Models for the Initial Stages of Oxidative Addition. Synthesis, Characterization, and Mechanistic Investigation of η^1-I$_2$ Organometallic "Pincer" Complexes of Platinum. X-ray Crystal Structures of [PtI(C$_6$H$_3${CH$_2$NMe$_2$}$_2$-2,6)(η^1-I$_2$)] and *exo-meso*-[Pt(η^1-I$_3$)(η^1-I$_2$)(C$_6$H$_3${CH$_2$N(*t*-Bu)Me}$_2$-2,6)]

Robert A. Gossage,[†,#] Alexander D. Ryabov,[∥] Anthony L. Spek,[‡] Derk J. Stufkens,[§] Johannus A. M. van Beek,[§] Rudi van Eldik,[⊥] and Gerard van Koten*,[†]

Contribution from the Department of Metal-Mediated Synthesis, Debye Institute, and Laboratory of Crystal Chemistry, The Bijvoet Center for Biomolecular Research, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands, Anorganisch Chemisch Laboratorium, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands, Institut für Anorganische Chemie, Universität Erlangen-Nürnberg, Egerlandstrasse 1, 91058 Erlangen, Germany, and Division of Chemistry, M. V. Lomonosov Institute, Moscow State University, 119899 Moscow, Russia

Received June 16, 1998

Abstract: The reaction of I$_2$ with platinum "pincer" complexes of the general formula [PtI(NCN″)] (NCN″ = [C$_6$H$_3$(CH$_2$NRR′)$_2$-2,6]$^-$; R = R′ = Me or Et; or R = Me, R′ = *t*-Bu) is reported. All three complexes contain an end-on (η^1) I$_2$ unit, and these compounds represent the only known isolable organometallic species which contain I$_2$ in this bonding motif. These compounds can be envisioned as representing the initial stages of oxidative addition of dihalides to d^8 transition metal complexes. The complexes [PtI{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}-(η^1-I$_2$)] (**1**) and *exo-meso*-[PtI$_3${C$_6$H$_3$(CH$_2$NMe[*t*-Bu])$_2$-2,6}(η^1-I$_2$)] (**3b**) have been structurally characterized by single-crystal X-ray diffraction methods. Mechanistic and spectroscopic (IR, Raman, NMR, UV/vis) investigations have led to the conclusion that complex **1** is formed via a 1,2-shift of the dihalide from the primary product [Pt(η^1-I$_3$){C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-2,6}]. The role of the metal-bound halide anion as the point of initial attack of I$_2$ is described. The results of these investigations are discussed in terms of the basic mechanism of oxidative addition and its implications for catalysis.

Introduction

The study of the interaction of simple diatomic molecules with d^8 transition metals is crucial for a better understanding of the mechanism of oxidative addition and reductive elimination reactions.[1−3] Reagents such as dihydrogen and alkyl or hydrogen halides react with a variety of mononuclear transition metal complexes[1−5] via a concerted addition mechanism to give a d^6 adduct in which the fragments that have been introduced are in a cis position to one another.[5−7] Oxidative addition reactions based on free-radical chain or nonchain processes usually afford both cis and trans products.[1−4] The oxidative addition of dihalogen molecules is distinctly different, however, and typically yields trans addition products only.[8,9] A possible explanation for this very different behavior is that H$_2$ generally attacks a metal center side-on, while in an imaginary η^2-X$_2$ complex,

the filled p-orbitals of X$_2$ will have a strong repulsive interaction with the electrons of the d$_{z^2}$ orbital of M and hence disfavor the formation of such an adduct. As a consequence, X$_2$ addition to M should be mechanistically different from that of H$_2$. Early kinetic work dealing with the oxidative addition of halogen

---

(2) (a) van Leeuwen, P. W. N. M.; van Koten, G. Homogeneous Catalysis with Transition Metal Complexes. In *Catalysis: An Integrated Approach to Homogeneous, Heterogeneous and Industrial Catalysis*; Moulijn, J. A., van Leeuwen, P. W. N. M., van Santen, R. A., Eds.; Elsevier: Amsterdam, 1993; Chapter 6. (b) Taqui Khan, M. M.; Martell, A. E. *Homogeneous Catalysis by Metal Complexes*; Academic: London, 1974; Vol. I, Chapter 1, and Vol. II, Chapter 4. (c) Parshall, G. W.; Ittel, S. D. *Homogeneous Catalysis: The Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes,* 2nd ed.; Wiley: New York, 1992; Chapters 3 and 12. (d) Brunner, H. Hydrogenation. In *Applied Homogeneous Catalysis with Organometallic Compounds, Vol. 1*; Cornils, B., Herrmann, W. A., Eds.; VCH: Weiheim, 1996; Chapter 2.2. (e) Noels, A. F.; Hubert, A. J. Transition Metal Catalyzed Reductions of Organic Molecules by Molecular Hydrogen and Hydrides, An Overview. In *Industrial Applications of Homogeneous Catalysis*; Morteaux, A., Petit, F., Eds.; Reidel: Dordrecht, 1988; pp 65−92.

(3) Dickson, S. R. *Homogeneous Catalysis with Complexes of Rhodium and Iridium*; Reidel: Boston, 1985.

(4) For examples of free-radical oxidative addition that leads to single geometric isomers only, see: (a) Bradley, J. S.; Connor, D. E.; Dolphin, D.; Labinger, J. A.; Osborn, J. A. *J. Am. Chem. Soc.* **1972**, *94*, 4043−4044. (b) Labinger, J. A.; Kramer, A. V.; Osborn, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 7903−7904. (c) Lappert, M. F.; Lednor, P. W. *J. Chem. Soc., Chem. Commun.* **1973**, 948−949. (d) Hargreaves, N. G.; Puddephatt, R. J.; Sutcliffe, L. H.; Thompson, P. J. *J. Chem. Soc., Chem. Commun.* **1973**, 861−862. Also see: (e) Byers, B. H.; Brown, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 2527−2532.

---

* To whom correspondence should be addressed. Fax: +31-30-252361. E-mail: g.vankoten@chem.uu.nl.
[†] Debye Institute, Utrecht University.
[‡] The Bijvoet Center for Biomolecular Research, Utrecht University.
[§] University of Amsterdam.
[⊥] Universität Erlangen-Nürnberg.
[∥] Moscow State University.
[#] Current address: AnorMED Inc., #100 20353-64th Ave., Langley, BC, Canada V2Y 1N5.

(1) (a) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry,* 5th ed.; Wiley: New York, 1988; Chapter 28.1−28.12 and references therein. (b) Elschenbroich, C.; Salzer, A. *Organometallics: A Concise Introduction,* 2nd ed.; VCH: Weinheim, 1992,; Chapter 17.

η¹-I₂ Organometallic "Pincer" Complexes of Platinum

J. Am. Chem. Soc., Vol. 121, No. 11, 1999 2489

molecules to d^8 TM complexes had strongly suggested the end-on attack mode of the dihalide to form an η^1-X_2 complex to be the inital step.[10] Calculations on the model system $[PtCl_4]^{2-}\cdots F_2$ by Bickelhaupt and co-workers have also supported this idea.[11] Some time ago, we briefly communicated the successful isolation of the first example of an organometallic complex with I_2 bonded in the relevant η^1-X_2 (end-on) bonding mode.[12a] Since then, we have expanded our investigations to include other Group 10 metals containing similar ligands of the general formula $[C_6H_2(CH_2NMe_2)_2$-2,6-R-4]$^-$ (abbreviated as NCN′ in the case of R = H). These versatile "pincer" ligands have two N-donor atoms and a formal aryl carbanion available for coordination to a metal center.[12,13]

In this report, we expand our earlier preliminary communication on the isolation of three organometallic Pt^{II} complexes, **1**, **2**, and **3** (see Figure 1), containing an end-on (η^1)-bound I_2 ligand.[12a,b] This work also includes some mechanistic details of our original Pt system. The results presented are intended to serve not only as static models of the intimate first stages of oxidative addition of halogen molecules to d^8 TM centers (i.e.,
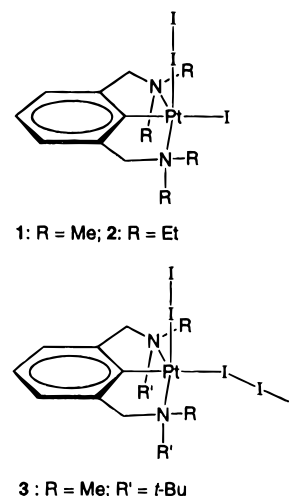

Figure 1. Complexes of I_2 with platinum "pincer" compounds [PtI-(NCN″)].

of relevance to the general understanding of the mechanism of oxidative addition and hence catalysis) but also as representatives of some fundamentally interesting structural features related to synthetic conductive "metallic" materials.[14]

Experimental Section

A. General. The syntheses of [PtX(NCN′)] (X = Cl, Br, I),[12g] [Pt-(NCN′)(OH₂)]BF₄,[15] and [PtI(C₆H₃{CH₂NR¹R²}₂-2,6)] (NCN′Et, R¹ = R² = Et; NCN′Bu, R¹ = t-Bu, R² = Me)[12f] have been described. Solvents were freshly distilled before use. Tetraethylammonium iodide and I_2 were Merck reagents. The former was used as received, while the latter was further purified by sublimation. Tetra-n-butylammonium iodide (Fluka) was recrystallized thrice from EtOH/H₂O (1/2 v/v) to remove traces of I_2. NMR spectra (¹H) were recorded on Bruker AC 100 (100 MHz) or WM 250 (250 MHz) spectrometers. Chemical shifts are reported in ppm using tetramethylsilane as external standard (δ = 0.00 ppm). The UV/vis spectra were recorded on a Perkin-Elmer Lamba 5 spectrometer. Resonance Raman measurements were carried out with a Jobin-Yvon Ramanor HG2S with a Spectra Physics 171 argon ion laser both as solutions (CH₂Cl₂) and as solids mixed with glass (SiO₂) powder. Far-infrared spectra were recorded on a Nicolet 7199 B FT-IR spectrophotometer on powdered samples sandwiched between polyethylene films or as Nujol mulls. IR spectra were recorded on a

(5) (a) Walper, M.; Kelm, H. *Z. Phys. Chem. N. F.* **1978**, *113*, 207−216. (b) Luo, X.-L.; Michos, D.; Crabtree, R. H.; Hall, M. B. *Inorg. Chim. Acta* **1992**, *198−200*, 429−435.

