44 *Inorg. Chem.* **1998,** *37,* 44−49

Role of *o*-Methylene-Bridged Bis(aniline) as a Spectroscopic Probe for the Metal Coordination Environment

William Lesueur, Andrew J. Rogers, and Carlo Floriani*

Institut de Chimie Minérale et Analytique, BCH, Université de Lausanne,
CH-1015 Lausanne, Switzerland

Angiola Chiesi-Villa and Corrado Rizzoli

Dipartimento di Chimica, Università di Parma, I-43100 Parma, Italy

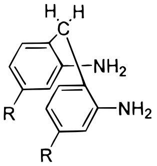
Received May 19, 1997

Reaction of the bidentate ligand 2,2′-methylenebis(5-(dimethylamino)aniline) (**2**, L) with $PdCl_2$ and K_2PtCl_4 and the bidentate ligand 2,2′-methylenebis(5-(acetylamino)aniline (**5**, L′) with K_2PtCl_4 in polar solvents gave the complexes $[PdCl_2(L)]$ (**6**), $[PtCl_2(L)]$ (**8**), and $[(L')PtCl_2]$ (**7**), respectively. Treatment of **2** with K_2PtCl_4 in the presence of DMSO resulted in the solvolysis of a chloride ion to give [(L)Pt(Cl)(DMSO)]Cl (**9**). The resulting eight-membered metallocyclic rings have rigid elongated chair conformations forcing one of the two bridging methylene hydrogens (H_{endo}) in close proximity to the metal centre. An ^{1}H NMR study revealed that they are now diastereomeric (H_{endo}, H_{exo}); the higher field signal position does not vary irrespective of the ligand or metal, whereas the proton corresponding to the lower field signal is apparently more sensitive to the metal coordination environment. The ability of this spectroscopic probe to predict the bonding mode of the metal was also studied by reacting **2** with $K[PtCl_3(C_2H_4)]\cdot H_2O$ to give $[Pt_2(\mu\text{-}L)Cl_4(C_2H_4)_2]$ (**10**), which occurred irrespective of the L/Pt ratio. The corresponding methylene hydrogens were not diastereomeric, showing only one singlet in the ^{1}H NMR spectrum. Crystal structures of **6** and **9** have been determined: **6** is triclinic, space group $P\bar{1}$, $a = 10.179(2)$ Å, $b = 12.136(2)$ Å, $c = 9.686(2)$ Å, $\alpha = 97.79(1)°$, $\beta = 95.98(2)°$, $\gamma = 78.02(1)°$, $V = 1156.1(4)$, $Z = 2$, and $R = 0.034$; **9** is triclinic, space group $P\bar{1}$, $a = 12.348(1)$ Å, $b = 12.407(1)$ Å, $c = 10.159(1)$ Å, $\alpha = 103.02(1)°$, $\beta = 104.87(2)°$, $\gamma = 117.09(1)°$, $V = 1313.0(3)$, $Z = 2$, and $R = 0.035$.

Introduction

The focus of this paper is on the design and use of bidentate amine ligands capable of acting as spectroscopic probes when coordinated to a metal centre, the long-term goal being to predict spectroscopically the coordination environment, or subtle changes thereof, of a metal ion.

Chelating bidentate amines are among the classical ligands in coordination chemistry[1] and have found renewed favor with the discovery that the cytostatic properties of some *cis*-diaminoplatinum(II)−X_2 and more recently *cis*-diaminopalladium(II)−X_2 complexes are, to some extent, dependent on the nature of the chelating diamino ligand.[2,3] Considerable effort has focused on determining the structure−activity relationship and the thermodynamic and kinetic stability of potentially reactive species.[2,4,5] Aspects such as the coordination environment about the platinum ion are not always so clear with other coordination geometries now thought to result in active compounds.[6] An interesting perspective in this area centres on using ligands capable of engendering more chemical and spectroscopic information than earlier ligand systems. Work in our laboratories has shown that ligands of the type shown in Figure 1, when coordinated to a metal, can show changes to the methylene resonance(s) and its position(s) and that these changes are diagnostic of the coordination environment of the metal.[7] With this perspective in mind we wish to extend this series of compounds to include amino derivatives with the following skeleton:



This ligand skeleton is appealing for a number of reasons. First, complexation to a metal fragment results in an eight-membered ring with some conformational rigidity. This can result in the methylene hydrogens becoming diastereotopic with

---

* To whom correspondence should be addressed.

(1) House, D. A. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Gillard, R. D., McCleverty, J. A. Eds.; Pergamon: Oxford, U.K., 1986; Vol. 2, Chapter 13.1, p 23 and references therein.

(2) Bloemink, M. J.; Reedijk, J. In *Metal Ions in Biological Systems*; Sigel, H., Sigel, A., Eds.; M. Dekker: New York, 1996; Vol 32, pp 641−685. Reedijk, J. *Chem. Commun.* **1996**, 801. Reedijk, J. *Inorg. Chim. Acta* **1992**, *198−200*, 873. Sundquist, W. I.; Lippard, S. J. *Coord. Chem. Rev.* **1990**, *100*, 293; **1989**, *95*, 129. Sherman, S. E.; Lippard, S. J. *Chem. Rev.* **1987**, *87*, 1153.

(3) Barnham, K. J.; Bauer, C. J.; Djuran, M. I.; Mazid, M. A.; Rau, T.; Sadler, P. J. *Inorg. Chem.* **1995**, *34*, 2826. Barnham, K. J.; Djuran, M. I.; Frey, U.; Mazid, M. A.; Sadler, P. J. *J. Chem. Soc., Chem. Commun.* **1994**, 65.

(4) Miller, S. E.; House, D. A. *Inorg. Chim. Acta* **1989**, *166*, 189; **1989**, *161*, 131; **1990**, *173*, 53; **1991**, *187*, 125. Miller, S. E.; Gerard, K. J.; House, D. A. *Inorg. Chim. Acta* **1991**, *190*, 135.

