri, M.; Balzani, V.; Deuschel-Cornioley, C.; von Zelewsky, A. *Adv. Photochem.* **1992**, *17*, 1.

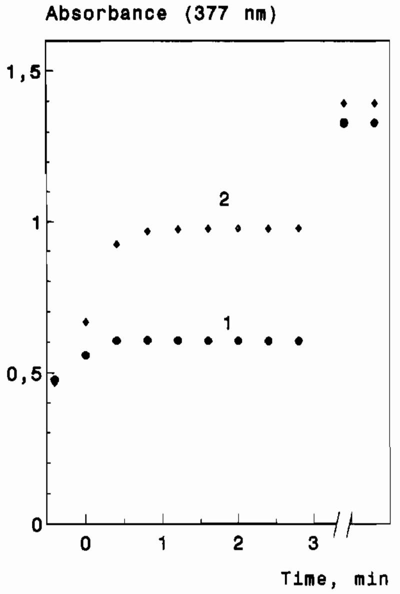
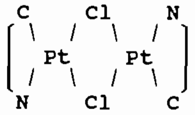


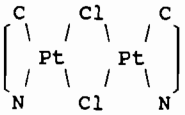
Figure 5. Progress in the formation of **3a** from **1a** and *trans*-**2a** in $CHCl_3$ at room temperature when (1) only **1a** was initially irradiated (10 min) and (2) only *trans*-**2a** was irradiated ([**1a**] = [**2a**] = 2.06 × 10^{-3} M). The level of absorbance in the upper right corner was achieved after irradiation of both solutions for 10 min after leveling off; for explanations, see text.

chemical trans to cis isomerization of **2** plays a key role. A solution of **1a** in $CHCl_3$ (2.06 × 10^{-3} M) was placed into one compartment of a tandem quartz cell and irradiated for 10 min. The solution of **2a** (2.06 × 10^{-3} M), which was not pre-irradiated, was then added into the other compartment of the cell, and the absorbance was measured at 377 nm (valley of *trans*-**2a**). Both the solutions were then rapidly mixed, and the formation of **3a** was monitored. The sequence was then changed, and only solution **2a** was irradiated. The increase in absorbance is significantly stronger when the ligand was irradiated (Figure 5) or, in other words, when more *cis*-**2a** is present. When both the solutions are irradiated for an additional 10 min, the absorbance increases further and reaches practically identical values. This data suggests that it is *cis*-**2** that is actually involved; its reaction with the dimer **1** is rather fast, and the platinum moiety is a trap for *cis*-**2**. A comparison of the quantum yields of the forward and reverse isomerizations[29] suggests that the equilibrium mixture will contain between 22 and 62% *cis*-**2** (depending on the wavelength). Trace 2 in Figure 5 corresponds to the binding of the photochemically generated "equilibrium" *cis*-**2**. When azobenzene is irradiated in the presence of **1**, the latter converts *cis*-**2** into **3** and shifts the equilibrium *trans*-**2** ⇌ *cis*-**2** far to the right, thus providing high yields of complexes **3** (79% in the case of **3a**).

Vibrational Spectra. Free *N*,*N*-dimethylbenzylamine has two bands at 698 and 737 cm^{-1} due to a monosubstituted phenyl ring.[31] In **1a** there are bands at 738 and 746 cm^{-1}. Since only one frequency is typical of 1,2-disubstitution, the two arise from *ab-hg* and *ab-gh* isomers comprising dimer **1a** (in accord with ^1H NMR data; see below). On examination of monomeric complexes of the type $[Pt(C_6H_4CH_2NMe_2)Cl(L)]$, the two bands collapse into one sharp peak at 745.5 and 747 cm^{-1} for L = 2-Phpy and 4-Mepy, respectively. The IR spectrum of *trans*-**2** has two bands at 689 and 776 cm^{-1}. In the case of **3a** three bands of approximately equal intensity at 689, 717, and 769 cm^{-1} are observed together with a stronger peak at 743 cm^{-1}. The spectrum of *d*-**3a** prepared from d_{10}-azobenzene and **1a** does not have the former triad, but the sharp band at 743 is present and, thus, should be ascribed to the orthoplatinated fragment. The triad in *d*-**3a** is seen at 530, 548, and 677 cm^{-1}. In the case of **3c** it is at 686, 719, and 760 cm^{-1}, reflecting the influence of the platinacycle with the electron-donating group.