(6) (a) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1965**, *87*, 16−21. (b) Harrod, J. F.; Smith, C. A. *Can. J. Chem.* **1970**, *48*, 870−871. (c) Fawcett, J. P.; Harrod, J. F. *Can. J. Chem.* **1976**, *54*, 3102−3109. (d) Auburn, M. J.; Holmes-Smith, R.; Stobart, S. R. *J. Am. Chem. Soc.* **1984**, *106*, 1314−1318. (e) Auburn, M. J.; Stobart, S. R. *Inorg. Chem.* **1985**, *24*, 318−323. (f) Procopio, L. J.; Carroll, P. J.; Berry, D. H. *J. Am. Chem. Soc.* **1994**, *116*, 177−185. (g) Saillard, J.-Y.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 2006−2026. (h) Halpern, J. *Inorg. Chim. Acta* **1985**, *100*, 41−48. (i) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403−424. (j) Crabtree, R. H. *Chem. Rev.* **1985**, *85*, 245−269. (k) Green, M. L. H.; O'Hare, D. *Pure Appl. Chem.* **1985**, *57*, 1897−1910. (l) Schubert, U. *Adv. Organomet. Chem.* **1990**, *30*, 151−187. (m) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299−338.

(7) Burk, M. J.; McGrath, M. P.; Wheeler, R.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 5034−5039.

(8) (a) Chatt, J.; Shaw, B. L. *J. Chem. Soc.* **1959**, 4020−4033. (b) Hodges, K. D.; Rund J. V. *Inorg. Chem.* **1975**, *14*, 525−528. (c) Hunziker, M.; Rihs, G. *Inorg. Chim. Acta* **1985**, *102*, 39−43. (d) Vicente, J.; Chicote, M.-T.; Martin, J.; Jones, P. G.; Fittschen, C. *J. Chem. Soc., Dalton Trans.* **1987**, 881−886. (e) Jones, R.; Kelly, P. F.; Williams, D. J.; Woollins, J. D. *J. Chem. Soc., Dalton Trans.* **1988**, 1569−1576. (f) van Koten, G.; Terheijden, J.; van Beek, J. A. M.; Wehman-Ooyevaar, I. C. M.; Muller, F.; Stam, C. H. *Organometallics* **1990**, *9*, 903−912.

(9) A detailed discussion of oxidative addition reactions involving Pt^{II} complexes has recently appeared: Rendina, L. M.; Puddephatt, R. J. *Chem. Rev.* **1997**, *97*, 1735−1754 and references therein.

(10) (a) Teggins, J. E.; Martin, D. S., Jr. *Inorg. Chem.* **1967**, *6*, 1003−1006. (b) Poë, A. J.; Vaughan, D. H. *Inorg. Chim. Acta* **1968**, *2*, 159−165. (c) Jones, M. M.; Morgan, K. A. *J. Inorg. Nucl. Chem.* **1972**, *34*, 259−274; 275−296. (d) Hopgood, D.; Jenkins, R. A. *J. Am. Chem. Soc.* **1973**, *95*, 4461−4463. (e) Kuwae, R.; Tanaka, T.; Kawakami, K. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 437−440. (f) van Zyl, G. J.; Lamprecht, G. J.; Leipoldt, J. G. *Inorg. Chim. Acta* **1987**, *129*, 35−37. (g) Drougge, L.; Elding, L. I. *Inorg. Chem.* **1988**, *27*, 795−798. (h) Appleton, T. G.; Clark, H. C.; Manzer, L. E. *J. Organomet. Chem.* **1974**, *65*, 275−287. (i) For studies on the oxidative addition of Cl₂ to Pt^{II} complexes forming stable Pt^{III} dimeric species, see: Bandoli, G.; Caputo, P. A.; Intini, F. P.; Sivo, M. F.; Natile, G. *J. Am. Chem. Soc.* **1997**, *119*, 10370−10376.

(11) Bickelhaupt, F. M.; Baerends, E. J.; Ravenek, W. *Inorg. Chem.* **1990**, *29* 350−354.

(12) (a) van Beek, J. A. M.; van Koten, G.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 5010−5011. (b) van Koten, G. *Pure Appl. Chem.* **1990**, *62*, 1155−1159. (c) Muijsters, J. C.; Niemantsverdriet, J. W.; Wehman-Ooyevaar, I. C. M.; Grove, D. M.; van Koten, G. *Inorg. Chem.* **1992**, *31*, 2655−2658. (d) Baerends, E. J. *Chem. Mag. (Rijswijk, Neth.)* 1993 (Maart), 98. (e) van Beek, J. A. M.; van Koten, G.; Wehman-Ooyevaar, C. M.; Smeets, W. J. J.; van der Sluis, P.; Spek, A. L. *J. Chem. Soc., Dalton Trans.* **1991**, 883−893. (f) van Beek, J. A. M.; van Koten, G.; Dekker, G. P. C. M.; Wissing, E.; Zoutberg, M. C.; Stam, C. H. *J. Organomet. Chem.* **1990**, *394*, 659−678. (g) Terheijden, J.; van Koten, G.; Muller, F.; Grove, D. M.; Vrieze, K.; Nielsen, E.; Stam, C. H. *J. Organomet. Chem.* **1986**, *315*, 401−417. (h) Jastrzebski, J. T. B. H.; van der Schaaf, P. A.; Boersma, J.; van Koten, G.; de Wit, M.; Wang, Y.; Heijdenrijk, D.; Stam, C. H. *J. Organomet. Chem.* **1991**, *407*, 301−311.

(13) (a) Rietveld, M. H. P.; Grove, D. M.; van Koten, G. *New J. Chem.* **1997**, *21*, 751−771. (b) van Koten, G. *Pure Appl. Chem.* **1989**, *61*, 1681−1694. For very recent examples of "pincer" chemistry, see: (c) Dani, P.; Karlen, T.; Gossage, R. A.; Smeets, W. J. J.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **1997**, *119*, 11317−11318. (d) Steenwinkel, P.; Gossage, R. A.; van Koten, G. *Chem. Eur. J.* **1998**, *4*, 759−764. (e) Lagunas, M.-C.; Gossage, R. A.; Spek, A. L.; van Koten, G. *Organometallics* **1998**, *17*, 731−741. (f) Lee, D. W.; Kaska, W. C.; Jensen, C. M. *Organometallics* **1998**, *17*, 1−3 and references therein. (g) Albrecht, M.; Gossage, R. A.; Spek, A. L.; van Koten, G. *Chem. Commun.* **1998**, 1003−1004. (h) Kleijn, H.; Jastrzebski, J. T. B. H.; Gossage, R. A.; Grove, D. M.; van Koten, G. *Tetrahedron* **1998**, *54*, 1145−1154. (i) Schlengermann, R.; Sieler, J.; Jelonek, S.; Hey-Hawkins, H. *Chem. Commun.* **1997**, 197−198. (j) Frey, U.; Grove, D. M.; van Koten, G. *Inorg. Chim. Acta* **1998**, *269*, 322−325.

(14) (a) Ferraro, J. R.; Williams, J. M. *Introduction to Synthetic Electrical Conductors*; Academic Press: New York, 1987. (b) Lin, L.-S.; Marks, T. J.; Kannewurf, C. R.; Lyding, J. W.; McClure, M. S.; Ratajack, M. T.; Whang, T.-C. *J. Chem. Soc., Chem. Commun.* **1980**, 954−955. (c) Hunziker, M.; Loeliger, H.; Rihs, G.; Hilti, B. *Helv. Chim. Acta* **1981**, *64*, 2544−2554. (d) Vicente, R.; Ribas, J.; Sourisseau, C. *Polyhedron* **1986**, *5*, 2033−2038. (e) Braga, D.; Grepioni, F. *Acc. Chem. Res.* **1994**, *27*, 51−56. (f) Caneschi, A.; Gatteschi, D.; Pardi, L.; Sessoli, R. In *Clusters, Chains, and Layered Molecules: The Chemist's Way to Magnetic Materials*; Williams, A. F., Floriani, C., Merbach, A. E., Eds.; Perspectives in Coordination Chemistry; VCH: Weinheim, 1992; pp 109−128. (g) Carter, F. L., Siatkowski, R. E., Wohltjen, H., Eds. *Molecular Electronic Devices*; North-Holland: Amsterdam, 1988.

(15) Grove, D. M.; van Koten, G.; Louwen, J. N.; Noltes, J. G.; Spek, A. L. *J. Am. Chem. Soc.* **1982**, *104*, 6609−6616.

Perkin-Elmer 283 spectrophotometer. Mass spectra (FD and FI) were measured on a Varian MAT 711 spectrometer. Elemental analyses were carried out at the Institute for Applied Chemistry, TNO, Zeist, The Netherlands. Equilibrium measurements were made on a Shimadzu UV-250 spectrophotometer equipped with a temperature-controlled (±0.1 °C) cell compartment. A spectrophotometric cuvette, with a round-bottom flask equipped with a stopper directly attached to it, was used to provide correction for the addition of weighed amounts of I_2 or iodides to avoid dilution. The rates of the fast reactions were measured by using a Dionex D110 stopped-flow instrument.

B. Syntheses. The synthesis of $[PtI(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)(\eta^1\text{-}I_2)]$ (**1**) is described in detail as a representative example. All other complexes were made from the appropriate starting materials ($[PtX\text{-}(NCN')]$ { X = Cl, Br, I}[12g,16] or $[Pt(NCN')(OH_2)]BF_4$ with I_2 or IBr) in a similar fashion.

$[PtI(NCN')(\eta^1\text{-}I_2)]$ (1). To a clear yellow solution of $[PtI(NCN')]$ (0.30 g, 0.6 mmol; CH_2Cl_2, 10 mL) was added iodine (0.17 g, 0.65 mmol). Immediately, a very dark (black) solution was obtained, which was stirred at ambient temperature for 15 min. After this time, the volume of the mixture was reduced to 4 mL (in vacuo), upon which a precipitate formed. Hexane was added (40 mL), and the precipitate was filtered off, washed (hexane, 2 × 10 mL), and dried in vacuo. This procedure gave the product (**1**) as a dark brown/black solid (yield, 0.42 g; 90%). Crystals of **1** that were suitable for X-ray structure analysis were obtained from a solution of **1** in a mixture of CH_2Cl_2 and hexane. Anal. Calcd (found) for $C_{12}H_{19}I_3N_2Pt$: C, 18.79 (19.07); H, 2.50 (2.53); N, 3.65 (3.62); I, 49.63 (49.33).

$[PtI(NCN'Et)(\eta^1\text{-}I_2)]$ (2). The reaction of $[PtI(NCN'Et)]$ (0.34 g, 0.6 mmol) with I_2 (0.152 g, 0.6 mmol) yielded 0.38 g (75%) of **2** as a dark brown/black solid. Anal. Calcd (found) for $C_{16}H_{27}I_3N_2Pt$: C, 23.34 (23.15); H, 3.31 (3.23); N, 3.40 (3.37).

$[PtI(NCN'Bu)(\eta^1\text{-}I_2)]$ (3a). The reaction of $[PtI(NCN'Bu)]$ (0.36 g, 0.6 mmol; the *meso*-form is present as the largest fraction [89%] of this material; residual components are the *rac*-isomers[12f]) with I_2 (0.152 g, 0.6 mmol) yielded 0.36 g (70%) of **3a** as a dark solid with a greenish shine. Anal. Calcd (found) for $C_{18}H_{31}I_3N_2Pt$: C, 25.40 (25.16); H, 3.67 (3.40); N, 3.29 (3.12). A sample of **3a**, which was recrystallized from CH_2Cl_2/hexane, yielded X-ray quality crystals of $[PtI_3(NCN'Bu)(\eta^1\text{-}I_2)]$ (**3b**) as the *exo-meso*-form (see Results section).