S0020-1669(97)00601-0 CCC: $15.00

one (H_{endo}) becoming spectroscopically (NMR) sensitive to the coordination environment of the metal. Second, we recognized that the topology of the fragment is that of half a calix[4]arene, a ligand of considerable interest in coordination and organometallic chemistry.[8,9]

Herein we report the synthesis of diamino ligands which have this reference skeleton and their complexation of $PtCl_2$ and $PdCl_2$ moieties, as well as their hydrolysis products and structural identification.

Experimental Section

General Procedures. All the preparations of metal complexes were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. Infrared spectra were recorded with a Perkin-Elmer 883 spectrophotometer; ^{1}H NMR spectra were measured on 200-AC and 400-DPX Bruker instruments, at 298 and 343 K.

Preparation of 1.[10] This preparation is essentially that reported by Pinnow.[11] To a cooled (0 °C) solution of 4,4′-methylenebis(*N*,*N*-dimethylaniline) (30.0 g, 118 mmol) in sulfuric acid (140 mL, 96%) was added dropwise over 3 h a solution of sulfuric acid (17 mL, 96%) and nitric acid (17 mL, 60%). At the end of the addition the flask contents were transferred to a large beaker containing ice (*ca.* 1 kg) and, with vigorous stirring, carefully made basic with a mixture of ice (*ca.* 1 kg) and ammonia (25%). The resulting orange solid was collected by filtration and washed thoroughly with water. The solid was then refluxed in ethanol (300 mL) for 30 min, collected by filtration, and finally dried in the air. Yield: 38.3 g, 94%. Mp: 190−191 °C. Anal. Calcd for $C_{17}H_{20}N_4O_4$: C, 59.29; H, 5.85; N, 16.27. Found: C, 58.91; H, 6.07; N, 16.02. ^{1}H NMR (CD_2Cl_2, 298 K): δ 7.21 (d, 2H, Ar-H), 6.96 (d, 2H, Ar-H), 6.81 (dd, 2H, Ar-H), 4.30 (s, 2H, CH_2), 2.97 (s, 12H, NCH_3).

Preparation of 2,2′-Methylenebis(5-(dimethylamino)aniline), 2, L. This preparation is essentially that reported by Pinnow.[11] To a cooled (0 °C) solution of **1** (10.0 g, 29.0 mmol), HCl (240 mL, 36%), and water (60 mL) (the mixture was gently heated to aid solubility) was slowly added powdered tin (20.0 g) resulting in the formation of an orange solution and the evolution of gas. The solution acidity was then adjusted to *ca.* 6 and H_2S added to remove the tin byproduct. The mixture was filtered and NaOH added until the point of precipitation. The resulting solid was washed thoroughly with water and then ethanol (*ca.* 300 mL). Yield: 72%. Mp: 139−140 °C (lit.[11] mp 139−140 °C). Anal. Calcd for $C_{17}H_{24}N_4$: C, 71.79; H, 8.51; N, 19.70. Found: C, 72.02; H, 8.61; N, 19.45. ^{1}H NMR (d_6-acetone, 298 K): δ 6.72 (d, 2H, Ar-H), 6.15 (d, 2H, Ar-H), 6.04 (dd, 2H, Ar-H), 4.19 (brd s, 4H, NH_2), 3.50 (s, 2H, CH_2), 2.80 (s, 12H, NCH_3).

Preparation of 3.[12] To a cooled (0 °C), stirred solution of (*p*,*p*′-diaminodiphenyl)methane (50.0 g, 250 mmol) and sulfuric acid (270 mL, 96%) (previously warmed (80 °C) to aid dissolution) was added dropwise over 3 h a solution of sulfuric acid (110 mL, 96%) and KNO_3 (51 g, 0.50 mol). The reaction vessel was allowed to warm to room temperature and stirred for 1 h, and the contents were then emptied, with vigorous stirring, into a large beaker of ice (*ca.* 3 kg). A second beaker containing ice (2 kg) and ammonia (25%) was then slowly added, with vigorous stirring, until the mixture became basic. (N.B.: It is important that the temperature is strictly controlled.) An orange solid resulted which was collected by filtration and washed with water until the washings were neutral. The solid was refluxed in ethanol (2.5 L) and activated charcoal for 15 min and then filtered, while hot, through a bed of Celite. The filtrate was concentrated to the point of precipitation and left to stand for 2 h (crude yield: 74%). Recrystallization in the minimum volume of ethanol gave the desired product as red/orange crystals in 54% yield. Mp: 203 °C. Anal. Calcd for $C_{13}H_{12}N_4O_4$: C, 54.17; H, 4.20; N, 19.44. Found: C, 55.0; H, 4.12; N, 19.13. ^{1}H NMR (CD_2Cl_2, 298 K): δ 7.25 (d, 2H, Ar-H), 6.90 (d, 2H, Ar-H), 6.80 (dd, 2H, Ar-H), 4.29 (s, 2H, CH_2), 3.98 (brd s, 4H, NH_2).

Preparation of 4. This method is essentially that reported by Duval.[12] A mixture of **3** (50 g, 0.17 mol) and acetic anhydride (50 mL) was heated to the point of reflux and then allowed to cool to room temperature. After *ca.* 15 min water (*ca.* 500 mL) was added and the mixture again heated to the point of reflux. After cooling, the resulting yellow solid was recrystallized in the minimum volume of ethanol (10.8 g, 84%). Mp: 230 °C (lit.[12] mp 229 °C). Anal. Calcd for $C_{17}H_{16}N_4O_6$: C, 54.84; H, 4.33; N, 15.05. Found: C, 55.02; H, 4.12; N, 15.12. ^{1}H NMR (d_6-acetone, 298 K): δ 9.31 (brd s, 2H, NH), 8.23 (d, 2H, Ar-H), 7.51 (dd, 2H, Ar-H), 6.94 (d, 2H, Ar-H), 4.25 (s, 2H, CH_2), 1.89 (s, 6H, $NCOCH_3$).