ab-hg



ab-gh

^1H and ^2H NMR Data. It has already been demonstrated[32] that orthoplatinated *N*,*N*-dimethylbenzylamine derivatives **1** exist in solution as a mixture of approximately equal amounts of *ab-hg* and *ab-gh* isomers accounting for two sets of signals in the ^1H NMR spectra at 400 MHz; see Experimental Section. On complexation with azobenzenes, the positions of resonances of aliphatic and aromatic protons change significantly. The assignment of the latter was made on the basis of comparison of the ^1H NMR spectra of all complexes **3** and ^1H NMR and ^2H NMR spectra of the deuterated compound *d*-**3a**. It should again be pointed out that compounds **3** are unstable in solution and, hence, we never observed a clean spectral pattern exclusively from **3**. Signals from dissociation products were always present. In C_6D_6 in particular, these were the starting dimer **1** and free azobenzene, the amount of which did not exceed 15–20% as compared to **3**. In $CDCl_3$ as a solvent, an additional set, resembling typical features of monomeric compounds of the type $[Pt(C_6H_4CH_2NMe_2)Cl(L)]$, was also observed, but the concentration of these species was even lower than above.

The resonances from *N*-methyl and *N*-methylene C–H protons are affected most on binding of **1** to *cis*-**2**. In complexes **3**, the *N*-methyl groups become diastereotopic and the signals are shifted upfield. The N–CH_3 resonances have broad shoulders because of the ^3J(Pt–H) coupling (it is not always possible to determine the exact position of ^{195}Pt satellites operating at 400 MHz[33]). Nonequivalence of the N–CH_2 protons is even more pronounced, and they are observed as an AX quartet. The N–CH_3 and N–CH_2 resonances are remarkably sharp at ambient temperature pointing to the absence of a dynamic process involving the cycloplatinated rings. The possible reason is that, if coordinated to two adjacent nitrogens of *cis*-**2**, the platinacycles loose the ability to rotate freely around the azobenzene N–Pt bonds because of steric limitations. There might be an electronic stabilization, since the most efficient MLCT of the type $d_{xy} \rightarrow \pi^*(N{=}N)$ will occur when the platinum plane is perpendicular to the plane of the N=N double bond.

Other features worth mentioning are strong broadening of the azobenzene H2′ and H6′ protons (ortho to the N=N bond) observed in both the ^1H NMR and ^2H NMR spectra and a downfield drift of the proton H6 of the orthoplatinated ring (ortho to the Pt–C bond). The latter reaches, in particular, 0.56 ppm for **3a** and **3d** and reflects the approach of the chloro ligand to H6 in **3**. The broadening of H2′ and H6′, accompanied by a downfield shift, also fits the structural model **3**. The phenyl rings of azobenzene may have more freedom to rotate around the C–N bonds in complexes **3**. The N–C(phenyl) bonds are in fact longer in both *cis*-**2a**[20] and **3a** as compared to *trans*-**2a**.[20] The rotation would explain both the broadening and the downfield shift, since the H2′ and H6′ protons will thus approach the axial sites of Pt(II), but such interactions cause both effects in Pt(II)[33] and Pd(II)[34–36] complexes.

---

(31) Bellami, L. J. *The Infra-Red Spectra of Complex Molecules*; Wiley: New York, 1954.

(32) Affolter, S. A Comparison of Cyclopalladated Compounds with Respect to Their Reactivity toward Selected Reagents. Dissertation ETH No. 9134, Zürich, 1990.

(33) Anklin, C. G.; Pregosin, P. S. *Magn. Reson. Chem.* **1985**, *23*, 671.

(34) Deeming, A. J.; Rothwell, I. P.; Hursthouse, M. B.; New, L. *J. Chem. Soc., Dalton Trans.* **1978**, 1490.

(35) Jones, T. C.; Nielson, A. J.; Rickard, C. E. *Aust. J. Chem.* **1984**, *37*, 2179.

(36) Ryabov, A. D. *Inorg. Chem.* **1987**, *26*, 1252.