C. Reactivity of Complexes 1−3. Reaction of 1 with 1 Equiv of NEt₃. To a solution of **1** (0.31 g, 0.441 mmol) in 4 mL of CH_2Cl_2 was added 1 mL of a 0.41 M solution (CH_2Cl_2) of NEt_3. The reaction mixture was stirred for 30 min. Subsequently, 20 mL of hexane was added, and the resulting precipitate was filtered off to yield 0.01 g of a dark solid. Spectroscopic investigation (^{1}H NMR and IR) of this solid indicated that it was a mixture of **1** and Et_3NI_2. The filtrate was cooled to −20 °C, and after 1 h, 0.10 g of $[PtI(NCN')]$ (0.19 mmol) was collected.

Reaction of 1 with 30 Equiv of NEt₃. The addition of NEt_3 (2.08 mL, 15.0 mmol) to a solution of **1** (0.38 g, 0.50 mmol) in 20 mL of CH_2Cl_2 caused a color change of the mixture from dark brown/red to yellow/orange. After being stirred for 2 h, the solution was reduced in volume to 5 mL, and pentane (40 mL) was added. The resultant white precipitate was collected on a suction filter while a dark-colored, waxy solid was left behind in the reaction flask. Both solids were then dried in vacuo. Yield: 0.14 g of $[PtI(NCN')]$ (0.27 mmol) and 0.07 g of Et_3NI_2 (0.20 mmol).

Reaction of 1 with Na₂S₂O₃·H₂O. To a suspension of **1** (0.09 g, 0.12 mmol) in 10 mL of acetone was added $Na_2S_2O_3$·5H_2O (0.03 g, 0.12 mmol). No reaction was observed, but upon subsequent addition of 0.5 mL of H_2O to dissolve the sodium salt, the color of the reaction mixture turned orange, and all solids subsequently dissolved. After the mixture was stirred for 30 min, volatiles were removed (in vacuo), and the residue was extracted with CH_2Cl_2 (25 mL). This extract was washed with H_2O (2 × 10 mL) and then dried (Na_2SO_4). Following filtration, the solution was concentrated to 4 mL, and hexane (40 mL)

was added. The resulting precipitate was filtered off and dried in vacuo. Yield: 0.03 g of $[PtI(NCN')]$ (0.06 mmol; 50%).

Tests for I₂ with Starch. A saturated individual solution of each of compounds **1−3** in 5 mL of ethanol (prepared by heating a suspension of **1−3** in ethanol to reflux temperature, after which the solid was filtered off) was added to a hot solution of starch in 5 mL of H_2O. Solutions of complexes **1** and **2** did not afford a blue color, but conversely solutions of complex **3** turned a deep blue color.

D. Crystallography. Data Collection and Structure Determination of $[PtI(NCN')(\eta^1\text{-}I_2)]$ (1). A purple crystal of **1** was glued on top of a glass fiber and transferred to an Enraf-Nonius CAD-4F diffractometer for data collection (Zr-filtered Mo Kα radiation). Unit cell parameters were checked for the presence of higher lattice symmetry.[17] Data were corrected for Lorentz polarization, for a small linear increase (2%) of the intensities during the 47 h of X-ray exposure time, and for absorption (Gaussian integration on a 16 × 6 × 6 grid [transmission range 0.351: 0.658]). Standard deviations, as obtained by counting statistics, were increased according to an analysis of the excess variance of the four reference reflections: $\sigma^2(I) = \sigma_{cs}(I) + (0.044(I))^2$.[17b] The structure was solved by standard Patterson methods (SHELXS84).[17c] Refinement on *F* was carried out by full-matrix least-squares techniques. The H atoms were introduced on calculated positions (C−H = 0.98 Å) and included in the refinement riding on their carrier atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. The H atoms were refined with one common isotropic thermal parameter ($U = 0.046(8)$ Å^2). Weights were introduced in the final refinement cycles. Convergence was reached at $R = 0.024$. The absolute structure was checked by refinement with opposite f'' anomalous dispersion factors resulting in significantly higher $R = 0.0627$, w$R = 0.0844$. Neutral atom scattering factors were taken from ref 17d and corrected for anomalous dispersion.[17e]

Data Collection and Structure Determination of $[PtI_3(NCN'Bu)]\text{-}(\eta^1\text{-}I_2)]$ (3b). A brown, block-shaped crystal of **3b** was glued on top of a glass fiber and transferred to an Enraf-Nonius CAD-4F diffractometer for data collection. Unit cell parameters were determined from a least-squares treatment of the setting angles of 25 reflections with $15.3 < \theta < 18.3°$. The unit cell parameters were checked for the presence of higher lattice symmetry.[17a] Data were corrected for Lorentz polarization, for a linear decay (9.1%) of the intensities during the 103 h of X-ray exposure time, and for absorption (PLATON/ABS PSI).[17k] Standard deviation, as obtained by counting statistics, was increased according to an analysis of the excess variance of the two reference reflections: $\sigma^2(I) = \sigma^2_{cs}(I) + (0.062(I))^2$.[17b] The Pt and I atoms were found with direct methods (SHELXS86),[17i] and the remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses. Refinement on F^2 was carried out by full-matrix least-squares techniques. Hydrogen atoms were introduced on calculated positions and included in the refinement riding on their carrier atoms [SHELXL97].[17j] Twenty-nine reflections, which were considered to be too strong and were hampered by attenuation filter malfunction, were excluded from the final refinement cycles. Weights were introduced, and convergence was reached at $R = 0.051$. The residual electron density near Pt and I is interpreted as residual absorption artifacts. All other calculations were performed with PLATON (geometrical calculations and illustrations) on a Dec Alpha computer. Additional numerical details of both structure determinations are given in Table 1.

(16) The complexes $[PtI(NCN'Et)]$ and $[PtI(NCN'Bu)]$ are synthesized in a fashion similar to that described for $[PtI(NCN')]$, i.e., by reacting the in situ lithiated aryl ligand (1 equiv of *n*-BuLi) with 0.8 equiv of $[PtCl_2\text{-}(SEt_2)_2]$, followed by reaction with NaI.[12g,13a,b]

(17) (a) Spek, A. L. *J. Appl. Crystallogr.* **1988**, *21*, 578−579. (b) McCandlish, L. E.; Stout, G. H.; Andrews, L. C. *Acta Crystallogr.* **1975**, *A31*, 245−249. (c) Sheldrick, G. M. *SHELXS84. Program for crystal structure determination*; University of Göttingen, Germany, 1984. (d) Cromer, D. T.; Mann, J. B. *Acta Crystallogr.* **1968**, *A24*, 321−324. (e) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891−1898. (f) Sheldrick, G. M. *SHELX76. Crystal structure analysis package*; University of Cambridge, UK, 1976. (g) Spek, A. L. The EUCLID Package. In *Computational Crystallography*; Sayre, D., Ed.; Clarendon Press: Oxford, 1982. (h) Walker, N.; Stuart, D. *Acta Crystallogr.* **1983**, *A39*, 158−166. (i) Sheldrick, G. M. *SHELXS86. Program for crystal structure determination*; University of Göttingen, Germany, 1986. (j) Sheldrick, G. M. *SHELXL97. Program for crystal structure refinement*; University of Göttingen, Germany, 1997. (k) Spek, A. L. *PLATON: General Crystallographic Tool*; Utrecht University, The Netherlands, 1998.

Table 1. Crystal Data and Details of the Structure Determination for **1** and **3b**

	1	**3b**
Crystal Data		
empirical formula	$C_{12}H_{19}I_3N_2Pt$	$C_{18}H_{31}I_5N_2Pt$
formula weight (g mol^{-1})	767.09	1105.06
crystal system	orthorhombic	triclinic
a (Å)	7.976(2)	11.3887(10)
b (Å)	9.532(2)	11.7359(10)
c (Å)	23.577(7)	11.9973(10)
α (deg)		118.376(10)
β (deg)		94.289(10)
γ (deg)		103.292(10)
V (Å^3)	1792.5(8)	1341.0(3)
Z	4	2
D (calcd) (g cm^{-3})	2.842	2.737
F (000)	1368	992
μ (Mo Kα) (cm^{-1})	129.8	109.9
crystal size (mm)	$0.05 \times 0.11 \times 0.49$	$0.20 \times 0.30 \times 0.40$
Data Collection		
temperature (K)	294	293
radiation (Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
θ min, max (deg)	0.9, 27.3	1.9, 27.5
scan (deg)	$0.40 + 0.35 \tan\theta$	$0.65 + 0.35 \tan\theta$
data set	0:10; 0:12; 0:30	-14:14; -15:0; -13:15
total no. of unique data	2392, 2392	6442, 6145
R(int)		0.056
no. of obsd data [$I > \sigma(I)$]	2101	5781
Refinement		
N_{ref}, N_{par}	2101, 176	6145, 243
R, wR	0.0260,^{a} 0.0320^b	0.0512,^{a} 0.1452^c
S	2.02	1.11
w	$1/\sigma^2(F)$	d
max shift/error	0.03	0.00
min, max resd dens (e Å^3)	-0.73, 0.79	-3.46, 2.60

^{a} R $= (\sum|F_o| - |F_c|)/\sum|F_o|$. ^{b} wR $= [(\sum w(|F_o| - |F_c|)^2)/\sum w|F_o|^2]^{1/2}$. ^{c} wR2 $= [(\sum w(|F_o|^2 - |F_c|^2)^2)/\sum w(|F_o|^2)^2]^{1/2}$. ^{d} $1/[s^2(F_o^2) + (0.0921P)^2 + 9.5941P]$, where $P = (F_o^2 + 2F_c^2)/3$.

Results and Discussion

A. Synthesis and Properties of the I_2 Complexes. The reaction of the platinum(II) complexes [PtI(NCN′)], [PtI-(NCN′Et)], and [PtI(NCN′Bu)] with 1 equiv of I_2 results in the formation of very dark red/brown solids. Elemental analyses of these materials are consistent with molecular formulas corresponding to [PtI$_3$(NCN′)] (**1**), [PtI$_3$(NCN′Et)] (**2**), and [PtI$_3$-(NCN′Bu)] (**3a**), respectively. These compounds are highly soluble in chlorinated organic solvents. The solubilities are much lower in acetone, toluene, or C_6H_6 and are negligible in diethyl ether (Et$_2$O) or hexanes.

Compounds **1**–**3** can be dried in vacuo and washed, on a suction filter, with hexane without the apparent loss of I_2. When complex **3** is recrystallized (CH$_2$Cl$_2$/hexane), black crystals (with a green shine to them) are obtained which contain I_2 and [PtI-(NCN′Bu)] in a ratio of 2:1. Therefore, reactions were carried out in which [PtI(NCN′)], [PtI(NCN′Et)], and [PtI(NCN′Bu)] were treated with 2 equiv of I_2. The first two reactions afforded **1** and **2** as products without extra I_2 becoming incorporated into the lattice of the metal-containing product. The last reaction led to the formation of products with varying amounts of I_2 (i.e., [MI$_n$(L)]; M = Pt, L = NCN′ or NCN′Bu; $3 < n < 5$).