---

(5) See for example: Rau, T.; Shoukry, M.; van Eldik, R. *Inorg. Chem.* **1997**, *36*, 1454. Bloemink, M. J.; Engelking, H.; Karentzopoulos, S.; Krebs, B.; Reedijk, J. *Inorg. Chem.* **1996**, *35*, 619. Takahara, P. M.; Frederick, C. A.; Lippard, S. J. *J. Am. Chem. Soc.* **1996**, *118*, 12309. Prinsloo, F. F.; Pienaar, J. J.; van Eldik, R. *J. Chem. Soc., Dalton Trans.* **1995**, 3581. Elmroth, S. K. C.; Lippard, S. J. *J. Am. Chem. Soc.* **1994**, *116*, 3633. Frey, U.; Ranford, J. D.; Sadler, P. J. *Inorg. Chem.* **1993**, *32*, 1333. Bloemink, M. J.; Heetebrij, R. J.; Inagaki, K.; Kidani, Y.; Reedijk, J. *Inorg. Chem.* **1992**, *31*, 4656. Hohmann, H.; Hellquist, B.; van Eldik, R. *Inorg. Chem.* **1992**, *31*, 345. Frommer, G.; Lippert, B. *Inorg. Chem.* **1990**, *29*, 3259. Inagaki, K.; Alink, M.; Nagai, A.; Kidani, Y.; Reedijk, J. *Inorg. Chem.* **1990**, *29*, 2183. van Garderen, C. J.; Altona, C.; Reedijk, J. *Inorg. Chem.* **1990**, *29*, 1481. Frommer, G.; Schöllhorn, H.; Thewalt, U.; Lippert, B. *Inorg. Chem.* **1990**, *29*, 1417. Micklitz, W.; Sheldrick, W. S.; Lippert, B. *Inorg. Chem.* **1990**, *29*, 211. Arpalahti, J.; Lippert, B. *Inorg. Chem.* **1990**, *29*, 104. Bancroft, D. P.; Lepre, C. A.; Lippard, S. J. *J. Am. Chem. Soc.* **1990**, *112*, 6860. Hollis, L. S.; Amundsen, A. R.; Stern, E. W. *J. Med. Chem.* **1989**, *32*, 128. Breet, E. L. J.; van Eldik, R. *Inorg. Chem.* **1987**, *26*, 2517.

(6) Giandomenico, C. M.; Abrams, M. J.; Murrer, B. A.; Vollano, J. F.; Barnard, C. F. J.; Harrap, K. R.; Goddard, P. M.; Kelland, L. R.; Morgan, S. E. In *Proceedings of The Sixth International Symposium on Platinum and Other Metal Coordination Compounds in Cancer Chemotherapy*; Plenum: San Diego, CA, 1992; p 93. Giandomenico, C. M.; Abrams, M. J.; Murrer, B. A.; Vollano, J. F.; Rheinheimer, M. I.; Wyer, S. B.; Bossard, G. E.; Higgins, J. D. *Inorg. Chem.* **1995**, *34*, 1015.

(7) Lesueur, W.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1997**, *36*, 3354. Lesueur, W.; Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 66.

(8) Zanotti-Gerosa, A.; Solari, E.; Giannini, L.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Chem. Commun.* **1996**, 119. Hajek, F.; Graf E.; Hosseini, M. W. *Tetrahedron Lett.* **1996**, *37*, 1409. Acho, J. A.; Lippard, S. J. *Inorg. Chim. Acta* **1995**, *229*, 5. Acho, J. A.; Ren, T.; Yun, J. W.; Lippard, S. J. *Inorg. Chem.* **1995**, *34*, 5226. Acho, J. A.; Doerrer, L. H.; Lippard, S. J. *Inorg. Chem.* **1995**, *34*, 2542. Gibson, V. C.; Redshaw, C.; Clegg, W.; Elsegood, M. R. J. *J. Chem. Soc., Chem. Commun.* **1995**, 2371. Delaigue, X.; Hosseini, M. W.; Leize, E.; Kieffer, S.; Van Dorsselaer, A. *Tetrahedron Lett.* **1993**, *34*, 7561. Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1991**, *30*, 4465. Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1990**, 640. Corazza, F.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1990**, 1083. Hofmeister, G. E.; Alvarado, E.; Leary, J. A.; Yoon, D. I.; Pedersen, S. F. *J. Am. Chem. Soc.* **1990**, *112*, 8843. Hofmeister, G. E.; Kahn, F. E.; Pedersen, S. F. *J. Am. Chem. Soc.* **1989**, *111*, 2318. Furphy, B. M.; Harrowfield, J. M.; Kepert, D. L.; Skelton, B. W.; White, A. H.; Wilner, F. R. *Inorg. Chem.* **1987**, *26*, 4231. Bott, S. G.; Coleman, A. W.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1986**, 610. Olmstead, M. M.; Sigel, G.; Hope, H.; Xu, X.; Power, P. P. *J. Am. Chem. Soc.* **1985**, *107*, 8087.

(9) Giannini, L.; Solari, E.; Zanotti-Gerosa, A.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 753. Giannini, L.; Solari, E.; Zanotti-Gerosa, A.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 85. Castellano, B.; Zanotti-Gerosa, A.; Solari, E.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Organometallics* **1996**, *15*, 4894. Giannini, L.; Solari, E.; Zanotti-Gerosa, A.; Floriani, C.; Chiesi-Villa, A.; Rizzoli, C. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2825. Gardiner, M. G.; Lawrence, S. M.; Raston, C. L.; Skelton, B. W.; White, A. H. *Chem. Commun.* **1996**, 2491. Gardiner, M. G.; Koutsantonis, G. A.; Lawrence, S. M.; Nichols, P. J.; Raston, C. L. *Chem. Commun.* **1996**, 2035.

(10) Borkowski, W. L.; Wagner, E. C. *J. Org. Chem.* **1952**, *17*, 1128.

(11) Pinnow, J. *Ber.* **1894**, *27*, 3161.

(12) Duval, M. H. *Bull. Soc. Chim. Fr.* **1910**, *7*, 527. King, H. *J. Chem. Soc.* **1920**, *117*, 988.