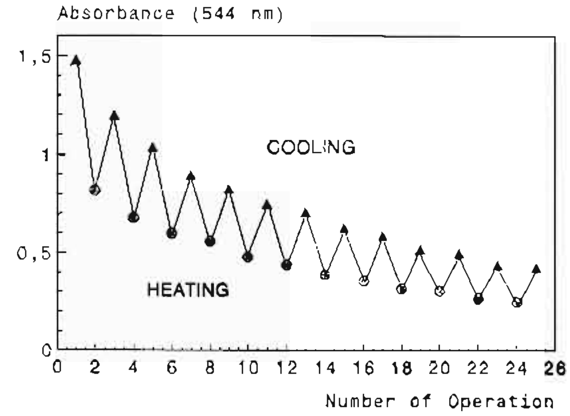


Figure 6. Visualization of the thermochroic behavior of complexes **3** by the example of **3d** (5.6×10^{-4} M) in C_6H_6–$CHCl_3$ (2:1). Absorbance was measured after keeping the solution at −7 °C (●) and +60 °C (▲) for 1 min. The temperature of the cell compartment was 17.7 °C. For additional explanations, see text.

General Properties of Complexes 3. The complexes are nonelectrolytes in chloroform. Even in C_6H_6 or $CHCl_3$ at room temperature they slowly decompose to yield the starting dimers **1** and *trans*-**2**, as was confirmed by the IR and ^1H NMR data for the former and by the UV–vis spectra for the latter. The decay occurs much faster even in weakly nucleophilic solvents, such as acetone and ethanol. Pyridines induce rapid fading of the solutions due to reactions shown in eq 3.

$$\mathbf{3a} + 2\ \text{4-Mepy} \longrightarrow 2[Pt(C_6H_4CH_2NMe_2)Cl(\text{4-Mepy})] + cis\text{-}PhN{=}NPh \quad (3)$$
$$\downarrow$$
$$trans\text{-}PhN{=}NPh$$

Perhaps the most remarkable feature of complexes **3** is their thermochroic behavior. Heating of brownish-red solutions of **3a** or **3c** in $CHCl_3$ or C_6H_6 causes fading, and these became yellow. Rapid cooling of the faded solutions brings the brownish-red color back although its intensity is somewhat lower as compared to the starting solutions. The changes can be followed spectrophotometrically, and the representative spectra are shown in Figure 2 by the example of **3c**. As seen, the intensity of the MLCT band decreases significantly on heating (dotted line), while cooling restores the band but not to the initial level (broken line). For complexes **3**, the absorbance is always lower after cooling. This is actually understandable, since on increasing the temperature the binding between Pt(II) and *cis*-**2** decreases[36] causing dissociation and, hence, elimination of the MLCT bands. There is evidence (see below) that dissociation of even one platinacycle is sufficient for fading, but if one platinum moiety is bound to *cis*-**2**, the latter is not protected from isomerization anymore. Consequently, a fraction of *cis*-**2** will rearrange into *trans*-**2** at higher temperatures when at least one (or both) platinacycles dissociate. Therefore, the broken line in Figure 2 has no chance to converge with the solid one. Absorbance measurements at a fixed wavelength following many consecutive "cooling" and "heating" cycles result in a plot as in Figure 6. After every cycle, a fraction of *cis*-**2** rearranges into the trans form and the intensity of the MLCT band progressively decreases. If one considers the plot to be a single thick line, it reminds one of a kinetic curve attributed to the thermal cis → trans isomerization of azobenzene.

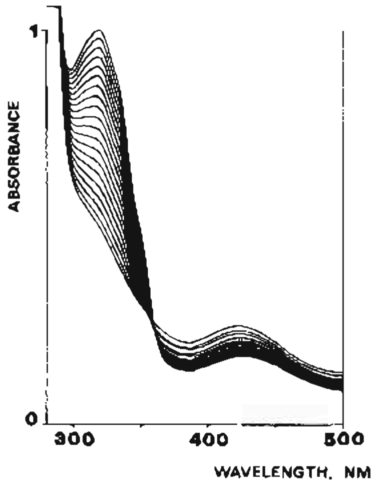


Figure 7. Spectral changes observed during the spontaneous decomposition of **3a** in benzene at 22 ± 2 °C. [**3a**] = 0.95×10^{-4} M; the interval between spectra is 60 min.