The treatment of solutions of **3** (MeOH) with a starch solution produced the blue coloration typical for the presence of free I_2, no doubt a consequence of release of the dihalide by **3** into the solution. Solutions of **1** and **2** gave negative I_2 tests.

[PtI(NCN′)(η^1-I_2)] (**1**) could also be synthesized by two other methods:

Method 1: the reaction of I_2 with (a) 1 equiv of [PtX(NCN′)] (X = Cl, Br) or (b) [Pt(NCN′)(OH$_2$)(BF$_4$)], producing (a) **1** and [Pt(X)$_3$(NCN′)] or (b) solely **1**.

Method 2: the treatment of XBr (X = Br or I) with 1 equiv of [PtX′(NCN′)] (X′ = Br or I). This mixture yields [Pt(Br)$_3$-(NCN′)] and **1** if X or X′ = I. The yields of product via both of these methods are high (80–90%), and the ratio of the products are roughly as expected from the halide stoichiometry that is used (i.e., the Br:I ratio). These experiments indicate directly that halide scrambling is an integral part of the chemistry of **1**.

A further situation may involve competition between Pt, coordinated I$^-$, and N centers for the binding of free I_2, and therefore this aspect could be an important factor in the mechanism of I_2 addition to Pt. To examine this possibility further, the addition of an organic base to complex **1** was investigated. The addition of 1 equiv of NEt$_3$ (CH$_2$Cl$_2$) to a mixture of **1** (CH$_2$Cl$_2$) produces an equilibrium mixture of **1**, Et$_3$NI$_2$,[18] and [PtI(NCN′)], while the addition of 30 equiv of NEt$_3$ to **1** (CH$_2$Cl$_2$) results only in the formation of Et$_3$NI$_2$ and [PtI(NCN′)]. When 2 equiv of a mild inorganic reducing agent such as hydrated Na$_2$S$_2$O$_3$ or KCN is added to a solution of **1**, I_2 is reduced and [PtI(NCN′)] is obtained.

Unfortunately, the spectroscopic data of the complexes **1**–**3** do not provide sufficient information to make any conclusive structural assignments. This situation is not uncommon in organometallic I_2 chemistry, where the unequivocal assignment for the presence of simple lattice I_2 or coordinated or free $(I_3)^-$ or I$^-$ fragments has been complicated at best.[10h] Complexes **1** and **3b** were therefore selected for analysis by single-crystal X-ray diffraction.

B. Molecular and Crystal Structures of [PtI(C$_6$H$_3$-{CH$_2$NMe$_2$}$_2$-2,6)(η^1-I$_2$)] (1) and *exo-meso*-[PtI$_3$(C$_6$H$_3$-{CH$_2$N(*t*-Bu)Me}$_2$-2,6)(η^1-I$_2$)] (3b). The molecular structures of **1** and **3b** are given in Figures 2 and 3, respectively, along with the adopted atomic numbering schemes. Selected bond lengths and bond angles are given in Tables 2 and 3. Space-filling models of **1** and **3b** are available as Supporting Information.

Complex **1** contains a platinum metal center which is five-coordinate and in a ligand geometry which is best described as distorted square-pyramidal. The metal has bonds to the aryl group (via C(1)) and to two trans-positioned nitrogen atoms of

(18) (a) Stromme, K. O. *Acta Chem. Scand.* **1959**, *13*, 268–274. For related η^1-X$_2$ (X = I, Br, or Cl) adducts, see: (b) Ruthe, F.; du Mont, W.-W.; Jones, P. G. *Chem. Commun.* **1997**, 1947–1948. (c) du Mont, W.-W.; Bätcher, M.; Pohl, S.; Saak, W. *Angew. Chem.* **1986**, *98*, 813–815; *Agnew. Chem.* **1987**, *99*, 945–947. (d) Godfrey, S. M.; Kelly, D. G.; McAuliffe, C. A.; Mackie, A. G.; Pritchard, R. G.; Watson, S. M. *J. Chem. Soc., Chem. Commun.* **1991**, 1163–1164. (e) Brickelbank, N.; Godfrey, S. M.; McAuliffe, C. A.; Pritchard, R. G. *J. Chem. Soc., Chem. Commun.* **1992**, 355–356. (f) Godfrey, S. M.; Jackson, S. L.; McAuliffe, C. A.; Prichard, R. G. *J. Chem. Soc., Dalton Trans.* **1997**, 4499–4502. (g) Godfrey, S. M.; McAuliffe, C. A.; Prichard, R. G.; Sarwar, S. *J. Chem. Soc., Dalton Trans.* **1997**, 1031–1035. (h) Bricklebank, N.; Godfrey, S. M.; Lane, H. P.; McAuliffe, C. A.; Pritchard, R. G.; Moreno, J.-M. *J. Chem. Soc., Dalton Trans.* **1995**, 2421–2424. (i) McAuliffe, C. A.; Beagley, B.; Gott, G. A.; Mackie, A. G.; MacRory, P. P.; Pritchard, R. G. *Angew. Chem.* **1987**, *99*, 237–238; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 264–265. (j) Breunig, H. J.; Denker, M.; Ebert, K. H.; Lork, E. *Z. Anorg. Allg. Chem.* **1997**, *623*, 1151–1156. (k) Stegemann, H.; Oprea, A.; Nagel, K.; Tebbe, K.-F. *Z. Anorg. Allg. Chem.* **1997**, *623*, 89–103. (l) du Mont, W.-W.; Stenzel, V.; Jeske, J.; Jones, P. G.; Sebald, A.; Pohl, S.; Saak, W.; Bätcher, M. *Inorg. Chem.* **1994**, *33*, 1502–1505. (m) Arca, M.; Devillanova, F. A.; Garau, A.; Isaia, F.; Lippolis, V.; Verani, G.; Demartin, F. *Z. Anorg. Allg. Chem.* **1998**, *624*, 745–749. (n) Godfrey, S. M.; McAuliffe, C. A.; Pritchard, R. G.; Sheffield, J. M. *Chem. Commun.* **1998**, 921–922. (o) Tefteller, W., Jr.; Zingaro, R. A. *Inorg. Chem.* **1966**, *5*, 2151–2156 and references therein. (p) Apperley, D. C.; Bricklebank, N.; Burns, S. L.; Hibbs, D. E.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1998**, 1289–1292.
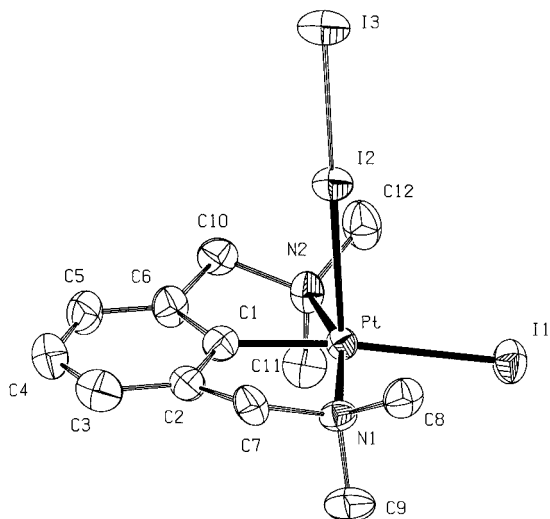
Figure 2. ORTEP diagram of complex **1**.
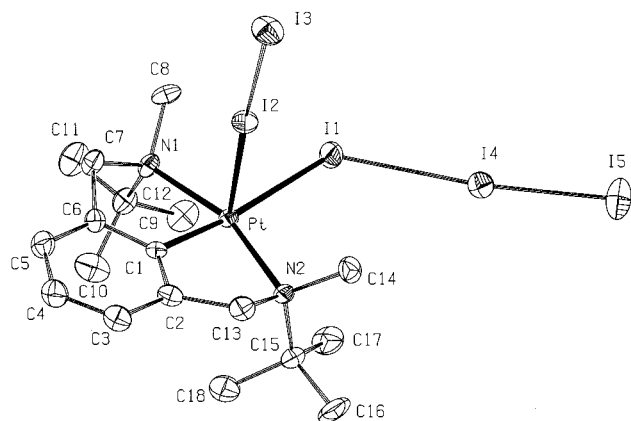
Figure 3. ORTEP diagram of complex **3b**.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **1**

Pt−I1	2.727(1)	I2−Pt−N1	94.5(2)
Pt−I2	2.895(1)	I2−Pt−N2	94.1(2)
Pt−C1	1.93(1)	I2−Pt−C1	84.0(3)
Pt−N1	2.115(8)	N1−Pt−N2	160.6(3)
Pt−N2	2.105(8)	N1−Pt−C1	82.4(4)
I2−I3	2.822(1)	N2−Pt−C1	81.2(4)
I1−Pt−I2	103.46(2)	Pt−I2−I3	179.42(4)
I1−Pt−N1	98.1(2)	Pt−N1−C8	116.5(6)
I1−Pt−N2	96.8(2)	Pt−N1−C9	105.0(6)
I1−Pt−C1	172.4(3)	Pt−N2−C11	105.0(7)
		Pt−N2−C12	117.0(7)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **3b**

Pt−I1	2.772(2)	I2−Pt−N1	95.1(2)
Pt−I2	2.906(2)	I2−Pt−N2	92.9(2)
Pt−C1	1.931(10)	I2−Pt−C1	82.5(3)
Pt−N1	2.152(9)	N1−Pt−N2	161.3(3)
Pt−N2	2.167(9)	N1−Pt−C1	81.8(4)
I2−I3	2.793(1)	N2−Pt−C1	82.4(4)
I1−I4	3.072(1)	Pt−I2−I3	176.91(4)
I4−I5	2.769(2)	Pt−I1−I4	126.82(4)
I1−Pt−I2	88.58(3)	I1−I4−I5	171.53(4)
I1−Pt−N1	96.1(2)	Pt−N1−C8	112.2(7)
I1−Pt−N2	100.9(2)	Pt−N1−C9	112.5(7)
I1−Pt−C1	171.6(3)	Pt−N2−C14	112.2(7)
		Pt−N2−C15	111.7(7)

179°, and the I−I bond lengths are in the range of 2.83(1)−3.41(1) Å.[18,20,21]

The platinum metal center in complex **3b** possesses a coordination sphere similar to that seen with compound **1**; notably, the η^1-coordination of an I_2 ligand to the metal. The Pt−I2 bond length is 2.906(1) Å, and the Pt−I2−I3 angle is 176.91(4)°. The I2−I3 bond distance is 2.793(1) Å. All of these values are similar to those for **1**. One obvious difference between **1** and **3b** is that, in the latter complex, the ligand trans to C(ipso) of the NCN′ system is an I_3 unit. This triiodide is asymmetric and can be considered as a donor−acceptor complex with iodide I1 as the donor atom and I4−I5 as the acceptor fragment (vide supra). The angle I1−I4−I5 is 171.53(4)°, and the I1−I4 and I4−I5 distances are 3.072(1) and 2.769(2) Å, respectively, and are typical when compared to those of related complexes.[22−28] Remarkably, the bulkier alkyl groups are in the axial positions, while the Me groups are in the equatorial positions. Thus, selective crystallization has led to the isolation of the *exo-meso*-form of this compound (i.e., the orientation of the groups on the N atoms is defined as *meso* due to the presence of a mirror plane bisecting the plane formed by Pt and the aryl ring of the NCN′Bu ligand; the coordination of the η^1-I_2 unit is on the *exo* face of the complex).