Preparation of 2,2′-methylenebis(5-(acetylamino)aniline), 5, L′. This method is essentially that described by Duval.[12] Compound **4** (11.6 g, 31.2 mmol) and a solution of $SnCl_2$ (20.0 g, 169 mmol) in HCl (80 mL, 36%) were heated to the point of reflux before being diluted with water. The mixture was made basic with NaOH (2 M) and the resulting white solid slurried in hot ethanol and then quickly filtered (10.8 g, 84%). Mp: 242−246 °C (lit.[12] mp 244 °C). Anal. Calcd for $C_{17}H_{20}N_4O_2$: C, 65.37; H, 6.45; N, 17.94. Found: C, 65.13; H, 6.31; N, 17.54. ^1H NMR (d_6-acetone/d_6-DMSO, 298 K): δ 9.49 (s, 2H, NH), 7.10 (s, 2H, Ar-H), 6.69 (d, 4H, Ar-H), 4.68 (brd s, 4H, NH_2), 3.51 (s, 2H, CH_2), 1.97 (s, 6H, $NCOCH_3$).

Preparation of [(L)PdCl$_2$], 6. A mixture of **2** (0.50 g, 1.76 mmol) and $PdCl_2$ (0.31 g, 1.76 mmol) in ethanol/DMF (100 mL/100 mL) was stirred for 1 h at room temperature to give an orange suspension. The mixture was then heated to reflux to give an orange solution which, on cooling, gave a red/orange microcrystaline solid. The solid was collected by filtration and dried in the air. Yield: 0.68 g (72%). Calcd for $C_{20}H_{31}N_5OPdCl_2$: C, 65.37; H, 6.45; N, 17.94. Found: C, 65.41; H, 6.63; N, 17.84. ^1H NMR (d_6-DMSO, 298 K): δ 7.94 (s, 1H, DMF), 7.24 (d, 2H, J_{HH} = 9 Hz, Ar-H), 6.96 (brd d, 2H, J_{HH} = 9 Hz, Ar-H), 6.52 (brd s, 4H, Ar-H), 5.96 (brd d, 2H, J_{HH} = 10 Hz, NH_2), 3.69 (d, 1H, J_{HH} = 14.6 Hz, CH_2), 3.40 (d, 1H, J_{HH} = 14.6 Hz, CH_2), 2.87 (s, 3H, DMF), 2.78 (s, 12H, NCH_3), 2.72 (s, 3H, DMF).

Preparation of [(L′)PtCl$_2$], 7. A mixture of **5** (0.50 g, 1.6 mmol) and K_2PtCl_4 (0.66 g, 1.6 mmol) in hot (50 °C) water/DMF (100/100 mL) was stirred for 1 h to give a yellow suspension. The solid was collected by filtration, washed with ethanol, and dried in the air. Yield: 0.91 g (98%). Anal. Calcd for $C_{20}H_{31}Cl_2N_5OPt$: C, 65.37; H, 6.45; N, 17.94. Found: C, 65.21; H, 6.32; N, 17.71. ^1H NMR (d_6-DMSO, 313 K): δ 9.92 (s, 1H, NH), 9.56 (s, 1H, NH), 7.40 (s, 2H, Ar-H), 7.01 (s, 2H, Ar-H), 6.63 (s, 2H, Ar-H), 5.0 (brd s, 4H, NH_2), 4.05 (brd d, 1H, CH_2), 3.50 (brd d, 1H, CH_2), 1.96 (s, 3H, CH_3), 1.99 (s, 3H, CH_3).

Preparation of [(L)PtCl$_2$], 8. To a stirred solution of **2** (0.50 g, 1.8 mmol) in the minimum volume of DMF was added a solution of K_2PtCl_4 (0.73 g, 1.8 mmol) in the minimum volume of water. To this beige suspension was added DMF (10 mL) and the mixture heated to reflux to give a red/violet solution and a dark red crystalline solid. The solid was collected and dried in the air. Yield: 0.66 g (68%). Anal. Calcd for $C_{17}H_{24}Cl_2N_4OPt$: C, 37.10; H, 4.39; N, 10.18. Found: C, 37.03; H, 4.42; N, 10.71. ^1H NMR (d_6-DMSO, 298 K): δ 7.64 (brd s, 2H, J_{HH} = 10.6 Hz, NH_2), 7.24 (d, 2H, J_{HH} = 9 Hz, Ar-H), 6.86 (brd d, 2H, J_{HH} = 10.6 Hz, Ar-H), 6.45 (brd s, 4H, Ar-H), 3.91 (d, 1H, J_{HH} = 14.8 Hz, CH_2), 3.38 (d, 1H, J_{HH} = 14.8 Hz, CH_2), 2.77 (s, 12H, NCH_3). IR (Nujol, cm^{-1}): NH_2 (3212, 1628), PtN (561, 488).

Preparation of [(L)Pt(Cl)(DMSO)]$^+$Cl$^-$, 9. To a stirred solution of **2** (1.00 g, 3.51 mmol) in ethanol (30 mL) was added a solution of K_2PtCl_4 (1.46 g, 3.51 mmol) in water (30 mL). To the resulting orange/rose suspension was added DMSO (15 mL) and the mixture heated to reflux to give a turbid red solution. The solution was filtered and left to stand for 12 h to give dark yellow crystals. Yield: 0.76 g (34%). Anal. Calcd for $C_{19}H_{30}N_4SOPtCl_2$: C, 36.31; H, 4.81; N, 8.91. Found: C, 36.57; H, 5.21; N, 8.69. ^1H NMR (CD_2Cl_2, 298 K): δ 7.21−7.28 (m, 2H, Ar-H), 6.51−6.72 (m, 4H, Ar-H), 5.96 (brd d, 2H, J_{HH} = 10 Hz, NH_2), 4.90 (d, 1H, J_{HH} = 15 Hz, CH_2), 3.56 (ovlap m, 4H, DMSO + CH_2), 3.21 (s, 3H, DMSO), 2.85 (s, 12H, NCH_3), 1.45 (s, 4H, NH_2). IR (Nujol, cm^{-1}): NH_2 (3256, 3199, 1625), S═O (1122), PtN (566, 491).