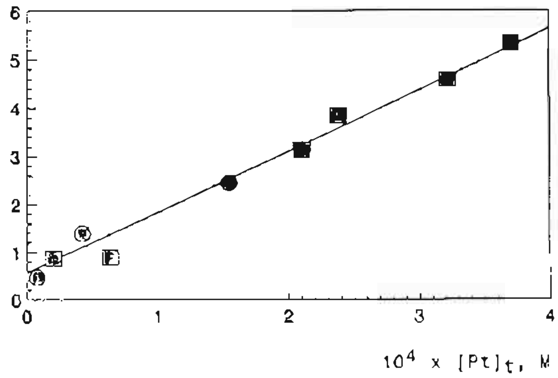


Figure 8. Pseudo-first-order rate constants for the thermal decomposition of **3a** (■) and **3c** (●) as a function of the total concentration of the complexes in benzene as solvent at 48.8 °C.

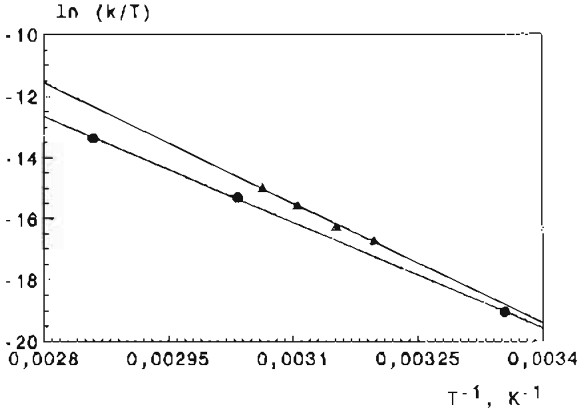


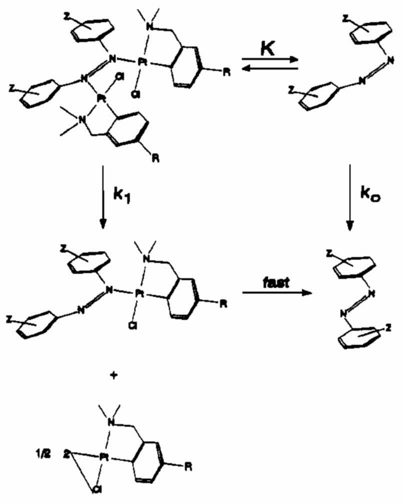
Figure 9. Temperature dependence of the thermal trans to cis isomerization of azobenzene in benzene: (●) Spontaneous isomerization (data from ref 37); (▲) values of k_0 (this work). For explanations, see text.

Kinetics of Decomposition of 3 in Benzene Solution. The spontaneous decomposition of **3** in solution was followed spectrophotometrically, and the typical spectra for **3a** are shown in Figure 7. The strong increase in absorbance at 320 nm is due to the formation of *trans*-**2**, and the decrease at 415 nm is due to the fading of the higher energy MLCT band. The reaction progress was monitored at 320 nm, and the results obtained are summarized in Figures 8 and 9. The former gives the values of k(obsd), calculated from the absorbance–time plots, against the total concentration of **3a** and **3c**. Interestingly, although the absorbance–time plots display a good first-order behavior for more than 3 half-lives, the values of k(obsd) do depend on concentration as in eq 6,

$$k(\text{obsd}) = k_0 + k[\text{Pt}]_t \quad (4)$$

where $[\text{Pt}]_t$ is the total concentration of **3**, $k_0 = (5.7 \pm 1.2) \times 10^{-5}\ s^{-1}$, and $k = 1.27 \pm 0.06\ M^{-1}\ s^{-1}$ at 48.8 °C. It is also seen from Figure 8 that the values of k(obsd) are insensitive to the