The molecular structures of **1** and **3b** both have characteristics that are common to many other NCN′ complexes.[13,32] For

the terdentate ligand system in addition to the iodo ligand which is located trans to C1. An additional interaction is observed between Pt and an intact I_2 unit. This is perhaps the most remarkable feature in the molecular structure of **1**, as the I_2 is end-on, η^1-coordinated to the platinum center. The Pt−I2 bond has a length of 2.895(1) Å and is part of a linear Pt−I2−I3 arrangement (angle = 179.43(4)°). The I−I bond distance of the coordinated halogen ligand (2.822(1) Å) is longer than that found in free I_2 (2.715(6) Å).[19] These features represent a previously unprecedented example of end-on η^1-X_2 coordination in an organometallic complex.[12a,b,f] Several of the features can, however, be compared to the bonding of I_2 to main-group elements.[18,20,21] For example, the E−I−I bond angles (where E is a donor atom; e.g., N, P, or As) are all between 173 and

(19) van Bolhuis, F.; Koster, P. B.; Migchelsen, T. *Acta Crystallogr.* **1967**, *23*, 90−91.

(20) (a) Hassel, O.; Romming, C. H. R. *Q. Rev., Chem. Soc.* **1962**, *16*, 1−18. (b) Bent, H. A. *Chem. Rev.* **1968**, *68*, 587−648. (c) Mulliken, R. S.; Person, W. B. *Molecular Complexes*; Wiley-Interscience: New York, 1969. (d) The band of free diiodine is located at 522 nm, with $\epsilon_{max} = 897$ (hexane solution). In the compound Et_3NI_2, this band is found at 414 nm, with $\epsilon_{max} = 2030$.

(21) Note that several examples of complexes with the general formula R_3PI_2 can exist in the neutral η^1-I_2−PR_3 *and/or* the ionic $[R_3PI]^+I^-$ forms in the solid state *or* in solution.[22f−h]

(22) Calderazzo, F.; Poli, R.; Zanazzi, P. F. *Gazz. Chim. Ital.* **1988**, *118*, 595−601.

(23) Ginn, S. G. W.; Wood, J. L. *Chem. Commun.* **1965**, 262−263.

(24) Milan, A.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1982**, 73−77.

(25) Buse, K. D.; Keller, H. J.; Pritzkow, H. *Inorg. Chem.* **1977**, *16*, 1072−1076.

(26) Gray, L. R.; Gulliver, D. J.; Levason, W.; Webster, M. *Inorg. Chem.* **1983**, *22*, 2362−2366.

(27) Gray, L. R.; Gulliver, D. J.; Levason, W.; Webster, M. *Acta Crystallogr.* **1983**, *C39*, 877−879.

(28) Alvarez, S.; Mota, F.; Novoa, J. *J. Am. Chem. Soc.* **1987**, *109*, 6586−6591.

(29) (a) van der Poel, H.; van Koten, G.; Kokkes, M.; Stam, C. H. *Inorg. Chem.* **1981**, *20*, 2941−2950. (b) van der Poel, H.; van Koten, G. *Inorg. Chem.* **1981**, *20*, 2950−2956.

(30) Koster, P. B.; Mighelse, T. *Acta Crystallogr.* **1967**, *23*, 90.

(31) (a) James, S. L.; Veldman, N.; Spek, A. L.; van Koten, G. *Chem. Commun.* **1996**, 253−254. (b) Davies, P. J.; Veldman, N.; Grove, D. M.; Spek, A. L.; Lutz, B. T. G.; van Koten, G. *Angew. Chem.* **1996**, *108*, 2078−2081; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1959−1961. (c) James, S. L.; Verspui, G.; Spek, A. L.; van Koten, G. *Chem. Commun.* **1996**, 1309−1310.

η^1-I_2 Organometallic "Pincer" Complexes of Platinum

J. Am. Chem. Soc., Vol. 121, No. 11, 1999 2493

example, the angle N1−Pt−N2 is less than the ideal value of 180° (160.7(3)° and 161(1)°, respectively). The angle C1−Pt−I1 also differs considerably from 180° (172.3(4)° in **1**, 169(1)° in **3b**). The bond lengths Pt−C$_{aryl}$, Pt−N, and Pt−I are also typical of similar bonds in other NCN' complexes of Pt.[13,29,32] The symmetry aspects with respect to the puckering of the two cyclometalated rings and the relative positions of the N-donor substituents is characteristic for the observed geometries.[29]

C. Crystal Structures. In compound **1**, infinite chains run along the *b*-directed screw axis as a result of the intermolecular contact of 3.595(2) Å of I1 of one molecule with I3 of another molecule (cf. ref 24), which has a similar interaction with a third molecule, etc. Thus, the solid-state structure of **1** contains what can be best described as intermolecular I$^-$···I$_2$ or I$_3^-$ units.

In complex **3b,** however, I$_3$ units are present, but these do not provide gross intermolecular contacts. No infinite chains are found, but only pairs of molecules linked to each other via I$_3$···I$_3$* interactions (I−I distance of 3.640(3) Å) are observed. The intermolecular interactions in "free" (crystalline) I$_2$ have been measured as 3.496(6) Å.[30] Thus, **3b** contains what may be described as a "dimeric" structure in terms of the I$_2$···I$_2$ or formally neutral I$_4$ units.

D. Spectroscopic Data. ^{1}H NMR. Earlier we described the molecular symmetry of a number of square-planar complexes [MX(NCN')] (M = Ni, Pd, or Pt; X = halide or pseudo-halide), and we have detailed the ^{1}H NMR spectra that can be expected from such compounds.[13,14,32] The change of molecular geometry as the metal center adjusts its coordination number from four (square-planar) to five (square-pyramidal) by the addition of another ligand (Y) has obvious consequences on the expected ^{1}H NMR spectra. We assume that the square-pyramidal complexes [PtX(NCN')Y] (X = halide, Y = neutral ligand at an apical site) studied here are similar in general symmetry (and structural) terms to those we have reported in our earlier work involving the simple NCN' ligand.[13,31,32]

These square-pyramidal complexes contain a different chemical environment above and below the plane containing the four basal ligands. This forces a situation in which ligands such as NCN'Bu contain N atoms that are chiral, and therefore four diastereomers should exist: *RR*, *RS*, *SR*, and *SS*. In contrast to the situation observed with square-planar complexes, the *RS* and *SR* forms are not identical (*meso*) compounds but are *endo-exo* diastereomers. The *RR* and *SS* forms (*rac*) are obviously enantiomers, and each consists of a pair of *endo-exo* diastereomers. Hence, three separate sets of resonances (*RS*, *SR*, and *endo-exo*; *rac*) should be observed in the ^{1}H NMR spectrum of a complex such as [PtX(NCN'Bu)Y] (Y = neutral donor), which contains a rigid Pt−Y interaction. The groups attached to N in the molecules of the enantiomeric pair (*RR/SS*) should also show different resonances. The ^{1}H NMR spectrum of **1** at room temperature in CDCl$_3$ solution shows only singlet resonance for both the methyl and the benzylic protons and an AB$_2$ pattern for the aryl protons (Table 4). A striking feature is the complete

Table 4. ^{1}H NMR Data for Complexes **1**, **2**, and **3b**^{a}

complex	aryl-*H*	aryl-C*H$_2$*	NC*H$_3$*	other
1	7.15^b	4.20^{c,d}	3.28^{c,e}	
	6.98			
2	7.00^b	4.09^f		3.61(m)^g
	6.73			2.97(m)^g
				1.52(t)^{b,h}
3b^i	6.96^b	4.30, 4.04^c	3.45^f	1.34^j
	6.65	4.54, 4.01^c	3.28^c	1.53^j

^{a} All data were recorded in CDCl$_3$ solution; chemical shifts are reported in ppm relative to external TMS (δ = 0.00 ppm). All signals are singlets unless otherwise stated; m = multiplet and t = triplet.^{b} J_{H-H} = 7 Hz. ^{c} J^{195}Pt$_{-H}$ is not resolved at room temperature. ^{d} J^{195}Pt$_{-H}$ = 38.3 Hz at 233 K. ^{e} J^{195}Pt$_{-H}$ = 29.8 Hz at 233 K. ^{f} J^{195}Pt$_{-H}$ = 37 Hz. ^{g} NC*H$_2$*CH$_3$. ^{h} NCH$_2$C*H$_3$*. ^{i} Two isomers are observed in a 7:1 ratio; only one AB$_2$ pattern is observed in the aromatic region; benzylic protons appear as an AB pattern with J_{H-H} = 15 and 13 Hz, respectively. ^{j} C−C*H$_3$*.

lack of observed coupling to the ^{195}Pt nucleus ($I = ^1/_2$) of these (slightly broad) signals. At a lower temperature (250 MHz, CD$_2$-Cl$_2$ solution), singlet patterns are still observed that do not change (T > 173 K). Below this temperature level, signal broadening is noted, but this appears to be due to an increase in solvent viscosity only. Even at temperatures as low as 133 K (CD$_2$Cl$_2$/Freon 22 solution; 1:2 ratio), no changes in the resonance patterns are observed. Platinum couplings do finally appear, however, at low temperatures. The ^{1}H NMR spectra of the complexes **2** and **3b** show an unexpected feature: they are strikingly similar to those of the parent square-planar complexes [PtI(NCN'Et)] and [PtI$_3$(NCN'Bu)], respectively. The only changes are subtle differences in the chemical shift values. The spectra of **3a** and **3b** show no significant differences, and both reveal the presence of only two isomers in a 7:1 molar ratio (see Table 4; the parent compound shows isomers in a similar ratio; selective crystallization of the *meso*-form was observed, see below).[14] The benzylic protons show two AB patterns, but $^3J(^{195}$Pt−^{1}H) coupling constants are not observed. The ^{1}H NMR spectra of **2** and **3** are temperature independent (250 MHz, CD$_2$-Cl$_2$, ambient to 173 K).

Resonance Raman and Far-IR Data. The Resonance Raman (RR) spectra give some information about the nature of the diiodine species that are present in solution or in the solid state. A band in the region 210−215 cm^{-1} indicates the presence of free I$_2$.[33] As this is the first report detailing η^1-I$_2$ organometallic complexes, there are no reports or data of other complexes to compare with. However, our interpretation is based on the frequencies found in the RR spectra of organic (donor−acceptor) I$_2$ complexes.[34] Thus, absorptions in the region 150−165 cm^{-1} are attributed to the stretching frequency of I$_2$ bonded η^1 to the platinum(II) center. Finally, bands near 120 cm^{-1} can be attributed to the symmetric stretching frequency of an I$_3^-$ species, although this assignment is not unambiguous.[35,36] The RR and far-IR spectral data can be found in Table 5.