Preparation of [Pt$_2$(μ-L)Cl$_4$(C$_2$H$_4$)$_2$], 10. To a cooled (0 °C), stirred solution of $K[PtCl_3(C_2H_4)]\cdot H_2O$ (0.50 g, 1.3 mmol) in methanol (5 mL) was added **2** (0.37 g, 1.3 mmol). A pale yellow solid resulted which was collected, washed with ether, and dried in the air. Yield: 0.76 g (34%). Anal. Calcd for $C_{21}H_{32}N_4Pt_2Cl_5K$: C, 26.63; H, 3.41; N, 5.92. Found: C, 26.70; H, 3.46; N, 5.91. ^1H NMR (CD_2Cl_2, 298 K): δ 6.94 (d, 2H, Ar-H), 6.72 (d, 2H, Ar-H), 6.53 (dd, 2H, Ar-H), 5.7 (brd, 4H, NH_2), 4.62 (t, 8H, J_{HPt} = 64 Hz, C_2H_2), 4.28 (s, 2H, CH_2) 2.95 (s, 12H, NCH_3). IR (Nujol, cm^{-1}): NH_2 (3190, 3119, 1629).

X-ray Crystallography for Complexes 6 and 9. Intensity data were collected at room temperature on a single-crystal four-circle diffractometer. Crystal data and refinement details for complexes **6** and **9** are given in Table 1. The reduced cells were obtained with use of TRACER.[13]

Table 1. Experimental Data for the X-ray Diffraction Studies on Crystalline Complexes **6** and **9**

	6	**9**
formula	$C_{17}H_{24}Cl_2N_4Pd\cdot C_3H_7NO$	$[C_{19}H_{30}ClN_4OPtS]^+[Cl]^-\cdot C_2H_6O$
a, Å	10.179(2)	12.348(1)
b, Å	12.136(2)	12.407(1)
c, Å	9.686(2)	10.159(1)
α, deg	97.79(1)	93.02(1)
β, deg	95.98(2)	104.87(1)
γ, deg	78.02(1)	117.09(1)
V, Å^3	1156.1(4)	1313.0(3)
Z	2	2
fw	534.8	674.6
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
t, °C =	22	22
λ, Å	0.710 69	0.710 69
ρ_{calc}, g cm^{-3}	1.536	1.706
μ, cm^{-1}	10.45	57.04
transm coeff	0.919−1.000	0.813−1.000
unique tot. data	4091	3669
unique obsd data	2797	2690
R^a	0.034	0.035
wR2^a	0.078	0.066
GOF^a	1.048	0.916

[a] $R = \sum|\Delta F|/\sum|F_o|$ for unique observed data [$I > 2\sigma(I)$]. $wR2 = [\sum w|\Delta F^2|^2/\sum w|F_o{}^2|^2]^{1/2}$ for unique observed data. $GOF = [\sum w|\Delta F^2|^2/(NO - NV)]^{1/2}$.

For intensities and background individual reflection profiles were analyzed.[14] Intensity data were corrected for Lorentz and polarization effects and for absorption.[15] The function minimized during the full-matrix least-squares refinement was $\sum w|\Delta F|^2$ using a weighting scheme based on counting statistics.[16] Anomalous scattering corrections were included in all structure factor calculations.[17b] Scattering factors for neutral atoms were taken from ref 17a for non-hydrogen atoms and from ref 18 for H atoms. Among the low-angle reflections, no correction for secondary extinction was deemed necessary.

The structures were solved by the heavy-atom method (Patterson and Fourier syntheses). Refinement was first done isotropically and then anisotropically for all the non-H atoms. The ethanol solvent molecule in complex **9** found to be disordered over two positions was isotropically refined. The H atoms except those associated with the ethanol molecule were located in a ΔF map and introduced in the refinement as fixed contributors with isotropic *U* values fixed at 0.08 Å^2 for **6** and 0.10 Å^2 for **9**. The final difference map showed no unusual features, with no significant peak above the general background. Final atomic coordinates of the non-hydrogen atoms are given in Table S2.[19]

Results and Discussion

Our decision on which ligands to use was strongly influenced by their synthetic accessibility. A number of these ligands were reported around the beginning of the century and have since then not been utilized. A detailed account of the synthesis of

---

(13) Lawton, S. L.; Jacobson, R. A. *TRACER (a cell reduction program)*; Ames Laboratory, Iowa State University of Science and Technology: Ames, IA, 1965.

(14) Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1974**, *A30*, 580−584.

(15) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *A24*, 351.

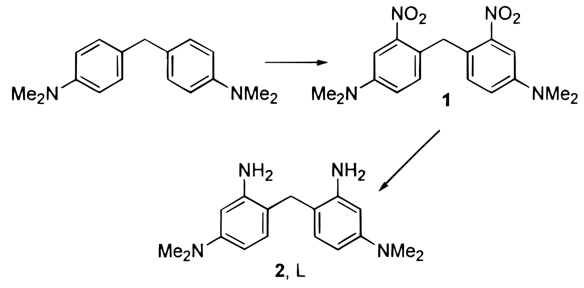
(16) SHELXL92 Gamma Test: Sheldrick, G. M. *Program for Crystal Structure Refinement*; University of Göttingen: Germany, Göttingen, 1992.

(17) (a) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, p 99. (b) *Ibid.*, p 149.

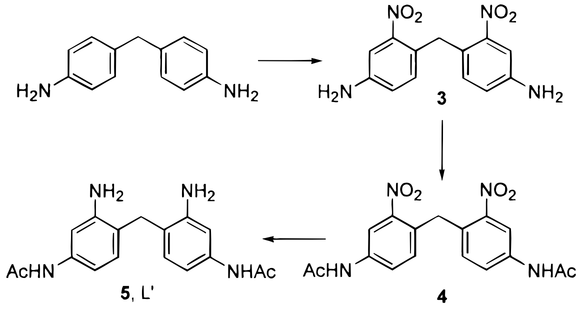
(18) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(19) See paragraph at the end of paper regarding Supporting Information.

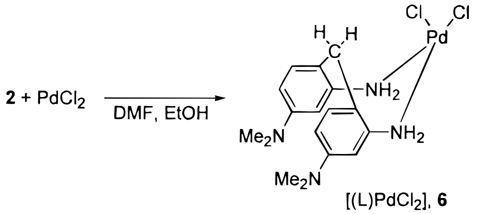
Scheme 1



Scheme 2



Scheme 3



compounds **1**−**5** is given in the Experimental Section and summarized in Schemes 1and 2, respectively.