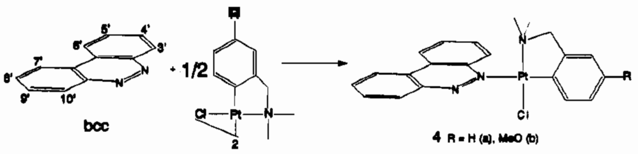
Scheme II



nature of the Pt moiety attached to *cis*-**2a**. The two-term rate law (4) suggests uncatalyzed (k_0) and Pt(II)-catalyzed (k) pathways for cis to trans isomerization of azobenzene. The kinetic data for the uncatalyzed isomerization obtained by Hartley[37] are compared to the rate constants k_0 in Figure 9. The two lines are rather close to each other, and the same is true for the corresponding activation parameters: $\Delta H^{*} = 100.5 \pm 8.7$ and 95.7 ± 2.0 kJ mol^{-1} and $\Delta S^{*} = -14 \pm 27$ and -34.7 ± 6.0 J K^{-1} mol^{-1} for k_0 and free *cis*-**2a**, respectively. The agreement is reasonably good, if one takes into account that the value of k_0 was calculated as shown in Figure 8 only at 48.8 °C; in other cases, the values of k(obsd) are plotted in Figure 9, which were obtained at low concentrations of **3**, ca. 0.1×10^{-4} M, where the k_0 pathway represents ca. 80% of the isomerization reaction. The decomposition of **3b** derived from *p*-azotoluene occurs 2–3 times faster as compared to **3a** and **3c**, reflecting the general tendency of substituted azobenzenes to isomerize faster.[37-39] The effective activation parameters, ΔH^{*} and ΔS^{*}, of 81 ± 8 kJ mol^{-1} and -64 ± 17 J K^{-1} mol^{-1}, respectively, are very close to those reported for free *cis*-**2b** in the enantiotropic, cholesteric phase (85 kJ mol^{-1} and -54 J K^{-1} mol^{-1}, respectively).[39] In this solvent, ΔH^{*} is lower and ΔS^{*} is significantly more negative compared to benzene or *n*-butyl stearate. It seems likely that the effectors capable of increasing the rate of cis to trans isomerization of azobenzenes will do it by reducing ΔH^{*}, and this reduction may partly be compensated by a decrease in ΔS^{*}.

The simplest mechanism to account for the dependence of k(obsd) on $[\mathrm{Pt}]_t$ or, in other words, the presence of the k pathway is shown in Scheme II, the crucial point of which is the step driven by k_1. Data in Figure 5 reveal evidence that the equilibration driven by K occurs much faster as compared to the rates of isomerization, implying that k_1 may be the rate-limiting step. The subsequent isomerization seems to be fast, since it is known that the Brönsted acids catalyze the cis → trans isomerization.[37] It is very likely that the same is true for Lewis acids, the Pt(II) complexes in particular, as is true for Lewis bases.[40] The isomerization is prohibited when two Pt centers are coordinated to both azobenzene nitrogens. When only one is coordinated, there are no steric restrictions imposed by the second platinacycle; hence, the isomerization can occur rather easily. Such an interpretation is in line with the general views on the mechanism of the thermal cis → trans isomerization of azobenzenes, which favor inversion rather than twisting of the central double bond.[29,38,39] Actually, two metal centers attached to *both* nitrogens of *cis*-**2** make the inversion principally impossible. Alternatively, the two metal centers "freeze" the thermodynamically less stable cis configuration. If only one metal center is bonded, it, in contrast, will favor the isomerization via the inversion at the adjacent N center.

Scheme III



The mechanism shown in Scheme II leads to the following expression for the reaction rate:

$$\text{rate} = \frac{\mathrm{d}[\mathit{trans}\text{-}\mathbf{2}]}{\mathrm{d}t} = -\frac{\mathrm{d}[\mathit{cis}\text{-}\mathbf{2}]}{\mathrm{d}t} = \left\{\frac{k_0K + k_1[\mathrm{Pt}]_t}{K + [\mathrm{Pt}]_t}\right\}[\mathit{cis}\text{-}\mathbf{2}] \tag{5}$$

If $K >> [\mathrm{Pt}]_t$, eq 5 transforms into

$$-\frac{\mathrm{d}[\mathit{cis}\text{-}\mathbf{2}]}{\mathrm{d}t} \approx (k_0 + k_1K^{-1}[\mathrm{Pt}]_t)[\mathit{cis}\text{-}\mathbf{2}] \tag{6}$$

or

$$k(\mathrm{obsd}) = k_0 + k_1K^{-1}[\mathrm{Pt}]_t \tag{7}$$

Equations 4 and 7 appear to be similar on the condition that $k = k_1K^{-1}$.