UV/Vis Data. The UV/vis spectra are not easy to interpret, but these results serve as a good starting point in establishing what sort of complex is obtained. The UV/vis spectra of the

(32) For further examples of square-planar (a−d), octahedral (e−f), and square-pyramidal (g) complexes with the NCN' ligand, see: (a) Grove, D. M.; van Koten, G.; Ubbels, H. J. C.; Vrieze, K.; Nieman, L. C.; Stam, C. H. *J. Chem. Soc., Dalton Trans.* **1986**, 717−724. (b) Grove, D. M.; van Koten, G.; Ubbels, H. J. C.; Spek, A. L. *J. Am. Chem. Soc.* **1982**, *104*, 4285−4286. (c) Grove, D. M.; van Koten, G.; Ubbels, H. J. C.; Zoet, R.; Spek, A. L. *Organometallics* **1984**, *3*, 1003−1009. (d) Terheijden, J.; van Koten, G.; de Booys, J. L.; Ubbels, H. J. C.; Stam, C. H. *Organometallics* **1983**, *2*, 1882−1883. (e) Grove, D. M.; van Koten, G.; Mul, W. P.; van der Zeijden, A. A. H.; Terheijden, J.; Zoutberg, M. C.; Stam, C. H. *Organometallics* **1986**, *5*, 322−326. (f) Terheijden, J.; van Koten, G.; Mul, W. P.; Stufkens, D. J.; Muller, F.; Stam, C. H. *Organometallics* **1986**, *5*, 519−525. (g) Grove, D. M.; van Koten, G.; Zoet, R.; Murrall, N. W.; Welch, A. J. *J. Am. Chem. Soc.* **1983**, *105*, 1379−1380.

(33) Downs, A. J.; Adams, C. J. In *Comprehensive Inorganic Chemistry, Vol. 2*; Trotman-Dickenson, A. F., Ed.; Pergamon Press: Oxford, 1973.

(34) Cataliotti, R. S.; Paliani, G.; Santini, S.; Zgierski, M. Z. *J. Mol. Struct.* **1986**, *142*, 171−177.

(35) (a) Barbati, A.; Calderazzo, F.; Poli, R.; Zanazzi, P. F. *J. Chem. Soc., Dalton Trans.* **1986**, 2569−2579. The structures of [PPh$_3$I]I$_3$ and [(Ph$_3$-PI)$_2$I]I$_3$ have been reported: (b) Cotton, F. A.; Kibala, P. A. *J. Am. Chem. Soc.* **1987**, *109*, 3308−3312.

(36) (a) Goggin, P. L.; Goodfellow, R. J.; Reed, F. J. S. *J. Chem. Soc., Dalton Trans.* **1974**, 576−585. (b) Goodfellow, R. J.; Taylor, B. F. *J. Chem. Soc., Dalton Trans.* **1974**, 1676−1684.
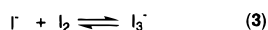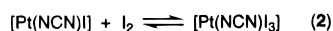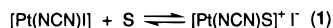
Table 5. Resonance Raman,[a] Far-Infared,[b] and UV/Vis Data[c] for Complexes **1**, **2**, and **3**

complex	Raman	far-IR	UV/vis
1	152,[d] 85[d] 153[f]	150, 135 132, 102 93	289, 311(sh)[e] 370, 500
2	151,[d] 80[d] 209,[f] 156[f] 123[f]	150	276, 301(sh) 365, 500
3	174,[d] 105[d] 210,[f] 155[f] 121[f]	150, 119	290, 313(sh) 370, 500

[a] Measurements in the solid state were performed by mixing the solids with glass powder; solutions were recorded in CH_2Cl_2. [b] **1** was measured as a solid; **2** as a Nujol mull, and **3** by both techniques using polyethylene windows. All values are in units of cm^{-1}. [c] Measured in CH_2Cl_2 solution, λ_{max} in nm. [d] Solid state. [e] sh = shoulder. [f] Solution.

starting complexes [PtX(NCN″)] (X = Cl, Br, I; NCN″ = NCN′, NCN′Bu, or NCN′Et) show one band in the region of 280−295 nm. Spectra of the oxidative addition products [Pt-(X)₃(NCN″)] do not display distinct bands. The spectra of the new I_2 complexes all show basically the same spectra, consisting of one very intense band between 275 and 290 nm, containing a shoulder in the region of 300−310 nm, a second strong band between 350 and 370 nm, and finally a fourth weak band at 500 nm (see Table 5).

E. Thermodynamic Investigations. In an attempt to gain further insight into the early stages of the reaction which results in the formation of complex **1**, we carried out a series of mechanistic investigations using UV/vis spectroscopy and stopped-flow techniques. Equations 1−3 show three possible equilibria that are likely to occur in solution for the complex [PtI(NCN′)] in the presence of excess I_2.

$$[Pt(NCN)I] + S \rightleftharpoons [Pt(NCN)S]^+ I^- \quad (1)$$

$$[Pt(NCN)I] + I_2 \rightleftharpoons [Pt(NCN)I_3] \quad (2)$$

$$I^- + I_2 \rightleftharpoons I_3^- \quad (3)$$

S = solvent molecule

The equilibrium to be considered is comprised of solvolysis of the iodo ligand (eq 1), since the coordinated aryl group exerts a strong trans labilizing influence on the Pt−I bond.[13a] Equation 2 shows the addition of I_2 to [PtI(NCN′)]. The site of addition is not specified here and can be either the iodo ligand or the Pt center (below). Finally, eq 3 is the well-known generation of the triiodo anion,[35] which appears to play a role in this chemistry.

The formation of I_3^- occurs very rapidly on mixing solutions of I_2 and I^- in CH_2Cl_2 as solvent, and this interaction is accompanied by the development of two intense bands in the UV region. The position of these bands and the ratio of their intensities is of diagnostic importance.

The generation of triiodo species is virtually irreversible in CH_2Cl_2 in the concentration range that was used in this study ([n-Bu₄NI] = (0.21−1.4) × 10⁻⁴ M; [I₂] = (1.7−6.9) × 10⁻⁴ M). There is no evidence that the solvolysis of the Pt−I bond (i.e., eq 1, Pt−I bond cleavage and formation of [Pt(NCN′)(S)]⁺I⁻ {S = solvent molecule}) plays any role in the CH_2Cl_2 solution.[37] Complex [Pt(NCN′)I] has an absorption maximum at 286 nm in this solvent, and the spectrum remains unchanged in the range of concentrations of [Pt(NCN′)I] and n-Bu₄NI ([0.63−6.04] × 10⁻⁵ and [0.47−5.74] × 10⁻⁴ M, respectively). The addition of I_2 to CH_2Cl_2 solutions of [Pt(NCN′)I] gives rise to immediate and drastic spectral changes (Table 6). The spectral parameters demonstrate that I_2 binds to the initial Pt complex ([Pt(NCN′)I])

Table 6. Spectral Characteristics of I_2, I^-, and [PtI(NCN′)][a]

system	$\lambda 1^b$	$\lambda 2^b$	$\epsilon 1^c$	$\epsilon 2^c$	A1/A2
$I_2 + I^-$	295	366	47 300	27 500	1.72
[PtI(NCN′)]	305	370	25 300	22 400	1.13

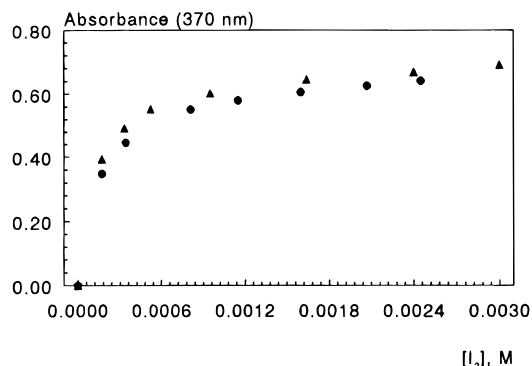[a] All data were collected in CH_2Cl_2 solution. [b] In nm. [c] In M^{-1} cm^{-1}.

Figure 4. Plot of absorbance at 370 nm for [PtI(NCN′)] in CH_2Cl_2 following the addition of I_2. Filled circles and filled triangles represent the data at 39.5 and 25.0 °C, respectively. The concentration of the Pt complex is 3.2 × 10⁻⁵ M. Filled circles and filled triangles represent the data at 39.5 and 25.0 °C, respectively. The concentration of the Pt complex is 3.2 × 10⁻⁵ M.

rather than to dissociation products. At the same time, a "two-headed" spectral profile is observed, which closely resembles the spectrum of free I_3^-, although it is slightly perturbed. This suggests that this anion has been formed and that it is *coordinated* in solution. Hence, this result strongly suggests that the complex [Pt(NCN′)(I₃)] is present. The latter conclusion is corroborated by the ¹H NMR data in CDCl₃ or CD₂Cl₂ solution (vide supra) and indicates that the initial coordination of I_2 to [Pt(NCN′)I] occurs at the metal-bound *halide* atom, and not on the Pt nucleus itself. From the plot of absorbance vs [I₂] (see Figure 4), it is obvious that the equilibrium shown in eq 2 is reversible in CH_2Cl_2 (note that iodine absorbs only slightly at this wavelength in this system). Plots of A^{-1} vs [I₂] are linear (not shown), in accordance with the formation of a 1:1 complex as shown in eq 2. Attempts to determine the enthalpy and entropy of complexation did not lead to data of sufficient quality. However, the values obtained suggest that the reaction is almost thermoneutral.

F. General Considerations. I_2 Complexes: Their Importance in Organometallic Chemistry. The reaction of organometallic compounds with halogen reagents can lead to many different products which arise from either oxidative addition, simple oxidation (with halides as counterions),[1,11a,38,39] Pt−C

(37) (a) In MeCN solution, complex [PtI(NCN)] rapidly undergoes solvolysis according to eq 1 (i.e., [PtI(NCN)] + MeCN ′ [Pt(NCN)-(MeCN)]⁺I⁻), and hence the liberated iodide reacts much faster with I_2 than with the solvated Pt complex. Stopped-flow investigations (MeCN solution) of residual unsolvated [PtI(NCN′)] indicate that the rate-determining step in the formation of **1** is the rearrangement of the observed intermediate, [Pt(I₃)(NCN′)], as k_{obs} is independent of [I₂]. The calculated values of $\Delta H\pi$ and $\Delta S\pi$, 62.1 ± 1.9 kJ mol⁻¹ and −19.5 ± 6.2 J K⁻¹ mol⁻¹, respectively, do not contradict this proposal: Ryabov A. D.; van Eldik, R. Unpublished results. Also see: (b) Ryabov, A. D.; Kazankov, G. M.; Yatsimirsky, A. K.; Kuz'mira, L. G.; Burtseva, O. Yu.; Dvortsova, N. V.; Polyakov, V. A. *Inorg. Chem.* **1992**, *31*, 3083−3090. (c) Schmülling, M.; Ryabov, A. D.; van Eldik, R. *J. Chem. Soc., Chem. Commun.* **1992**, 1609−1611. (d) Schmülling, M.; Ryabov, A. D.; van Eldik, R. *J. Chem. Soc., Dalton Trans.* **1994**, 1257−1263.