Metal Complexes. Scheme 3 outlines the reaction of **2** with $PdCl_2$. The reaction is straightforward and yields complex **6** as an orange/red crystalline solid which was analyzed in solution (^{1}H NMR) and solid state (*vide infra*).

The important feature of the NMR spectrum is the pair of doublets at 3.40 and 3.69 ppm which are due to the now diastereotopic bridging methylene hydrogens. In the free ligand they appear as a singlet at 3.50 ppm. The structure of **6** is given in Figure 1 with the selected bond distances and angles summarized in Table 2.

Coordination around palladium is not strictly planar and involves the N1 and N2 nitrogen atoms from the ligand (L) and two chlorine atoms. The N1 and N2 atoms are displaced by 0.190(4) and 0.251(4) Å on opposite sides of the plane through Pd, Cl1, and Cl2. The coordination of palladium to the ligand results in an eight-membered chelate ring which is puckered as indicated by the total puckering amplitude [1.137(5) Å].[20] The value of the ΔS(Pd) asymmetry parameter (0.054(2)) is consistent with the presence of a local mirror plane running through Pd and C7. The conformation of the ring could be described as an elongated chair, the dihedral angle between the N1,N2,C1,C13 and C1,C6,C8,C13 nearly planar moieties being 139.8(2)°. The Pd and C7 atoms are displaced from the best plane through all these atoms by 1.033(1) and 1.039(5) Å on opposite sides. The coordination plane is folded away from C7 resulting in a Pd···H71 distance of 3.75 Å and in a dihedral angle of 109.0(1)° with the N1,N2,C1,C13 plane. The N1 and N2 amine nitrogen atoms are linked to the DMF molecule of crystallization through hydrogen bond interactions and have the following geometry (Å, deg): N1···O1, 2.886(5); N1−H22, 0.84; O1···H22, 2.11; N1−H22···O1, 154; N2···O1, 2.933(6); N2−H23, 0.82; O1···H23, 2.17; N2−H23···O1, 155. The molecules are packed in columnar chains parallel to the [100] axis through $CH_3-\pi$ interactions involving the C19 methyl carbon of DMF and the C1···C6 aromatic ring of an adjacent complex molecule translated along the *a* axis. The range of carbon−carbon distances [3.773(9)−3.798(8) Å] is in good agreement with those observed for host−guest interactions in calixarenes.[21]

Similar structural and spectroscopic observations, though more emphasised, are observed for the analogous complexation

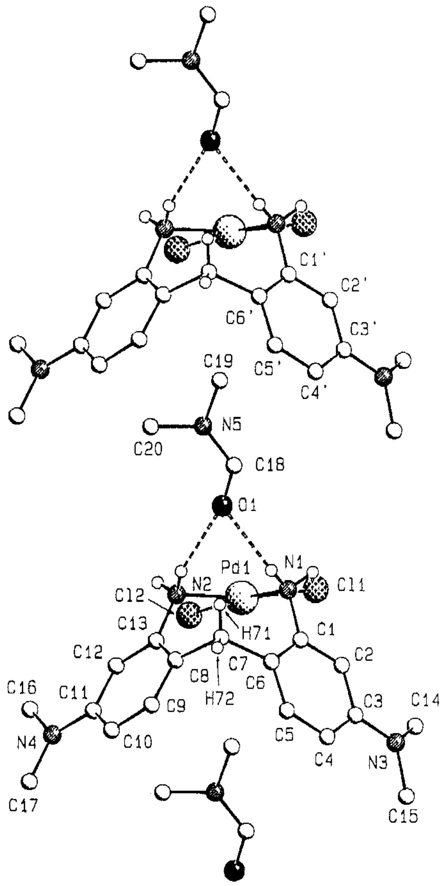


Figure 1. SCHAKAL view of the structure of complex **6**. A prime denotes a transformation of $x - 1, y, z$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes **6** (M = Pd, X = Cl2) and **9** (M = Pt, X = S1)

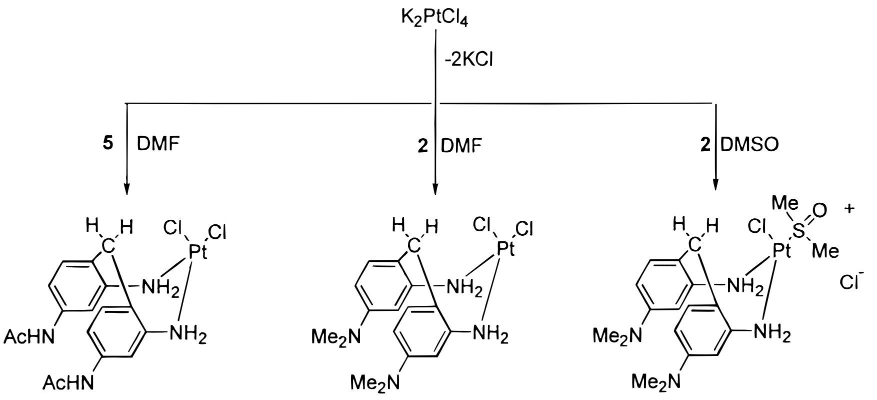
	6	9		6	9
M−Cl1	2.320(2)	2.289(4)	N4−C16	1.425(8)	1.457(16)
M−X	2.315(2)	2.207(2)	N4−C17	1.423(9)	1.441(18)
M−N1	2.056(4)	2.056(6)	C1−C6	1.383(7)	1.383(18)
M−N2	2.069(4)	2.077(9)	C6−C7	1.522(6)	1.535(15)
N1−C1	1.451(6)	1.447(13)	C7−C8	1.519(7)	1.511(11)
N2−C13	1.442(7)	1.473(15)	C8−C13	1.388(6)	1.394(13)
N3−C3	1.376(6)	1.408(14)	O1−C18	1.223(7)	1.779(11)
N3−C14	1.435(7)	1.40(2)	N5−C18	1.311(6)	
N3−C15	1.449(7)	1.447(14)	N5−C19	1.460(8)	
N4−C11	1.386(8)	1.372(12)	N5−C20	1.433(10)	

	6	9		6	9
N1−M−N2	90.2(1)	89.5(3)	Cl1−M−N1	87.0(1)	88.8(2)
X−M−N2	89.0(1)	90.6(2)	Cl1−M−X	94.4(1)	91.1(1)
X−M−N1	174.5(1)	176.3(2)	M−N1−C1	109.7(3)	118.9(6)
Cl1−M−N2	172.2(1)	178.0(2)	M−N2−C13	120.4(3)	114.7(5)
Cl1−M−N1	87.0(1)	88.8(2)			

---

(20) Cremer, D.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 1354.