Binding of Platinacycles 1 to Benzo[*c*]cinnoline, a Mimetic of *cis*-azobenzene. The instability of **3** arises from the tendency of *cis*-**2** to rearrange into the thermodynamically preferred trans form. It was tempting to test a stable mimetic of *cis*-**2** in the hope that the complexation will not be affected by ligand isomerization. Commercially available benzo[*c*]cinnoline (bcc, Scheme III) was used in which the "*cis*-azobenzene" N=N fragment already exists. Only a thermal interaction between **1** and bcc is, thus, to be expected. The reaction between bcc and **1a,b** is fast in $\mathrm{CHCl_3}$. The solutions turn yellow-orange from pale yellow, but the color is much weaker than that of the photochemical products **3**. Irradiation does also not increase the intensity of color. The thermal products, according to analytical data, are 1 to $^1/_2$ ligand to dimer adducts **4**; see Scheme III. Their UV–vis spectra have only the higher energy MLCT bands observed at 456 and 469 nm for **4a,b**, respectively (Table III). As in the case of **3**, the spectra are temperature dependent, and after a solution of **4a** is kept in benzene at 70 °C for 1 min, the absorbance at 456 nm is ca. 40% lower. Keeping the solution at 0 °C increases the optical density by ca. 25% compared to the initial value at 25 °C. Thermostating the solution at 25 °C in the cell compartment provides the initial spectrum, thus demonstrating complete reversibility, which is, of course, not surprising, since bcc is stable. Complex **4b** shows similar spectral changes.

The IR spectrum of bcc has a strong band at 760 cm^{-1} and a group of weaker ones at 734, 719, and 712 cm^{-1}. In complex **4a**, the three bands are at 758, 743, and 717 cm^{-1}, the relative intensity being approximately 3:2:1. The stretch at 743 cm^{-1}, as in the case of **3a**, refers to the cycloplatinated phenyl ring. It is absent in the spectrum of **4b**, while the remaining two are seen at 761 and 717 cm^{-1}. These data give evidence that the reaction shown in Scheme III is only an adduct formation.

The same conclusions came from the ^{1}H NMR data of **4**. The spectrum of bcc in $\mathrm{CDCl_3}$ is a set of three multiplets at δ 8.75 (H3′,10′), 8.56 (H6′,7′), and 7.90 (H4′,5′,8′,9′) with relative intensities 2:2:4. In complexes **4**, protons from bcc comprise a new 1:1:2:4 set, one proton (the most downfield in free bcc) being broad and shifted downfield by 1.6 ppm. One can also notice a broadening of two protons comprising the "4" signal of free bcc. The changes observed can be understood in terms of the structural model in Scheme III. Attachment of one platinacycle to bcc will

---

(37) Hartley, G. S. *J. Chem. Soc.* **1938**, 633.
(38) Talaty, E. R.; Fargo, J. C. *J. Chem. Soc., Chem. Commun.* **1967**, 65.
(39) Otruba, J. P., III; Weiss, R. G. *J. Org. Chem.* **1983**, *48*, 3448.
(40) Hall, C. D.; Beer, P. D. *J. Chem. Soc., Perkin Trans. 2* **1991**, 1947.

affect the resonances of protons from the "binding" site of bcc, i.e. H3′ and H4′, if Pt is bound to N2. The proton H3′ will be the most strongly affected, and it is the broad downfield resonance. The proton H4′ may also feel the Pt neighborhood, and this is a part of the multiplet at δ ca. 8.0. The protons from the orthoplatinated ring also feel the binding, especially H6, which as in the azobenzene case moves downfield and is well resolved both in **4a** and **4b**.

The aliphatic region of the spectra of **4** contrasts to that of complexes **3**. The signals from the $N-CH_3$ and $N-CH_2$ groups are very broad at ambient temperatures. At lower temperatures these comprise two singlets and an AB quartet, respectively, suggesting a dynamic process.[41,42] This may be a reversible dissociation, rotation around the Pt–N(bcc) bond, or "jumping" of the Pt center from one bcc nitrogen to another. The discrimination between these possibilities may constitute an elegant mechanistic NMR study. The tendency of complexes **4** to dissociate in solution is also seen from the ^1H NMR spectra. The typical signals from the dimers **1**, although weak ones, were observed together with the resonances from adducts **4** at ambient temperature.