(38) (a) Stephenson, N. C. *J. Inorg. Nucl. Chem.* **1962**, *24*, 791−795. (b) Stephenson, N. C. *J. Inorg. Nucl. Chem.* **1962**, *24*, 797−800.

(39) (a) Coronas, J. M.; Muller, G.; Rocamora, M. *J. Organomet. Chem.* **1986**, *301*, 227−236. (b) Johnston, L. J.; Baird, M. C. *Organometallics* **1988**, *7*, 2469−2475.

bond cleavage,[39] or halogenation of the metal-bound aromatic ring.[40] When I$_2$ is used, an additional possibility is the formation of polyiodide compounds, either by I$^-\cdots$I$_2$ interactions[28] or by incorporation of I$_2$ into stacks within the crystal lattice.[14,41]

The molecular structures of the compounds **1** and **3b** represent the first crystallographically characterized examples in which I$_2$ is bonded to an organometallic fragment in an η^1-bonding motif. The isolation of these complexes is interesting because they show very subtle interactions with what are traditionally viewed as somewhat reactive electrophiles. These reagents predominately lead to oxidative addition reactions. The η^1-I$_2$ metal coordination has been envisioned as representing an essential first step in the oxidative addition of dihalogens to d^8 square-planar transition metal complexes. In the case of the donation of two electrons from a platinum orbital to the dihalogen, the resulting oxidative addition would take place via an S$_N$2-type mechanism[9,13] and thus lead to the expected trans products.

Factors Influencing the η^1-Metal Dihalogen Bond. The η^1-I$_2$-Pt^{II} bond is a result of overlap of the filled d$_{z^2}$ platinum orbital with the empty σ^* orbital of I$_2$.[11,12a-e] Therefore, the complex may be more accurately described as a simple donor–acceptor complex (with I$_2$ as the acceptor), and the formal electron count at Pt remains 16.[12c] This is further corroborated by the X-ray data for complex **1** (vide supra). The structural similarities of **1** and **3** with organic donor–acceptor complexes (i.e., η^1-I$_2$-ER$_n$ complexes: R = alkyl or aryl group; E = N, P, SP, or SeP, n = 3; E = S, n = 2) support this.[18] We have encountered this situation earlier, such as in the case of η^1-complexation of SO$_2$ (via S) to [PtBr(NCN′)],[32g,h] the η^2-bonding of the Sn–Br bond of Me$_2$SnBr$_2$ to the neutral complex [Ir-(C$_6$H$_4${CH$_2$NMe$_2$}-2)(COD)] (COD = cyclooracta-1,5-diene) and in the compound [Pt(NCN′)(C$_{11}$H$_{16}$N$_2$)AgBr], which contains an intramolecular Pt$\cdots$Ag interaction.[12b,42]

The factors that influence the thermodynamic or kinetic preference for oxidative addition, donor–acceptor complexation (as in **1**), or nonbonding interactions between a metal fragment and I$_2$ can be summarized as follows:

(i) Ligand Rigidity and/or Steric Effects. In contrast to the present situation, the reaction of *cis*-[Pt(C$_6$H$_4${CH$_2$NMe$_2$}-2)$_2$] or *cis*-[Pt(C$_{10}$H$_6${NMe$_2$}-8)$_2$] with I$_2$ result in the formation of *trans*-(I)$_2$Pt^{IV} oxidative addition products.[8f] The starting materials for these reactions contain bidentate C,N-donor ligands and hence differ from (NCN″) in terms of ligand rigidity (i.e., stonger chelate binding, **3b**) and lower steric buttressing.

(ii) Ligand Donor Capacity. More basic ligands should increase the nucleophilic character of the metal center. This, in principle, shifts the balance to favor electron transfer or oxidative addition. Thus, the greater basicity of the (t-Bu)MeN donors in [PtI(NCN′Bu)] in comparison to the Me$_2$N donors in [PtI-(NCN′)] is reflected in an improved donor capacity of the iodide ligand trans to C(ipso), the result of which is the formation of a triiodide adduct in the reaction with I$_2$.

(iii) Acceptor Ligands. The fact that we have isolated Pt–I$_2$ complexes and no[43] dibromine, dichlorine, or interhalogen complexes is understandable from a standpoint that I$_2$ is the best electron acceptor but at the same time the mildest oxidizing agent of all the (inter)halogens (vide infra).[33]

The Nature of the Complexes in Solution. The spectroscopic data of the complexes in solution suggest that the structures in this phase are not necessarily retained in the solid state. All spectroscopic data point to the existence of equilibria between different forms of the reactants and products in solution. This may explain why material obtained from recrystallizing a reaction product which has a satisfactory elemental analysis for the molecular formula C$_{18}$H$_{31}$N$_2$PtI$_3$ (**3a**) also contains C$_{18}$H$_{31}$N$_2$-PtI$_5$ (**3b**) and probably the parent compound. In solution, however, both the crystalline material and the reaction product exhibit almost identical spectroscopic behavior. Obviously, one of the compounds present in solution crystallizes selectively.

The ^{1}H NMR spectrum of [PtI(NCN′)(η^1-I$_2$)] (**1**) can be accounted for by assuming that, at room temperature, the fast exchange limit is observed for a process in which the Pt–I$_2$ complex is undergoing some form of isomerization, such as the rapid interconversion between the η^1-I$_2$–Pt case and a Pt–I$_3$ complex (i.e., a 1,2-shift of the I$_2$ molecule along the Pt–I bond). This may be the reason for the apparently equal magnetic environment for the diastereotopic methyl (and benzylic) protons on the NMR time scale at ambient temperature. The low-temperature spectra reveal that this exchange process is fast on the NMR time scale.[44] Recall that the thermodynamic evidence above does suggest the formation of a weak complex, although the connection between this weak (thermodynamic) ground-state interaction and the η^1-I$_2$–Pt $\leftrightarrow$ Pt–I$_3$ isomerization is uncertain (vide supra). The slight broadening of the signals cannot be explained by exchange processes nor by chemical shift anisotropy (CSA). However, the formation of a paramagnetic complex as a reactive intermediate cannot be eliminated solely from these data.[11j,45] Thus, the ^{1}H NMR spectra for [Pt-(NCN′Et)(η^1-I$_2$)] (**2**) and [PtI$_3$(NCN′Bu)(η^1-I$_2$)] (**3b**) could also be accounted for by a process similar to that described for **1** above.[46]

In processes where free I$_2$ does not play a significant role, the diiodine molecules may be coordinated to another atom (i.e., not Pt or I) before binding to platinum; examples are known of metal complexes in which I$_2$ is bonded to one of the ligands, such as the NCN′ ligand.[47,48] Candidates for I$_2$ binding include the aryl ring or the N donor atoms of the terdentate NCN′ ligand system or possibly the solvent. In the case of CH$_2$Cl$_2$ or CDCl$_3$ as solvent, a role for the solvent as a donor or transfer agent

(40) (a) Coulson, R. D. *J. Chem. Soc., Dalton Trans.* **1973**, 2459−2462. (b) Walker, R.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1975**, 272−276. (c) Gupta, B. D.; Kumar, Roy, S. *Inorg. Chem.* **1989**, *28*, 11−18. (d) Sutter, J.-P.; Grove, D. M.; Beley, M.; Collin, J.-P.; Veldman, N.; Spek, A. L.; Sauvage, J.-P.; van Koten, G. *Angew. Chem.* **1994**, *106*, 1359−1362; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1282−1285. (e) Chattopadhyay, S.; Sinha, C.; Basu, P.; Chakravorty, A. *Organometallics* **1991**, *10*, 1135−1139. (f) Chattopadhyay, S.; Sinha, C.; Basu, P.; Chakravorty, A. *J. Organomet. Chem.* **1991**, *414*, 421−431.

(41) Hunziker, M.; Hilti, B.; Rihs, G. *Helv. Chim. Acta* **1981**, *64*, 82−89.

(42) van der Zeijden, A. A. H.; van Koten, G.; Wouters, J. M. A.; Wijsmuller, W. F. A.; Grove, D. M.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1988**, *110*, 5354−5361.

(43) Preliminary results indicate the existence of the dibromide complex [PtBr(NCN′Bu)(η^1-Br$_2$)] in solution at −56 °C: van Beek, J. A. M.; van Koten, G. Unpublished results. The structure of [Pt(Br)$_3$(NCN′)] (X-ray) confirms that oxidative addition of Br$_2$ to the Pt center of [PtBr(NCN′)] has occurred at room temperature: Albrecht, M.; Gossage, R. A.; van Koten, G.; Spek, A. L.; Smeets, W. J.; van Beek, J. A. M. Manuscript in preparation.

(44) We incorrectly reported the presence of $^3J(^{195}$Pt−^{1}H) in the spectrum of **1** at room temperature.[13a]

(45) The T_1 values for the resonances at δ = 3.28 (C*H$_3$*) and 4.20 ppm (C*H$_2$*) are 0.691(2) and 0.905(2) s, respectively (250 MHz) and 0.687(1) and 0.902(2) s, respectively (100 MHz). For CSA, see: (a) Brévard, C.; Granger, P. *Handbook of High-Resolution Multinuclear NMR*; John Wiley and Sons: New York, 1981. (b) Shaw, D. *Fourier Transform NMR Spectroscopy*, 2nd ed.; Elsevier: Amsterdam, 1984.

(46) For a theoretical investigation of 1,2-shifts in related [Pt^{II}(NCN′)L] complexes leading to arenium species, see: Ortiz, J. V.; Havlas, Z.; Hoffmann, R. *Helv. Chim. Acta* **1984**, *67*, 1−17.

(47) (a) Kuwae, R.; Tanaka, T.; Kawakami, K. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 427−340. (b) Kuwae, R.; Tanaka, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1067−1071.

(48) Hartl, H.; Steidl, S. *Z. Naturforsch.* **1977**, *B32*, 6−10.

can be ruled out. The aryl ring is a very weak donor, and an aryl-I_2 complex should exhibit some of the characteristics of solutions in which free diiodine is present.[20] The presence of free amine donors is sufficient to remove I_2 from complex **1** (vide supra). However, the N centers in complexes **1**–**3** are strongly coordinated to platinum, which rules them out as diiodine transfer agents.[32h] This leaves the iodide ligand bound trans to C(ipso) as the only candidate for binding the I_2 molecules in an intermediate stage of the exchange process. The nucleophilic character of the iodo ligand compares favorably with that of the Pt metal center, and a halide anion of this type has been previously shown to form stable donor–acceptor compounds with, for example, Group 10 metal complexes.[32g,h]

The proposed intermediate triiodide ion is well-known and has been previously observed both as "free" anions in solution and coordinated to metal centers.[20,23] Indeed, I_3^- may play a role in the exchange processes in solutions of **1**–**3**. Evidence for this includes the following:

(i) A triiodide fragment is found in the molecular structure of **3**.