Scheme 4



$[(L')PtCl_2]$, **7** $[(L)PtCl_2]$, **8** $[(L)Pt(Cl)(DMSO)]^+Cl^-$, **9**

of $PtCl_2$ by **2** and **5**. Scheme 4 outlines their syntheses. In the case of complexation with **2** both **8** and **9** have been isolated depending on the nature of the solvent. In the latter case the preliminary formation of the neutral species is followed by the solvent-induced ionization of the Pt−Cl bond.

Complexes **7**−**9** (see their characterization in the Experimental Section) display interesting ^{1}H NMR spectra as far as the bridging methylene is concerned. It appears as a singlet in the free ligand **5** at 3.51 ppm and as a pair of doublets separated by 0.55 ppm in complex **7**. For complexes **8** and **9** two different coordination environments for platinum are implied if we relate this to the diastereotopic proton separation. For **8**, this is $\Delta = 0.53$ ppm, while it is about 2.5 times greater ($\Delta = 1.34$ ppm) in **9**. We attribute this difference to the increased steric hindrance around the metal.

Although we do not have a completely satisfactory argument for explaining the separation of the two doublets derived from the diastereotopic hydrogens, the consequence on this parameter of the variation of the coordination number and/or steric hindrance at the metal is quite remarkable and eventually of great utility. In conclusion, we can say that the rigid conformation of the eight-membered metallacycle allowed the differentiation of the *exo* and *endo* protons of the bridging methylene. The conformational rigidity of the metallacycle is further supported by the ^{1}H NMR spectra of **6**−**8**, run in DMSO at 343 K, which did not show any significant change in the chemical shift of the *exo* and *endo* protons and in their separation. They do not collapse thus ruling out any ring inversion. Therefore, the *endo* proton is able to serve as a spectroscopic probe for structural correlations, particularly considering the separation of the two doublets.[22] The first argument concerning this structural−spectroscopic relationship is based on geometrical constraints and postulates a sort of weak interaction between the metal center and the H_{endo} proton. However, this kind of interaction is not supported by the number of cases we reported for the same skeleton but different donor atoms. An agostic type of interaction can be excluded, because this would result in a high-field shift for the proton which undergoes the agostic interaction.[23] This is clearly not the case.

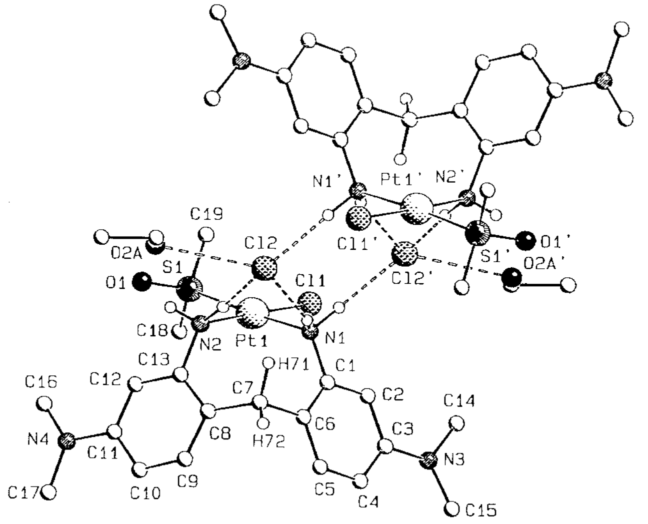


Figure 2. SCHAKAL view of the structure of complex **9**. Only the A position is given for the disordered ethanol solvent molecule. A prime denotes a transformation of $1 - x$, $1 - y$, $1 - z$.

Instead, the opposite trend was observed, a downfield shift of the signal assigned to H_{endo}, compared to the free ligand. This phenomenon may be explained in terms of an increased deshielding of the *endo* proton, because the formation of a metallacycle results in an additional ring current which opposes the external field.[24,25]

The structure of **9**, which is a partially hydrolyzed form of **8**, may be relevant in the context of hydrolyzed forms of *cis*-diaminodichloroplatinum(II) derivatives.[26] The structure consists of $[(L)Pt(Cl)(DMSO)]^+$ cations, chlorine anions, and ethanol solvent molecules in a stoichiometric ratio of 1/1/1 (Figure 2). Selected bond distances and angles are given in Table 2.

Coordination around platinum involves the N1 and N2 nitrogen atoms from the ligand, the Cl1 chlorine atom, and the S1 sulphur atom from a DMSO molecule. Coordination is not strictly planar, the N1 atom being displaced by 0.135(8) Å from

---

(21) Andreetti, G. D.; Ugozzoli, F. In *Calixarenes, A Versatile Class of Macrocyclic Compounds*; Vicens, J., Böhmer V., Eds.; Kluwer: Dordrecht, The Netherlands, 1991; p 88.

(22) Meek, D. W.; Nicpon, P. E.; Imhof Meek, V. *J. Am. Chem. Soc.* **1970**, *92*, 5351. *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis*; Verkade, J. G., Quin, L. D., Eds.; VCH: Weinheim, Germany, 1987.

(23) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. Brookhart, M.; Green, M. L. H.; Wong, L. L. *Prog. Inorg. Chem.* **1988**, *36*, 1.

(24) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(25) Lindner, E. *Adv. Heterocycl. Chem.* **1986**, *39*, 239.