Discussion

Complexes **3** are unique, since they contain coordinated *cis*-azobenzene as a bridging ligand that binds two orthoplatinated *N,N*-dimethylbenzylamine moieties. Such a binding mode provides low-energy MLCT transitions, and the energy of the latter depends on electronic capacities of both the azobenzene and platinacycle. The formation of **3** occurs photochemically due to initial light-induced trans to cis isomerization of azobenzene and can be completely reversed thermally. Intriguing questions are why only *cis*-**2** and not the trans form binds Pt(II) fragments and why the 1:1 (ligand to dimer) complexes **3** are formed in good yields even in a large excess of **2**. It should also be taken into account that Pd(II) analogs do not form the MLCT complexes although the thermal equilibrium (8) involving *trans*-**2** was reported and thermodynamically characterized in D_3CCOOD.[31] At the same time orthometalation of azobenzene by MCl_4^{2-} (M = Pd and Pt) leads to the products with MLCT bands at ca. 535 nm in both cases.[3,36]

$$[\mathrm{Pd(C_6H_4CH_2NMe_2)(OAc)}]_2 + 2\textit{trans}\text{-PhN=NPh} \rightleftharpoons 2[\mathrm{Pd(C_6H_4CH_2NMe_2)(OAc)}(\textit{trans}\text{-PhN=NPh})] \quad (8)$$

Comparison of the corresponding Pt(II) and Pd(II) cases suggests that electronic factors must play a decisive role. The bridging behavior of *cis*-**2** may be rationalized as follows. After irradiation, Pt dimer **1** reacts with *cis*-**2** to form a short-lived mononuclear complex (shown in Scheme II). A lone pair of electrons at nitrogen is likely the driving force for the bridge-splitting. The intermediate can either undergo a fast reverse cis → trans isomerization or be stabilized by coordinating the second platinacycle at the adjacent nitrogen. The coordination of the first metal center may induce some "flow-off" of the electron density localized on the orbitals of the N=N bond, thus favoring the back-bonding on coordination of the second platinacycle. There is most likely a delicate balance between the σ N → Pt bonding and π N ← Pt back-bonding provided by the strict correspondence between the *cis*-**2** and platinacycle orbitals. The back-bonding ability of Pt(II) complexes is generally higher as compared to related Pd(II) species. Therefore, inability of palladacycles to bind *cis*-**2** and thus to stabilize this form may be related to their lowered tendency to donate electrons for back-bonding. In this context, palladacycles are likely insufficiently "soft" to be involved in the complex formation shown in Scheme I.

Different binding of bcc may also be a consequence of the electronic factors. Strictly speaking, bcc is not a perfect model for *cis*-**2** since an additional C–C bond totally changes the electronic properties of the ligand and the orbitals of the nitrogen atoms are a part of a whole aromatic system. It may occur that the energy of the vacant π^* orbital localized in the vicinity of the N atoms is different (higher) as compared to the energy of the π^* orbital of *cis*-**2**, thus ruling out efficient interaction. As a result, only the σ N → Pt bonding plays a significant role in the case of bcc and this is insufficient for binding two platinum centers to both nitrogens of the ligand.

Conclusions. The photochemical reaction reported is an example of a process where a metal center traps and thus stabilizes a thermodynamically unstable ligand, *cis*-azobenzene in particular. *cis*-Azobenzene shows here a unique behavior by being a bridging, bidentate ligand. As a result, two platinum centers are located in a close proximity and the platinum planes are practically perpendicular to the plane of the N=N double bond. Despite the fact that the azobenzene nitrogens are trans to the Pt–C bonds and, hence, the corresponding Pt–N bonds are significantly elongated, the geometry of the complex is very favorable for the MLCT transitions, which are responsible for remarkable spectral and thermochroic properties of the compounds. Since the reaction occurs on irradiation by either sunlight or normal W-lamps and can be reversed thermally, it seems to be a remarkable demonstration experiment. It helps to visualize a photochemical trans to cis isomerization of azobenzene (organic photochemistry) and provides evidence for how the configuration of a ligand may affect its ability to bind metal centers (coordination chemistry).

Acknowledgments. A stipend from the Alexander von Humboldt Foundation to A.D.R. is gratefully acknowledged. R.v.E. acknowledges financial support from the Deutsche Forshungsgemeinschaft, the Fonds der Chemischen Industrie, and the Volkswagen-Stiftung. We thank Mr. Th. L. Snoeak for recording the Raman spectra.

Supplementary Material Available: Listings of positional and thermal parameters, complete bond lengths and angles, and crystallographic data (7 pages). Ordering information is given on any current masthead page.

---

(41) Deeming, A. J.; Rothwell, I. P. *J. Chem. Soc., Dalton Trans.* **1978**, 1490.

(42) Polyakov, V. A.; Ryabov, A. D. *Zh. Obsch. Khim.* **1989**, *58*, 1248.