(ii) The crystal structure of **1** reveals close intermolecular $I^- \cdots I_2$ contact distances which may be viewed as representing the presence of loose I_3^- units.

(iii) The RR spectra of **2** and **3** in solution show bands at 123 and 121 cm^{-1}, respectively. These can be attributed to the ν_2 or symmetric stretching frequency of an asymmetric I_3^- unit. Normally this value is found in the range 90–110 cm^{-1}.[14c,49] The observation of ν_2 suggests that the triiodide is asymmetric; this can be due to binding interactions with a platinum center. Unfortunately, the ^{195}Pt NMR spectra of **2** and **3** showed only one broad band, and no more information could be obtained.

(iv) A number of reactions, apart from that of [PtI(NCN′)] with I_2, yield complexes **1** and **3** (vide supra). This indicates that the halide ligand trans to C(ipso) of the (NCN′) system has been cleaved. By far the most likely way for this to occur is via a trihalide intermediate, since simple solvolysis has been ruled out (vide supra). This can then cleave from the platinum center and rearrange; e.g., I–Br–Br^- can convert to Br–I–Br^-,[28] followed by recoordination to the metal. This results in halide scrambling. The observed products can be accounted for if one considers that IBr or ICl can rearrange in solution to the dihalogens I_2 (which will coordinate) and X_2 (X = Br or Cl; this will lead to oxidative addition). The function of trihalides in the scrambling of halides in octahedral Pt^{IV} complexes has been previously described.[10g]

For complex **1**, chemical arguments are provided for the assumption that such trihalides are present and play a significant role in the solution behavior, but in contrast to those of **2** and **3**, the RR spectrum of **1** does not show any bands that can be attributed to I_3^-. The UV/vis data of complexes **1**–**3** do not obey the Lambert–Beer law, which again strongly suggests that there are equilibria processes in solution (cf. NMR data). This also means that the UV/vis spectra are comprised of overlapping bands, a situation which makes further interpretation extremely difficult. The method of constant addition,[50] in these cases of I_2, does not lead to "stable" bands. Thus, as long as I_2 is added, all peaks increase in intensity. Nevertheless, some conclusions can be drawn from the UV/vis data. The spectrum of **1** exhibits a clear pattern with intense bands. The band at 297 nm is attributed to a π–π^* transition in the ligand system and is similar to that found in many complexes with the NCN′ ligand.

(49) Sorai, M.; Nishimori, A.; Hendrickson, D. N.; Dong, F.-Y.; Cohn, M. J. *J. Am. Chem. Soc.* **1987**, *109*, 4266–4275.

(50) Bauman, R. P. *Absorption Spectroscopy*; John Wiley and Sons: New York, 1984.

Scheme 1
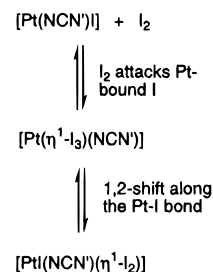
The band at 370 nm may be due to the coordinated I_2 (η^1-I_2–Pt), as coordinated diiodines usually show a blue shift and increased intensity.[20d] The band at 500 nm may be partly due to free I_2 in solution; however, this band and the accompanying band at 370 nm are far too intense to be attributed to free diiodine only. Most probably, these are the bands caused by the presence of triiodide ions. This anion is known to have a $\lambda_{max} = 295$ nm ($\epsilon = 4.51 \times 10^4$ M^{-1} cm^{-1}) and $\lambda_{max} = 365$ nm ($\epsilon = 2.53 \times 10^4$ M^{-1} cm^{-1}).[51] This helps to explain the constant increase in intensity of all bands upon addition of diiodine. Thus, the bands at 295 and 365–370 nm are probably due to formation of extra I_3^-, and the absorbance at 500 nm is due to free I_2 and to overlap with the shoulder of the bands at 365 nm. Although the spectra of **2** and **3** resemble that of **1**, the bands, especially those in the 365–370-nm region, are less intense.

An abundance of chemical and spectroscopic evidence has been found for the existence of complex exchange processes in the solutions of **1**, **2**, and **3**. All these data lead to the proposal for the exchange processes outlined in Scheme 1. The exchange can take place via dissociation/association of I_2, formation and dissociation of I_3^-, or intramolecular exchange via I_3^-. The formation of the final η^1-coordinated compound probably takes place by a 1,2-shift of the I_2 molecule, with the η^1-I_2 complex as the thermodynamically most stable species. Obviously, it is this species that is found in the solid state.

A final question is why complexes **1**, **2**, and **3** are stable at all. Noteworthy is the observation that replacement of coordinated iodide in [PtI(NCN′)] by a tolyl group results in facile oxidative addition by I_2 to form [Pt(I)$_2$(tolyl)(NCN′)].[8f] In analogy to the situation for the equilibrium η^2-H_2 coordination/dihydride formation, an equilibrium between η^1-I_2 coordination and Pt–(I)$_2$ formation can be envisioned. The I–I bond could be cleaved in an S_N2-type process, forming a Pt^{IV} cation and I^-; the attack of I^- then produces the neutral Pt^{IV}(I)$_2$ product.[8f,12,13] Obviously, the Pt(η^1-I_2) product is thermodynamically more stable than the oxidative addition products, i.e., the prerequisite cationic species [Pt(I)$_2$(NCN′)]$^+$ and the neutral complex [Pt-(I)$_3$(NCN′)]. In the latter case, this may be due to the steric interference between three (bulky) iodo ligands and the NCN′ system.[52]

One cannot rule out the possibility that the variety of the I_2 adducts observed here arise only during phase changes from the solution to the solid state, i.e. during recrystallization.[18n]

(51) Buckles, R. E.; Yuk, J. P.; Popov, A. I. *J. Am. Chem. Soc.* **1952**, *74*, 4379–4381.

(52) The complexation between [Pt(NCN′)I] and I_2 occurs very rapidly in CH_2Cl_2 (room temperature) and is, unfortunately, too fast to be measured by stopped-flow kinetics. Polar solvents appear to readily initiate the solvolysis of the ligand trans to the Pt–C bond, and the iodide anion thus formed will be the first species to react with I_2.[38] This has obvious serious consequences if the free iodide or free I_3^- resulting from it competes with the Pt complex (i.e., a catalyst) for attack on substrate molecules. In terms of catalyst performance, this may greatly affect reaction rates and/or product selectivity.

η^1-I_2 Organometallic "Pincer" Complexes of Platinum

J. Am. Chem. Soc., Vol. 121, No. 11, 1999 2497

The results here have not allowed us to unequivocally conclude exactly where, in apolar solvents, the incoming I_2 unit attacks first, but solvolysis of [Pt(NCN′)I] does not appear to play a significant role, and thus the formation of a coordinated I_3^- unit is strongly indicated. Thus, the source of complex **1** is very likely the result of a 1,2-shift from the thermodynamically unstable complex [Pt(η^1-I_3)(NCN′)] (i.e., initial attack of I_2 at I−Pt; Scheme 1). A combination of the kinetic and UV/vis data lends support to this latter complex being formed in the reaction profile. In either case, only 1:1 Pt:I_2 adducts are observed, and thus neither μ^2-I_2-bridged dimers[32g,h] nor (η^1-I_2)$_2$ complexes appear to any significant extent in this chemistry, both in a kinetic and thermodynamic sense.

This suggests that metal-bound halides, which are traditionally viewed merely as "spectator ligands", may be playing a very important function as intra(or inter-)molecular transfer agents or as mediators of substrate approach and/or entry to the reactive (presumably metallic) site.

This tendency for prior η^1-I_3 formation has been implied by in situ observation and by the isolation and crystallographic characterization of both classes of I_2-bonding; i.e., the η^1-I_2 case (complex **1**, a thermodynamic product that is probably formed via a 1,2-shift from an η^1-I_3 complex) and the isolable η^1-I_3 case (complex **3b**, a model of the hypothesized initial I_2 bonding mode [above] that leads to **1**).

Conclusions

This investigation has been used to examine some primary aspects of the mechanism of the oxidative addition of halogens to d^8 organometallic complexes. Compound **1**, [PtI(C_6H_3{CH_2-NMe_2}$_2$-2,6)(η^1-I_2)], is the first crystallographically characterized organometallic η^1-I_2 complex, and it is thus a model for an initial stage of oxidative addition of X_2 molecules to a transition metal. This chemistry is found to be very sensitive to changes in the metal center (i.e., Pt forms stable η^1-I_2 complexes, but Pd does not[53]) and the chelating ligand environment (cf. the reactivity of Pt[II] complexes containing monoanionic terdentate N,C,N′ [or ECE; E = P, S, etc.] donor ligands with related bidentate monoanionic C,N-analogues such as 2-{di-methylaminomethyl}benzenide). The presence of other ligands or anions appears to play a pivotal role in this chemistry, as is demonstrated by the reactivity of halogen molecules with [PtL-(NCN″)], specifically the very different outcome when the complex containing L = *p*-tolyl is used[8f] when compared to the case of L = halide.[12b] The function or necessity of these metal halide units in the halogen scrambling of dihalides (vide supra) and related reactivity,[12a,b,13a−c,32a−d,53] in addition to catalysis,[13d,f,32i,54] should not be underestimated. In this regard, the role of ancillary ionic ligands in palladium-mediated Heck reactions has recently been discussed by Shaw.[55]

Supporting Information Available: Tables of crystal data, fractional coordinates of the non-hydrogen atoms, anisotropic thermal parameters, fractional coordinates of the hydrogen atoms, bond distances and angles of the non-hydrogen atoms, and bond distances and angles of the hydrogen atoms for complexes **1** and **3b**, and space-filling models of these complexes (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

JA982095Z

(53) Reaction of [Pd(NCN′)I] with I_2 (1 equiv) yields a product which loses I_2 when washed with hexanes. However, recrystallization of this product from a CH_2Cl_2/hexanes mixture yields a crystalline material, from which black crystals with [PdI(NCN′)·(I_2)$_2$] stoichiometry were isolated. An X-ray structure determination revealed that this material consists of [PdI-(NCN′)] molecules and separate I_2 molecules (two per Pd) which, however, do have different close-contact interactions with each other: van Beek, J. A. M.; Spek, A. L.; Van Koten, G. *Acta Crystallogr.*, submitted.

(54) (a) Grove, D. M.; van Koten, G.; Verschuuren, A. H. M. *J. Mol. Catal.* **1988**, *45*, 169−174. (b) Grove, D. M.; Verschuuren, A. H. M.; van Koten, G.; van Beek, J. A. M. *J. Organomet. Chem.* **1989**, *372*, C1−C5. (c) Granel, C.; Dubois, Ph.; Jérôme, R.; Teyssié, Ph. *Macromolecules* **1996**, *29*, 8576−8582.

(55) Shaw, B. L. *New J. Chem.* **1998**, *22*, 77−79.