(26) Romeo, R.; Scolaro, L. M.; Nastasi, N.; Arena, G. *Inorg. Chem.* **1996**, *35*, 5087. Alibrandi, G.; Romeo, R.; Scolaro, L. M.; Tobe, M. L. *Inorg. Chem.* **1992**, *31*, 5061. Lempers, E. L. M.; Bloemink, M. J.; Reedijk, I. *Inorg. Chem.* **1991**, *30*, 201. Farrell, N.; Kiley, D. M.; Schmidt, W.; Hacker, M. P. *Inorg. Chem.* **1990**, *29*, 397. Bonivento, M.; Cattalini, L.; Marangoni, G.; Michelon, G.; Schwab, A. P.; Tobe, M. L. *Inorg. Chem.* **1980**, *19*, 1743.

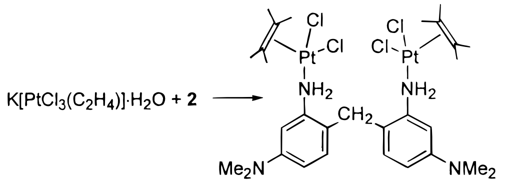
the mean plane through Pt, Cl1, S1, and N2. The orientation of the DMSO ligand leads the O1 oxygen atom to approach the N2 atom at a distance of 2.941(9) Å. The geometry of this contact [O1···H24, 2.24, N2−H24, 0.94 Å, O1···H24-N2, 130.3°] suggests it could be considered as an intramolecular hydrogen bond interaction.

The conformation of the eight-membered chelate ring is similar to that found in complex **6**, the total puckering amplitude being 1.118(8)Å [1] and the value of the ΔS(Pt) asymmetry parameter being 0.011(3). The conformation of the ring resembles an elongated chair with a dihedral angle between the N1,N2,C1,C13 and C1,C6,C8,C13 planar moieties of 144.7(4)°. The Pt and C7 atoms are displaced from the best plane through the eight atoms by 1.165(1) and 0.983(9) Å on opposite sides. The coordination plane is folded away from C7 resulting in a Pt···H71 distance of 3.62 Å and in a dihedral angle of 109.9(3)° with the N1,N2,C1,C13 plane. The Cl2 anion, though not involved in coordination [Pt···Cl2, 4.046(2) Å], is engaged in a network of hydrogen bonds involving the N1 and N2 amine nitrogens of a cation [Cl2···N1, 3.320(8); Cl2···H22, 2.49; N1-H22, 0.92 Å, Cl2···H22-N1, 150.4°; Cl2···N2, 3.195(6); Cl2···H23, 1.99; N2-H23, 1.22 Å, Cl2···H23-N2, 168.7°] and the N1 nitrogen of a centrosymmetric cation giving rise to the dimeric structure shown in Figure 2 [Cl2···N1′, 3.284(9); Cl2···H21′, 2.29; N1-H21, 1.10 Å; Cl2···H21′-N1′, 150.4; $' = 1 - x, 1 - y, 1 - z$]. The ethanol solvent molecule was found to be affected by a severe disorder which was solved by splitting each atom in two positions called A (65% of occupancy) and B (35% of occupancy). In position A the O2A oxygen atom approaches the Cl2 anion at a distance of 3.10(2) Å suggesting a hydrogen bond interaction. The failure in locating the hydrogen atom bonded to O2A prevents a more sound discussion on this subject. In position B the O2B oxygen atom gives rise to a minimum contact distance of 3.20(4) Å with the N2 nitrogen atom of an adjacent dimer related by the inversion centre at 0, $^1/_2$, 0.

The possibilty of detecting steric hindrance, changes in the coordination number, and eventually changes in the metal's bonding mode was also considered. For example, could our bidentate ligand act a a bis-monodentate ligand? This was evaluated by reacting the Zeiss compound $K[PtCl_3(C_2H_4)]\cdot H_2O$ with **2** (Scheme 5).

The dinuclear complex forms independent of the L/Pt ratio. In addition to all the analytical data reported in the Experimental Section, a major indication that L is functioning as a bis-monodentate ligand can be seen in the ^{1}H NMR spectrum where the bridging methylene hydrogens now appear as a singlet (4.28 ppm). The olefinic protons come out as a typical 1:4:1 triplet with $J_{Pt-H} = 64$ Hz, suggesting the same coordination environment for the two Pt atoms. Compounds which are potentially bidentate yet act as a bis-monodentate ligand have an interesting perspective in the often invoked relationship between mono- and dimetallic labile species in metal-assisted catalytic processes.[27]

Scheme 5



$[Pt_2(\mu\text{-}L)Cl_4(C_2H_4)_2]$, **10**

Concluding Remarks

Although it was not our intention to investigate the biological activity of the reported species, we felt that such molecules could eventually find use in areas such as the interaction of metal ions with large peptides or DNA strands. To some extent this is already being actively pursued but from the standpoint of the ligand by using for example ^{31}P or ^{15}N spectroscopies to investigate H-bonding, etc. The key feature with our work concerns the metal centre and the potential of these bis(amino) ligands to act as a spectroscopic ^{1}H NMR probe, sensitive to the coordination environment of the metal. This is particularly interesting in cases (e.g. as a result of hydrolysis) which do not lead to easily identifiable species. In addition, the appearance of the methylene signal in the ^{1}H NMR spectrum as either a pair of doublets or a singlet is particularly informative for assigning a bidentate or bis-monodentate bonding mode. We therefore believe that such systems have considerable promise.

Acknowledgment. We thank the "Fonds National Suisse de la Recherche Scientifique" (Bern, Switzerland, Grant No. 20-46′590.96), Ciba Specialty Chemicals (Basle, Switzerland), and Action COST D3 (European Program for Scientific Research) for financial support.

Supporting Information Available: Tables of experimental details associated with the data collections and structure refinement, final atomic coordinates for non-H atoms, hydrogen atom coordinates, thermal parameters, and bond distances and angles and ORTEP drawings for **7** and **10** (11 pages). Ordering information is given on any current masthead page.

IC9706010

---

(27) Parshall, W.; Ittel, S. D. *Homogeneous Catalysis*, 2nd ed.; Wiley: New York, 1992.