obtained with the following parameters: [{Cu(etam)(ClO₄)}₂]·2CH₃OH, $J = -72 \pm 5$ cm⁻¹, $g = 1.99$, $N\alpha$ fixed at 750×10^{-12} m³ mol⁻¹; [{Cu(pta)(ClO₄)}₂], $\bar{J} = -380 \pm 25$ cm⁻¹, $g = 2.10$, $N\alpha = 330 \times 10^{-12}$ m³ mol⁻¹; [{Cu(pta)(dmso)}₂](ClO₄)₂, $J = -430 \pm 25$ cm⁻¹, $g = 2.15$, $N\alpha = 1400 \times 10^{-12}$ m³ mol⁻¹. See Figure 5.

Spectroscopic Properties. The perchlorate compounds in acetonitrile all have a single broad asymmetric d–d band, plus a more intense band in the near-UV that is characteristic of dinuclear copper(II) compounds. The intensity of this band is notably greater for the pta compounds, which have the largest spin-coupling constant, J (λ, nm (ϵ, mol⁻¹ m²): eta, 617 (16), 386 (25); etam, 633 (14), 391 (33); etae, 625 (16), 388 (33); pta, 595 (13), 373 (160). The d–d bands for the solids are broad and asymmetric, the maxima for the perchlorate compounds shifting from 570 nm for the purple pta compound through 617 nm for the blue eta compound to 625 nm for the blue-green etam/eta compounds. The band shifts to lower energy for the dmso adducts.

The compounds shown to have weakly coordinated perchlorate groups show doublet ν_3(ClO₄⁻) bands in the infrared spectra (cm⁻¹): eta, 1098, 1063; pta, 1095, ca. 1073; etam, 1095, ca. 1073; etae, broad with poorly resolved detail. The dmso adducts show a singlet ν_3(ClO₄⁻) band (pta, 1085 cm⁻¹) or closer doublets, the splitting attributed to hydrogen-bonding interactions (eta, 1094, 1082 cm⁻¹; etam, 1096, 1081 cm⁻¹).

The compounds of eta and pta show a strong ν(NH) band near 3270 cm⁻¹.

Discussion. The structures of a number of dinuclear diamine olato compounds of Cu(II) have been determined and attempts made to correlate the antiferromagnetic spin-coupling parameter J with various structural parameters.[3] As a general observation, for similar ligands, the coupling is much larger when the chelate link to the oxygen, N–(CH₂)ₙ–O⁻, contains three or more members ($n > 2$) than when $n = 2$. Correlations of J with the O–Cu–O angle, planarity about the bridging oxygen atom (as evidenced by the sum of the bond angles at the oxygen), Cu–Cu distance, tetrahedral distortion of the N₂CuO₂ plane (τ = dihedral angle between N₄Cu₂ and Cu₂O₂ least-squares planes), magnitude of axial interactions (displacement of Cu from the N₂O₂ plane and the distance of Cu to the axial donor atom), Cu–O and Cu–O′ distances, etc., have been reported and are often satisfactory for closely similar groups of compounds. These parameters are interrelated, and all may have some relevance to the extent to which electron spins on the copper atoms can be coupled via the orbitals of the bridging oxygen atom.

The values of these parameters (Table V) for the highly spin-coupled pta compound, relative to the non-spin-coupled or very weakly spin-coupled eta compounds all shift in the directions expected.

For the ligand etam, with the 7-(methoxymethyl) substituent on the cage, the perchlorato compound shows an intermediate level of spin coupling ($J = -72$ cm⁻¹), but unfortunately a crystal suitable for a structural study could not be found. The dmso adduct of the compound, which obeys the Curie–Weiss relationship down to 95 K ($\Theta = 4$ K), indicating very little spin coupling, was structurally investigated, and the relevant structural parameters are closer to the values for the eta compounds. The Cu–O (apical) distances are shorter; the displacement of the Cu from the mean equatorial plane, Δ(Cu), and the tetrahedral distortion of the equatorial donor atoms τ are larger for the dmso adducts 2 and 3 than for the perchlorato compounds 1 and 4. The smaller spin coupling for the etam–dmso adduct than for the perchlorato compound thus arises essentially from the stronger axial interaction of the dmso oxygen, but unfortunately the way this interaction affects the structural parameters is unknown.

Supplementary Material Available: Details of diffraction data collection and structure solution and listings of anisotropic thermal parameters (Table VI), hydrogen atom coordinates (Table VII), bond lengths and angles involving hydrogen atoms for [{Cu(pta)(ClO₄)}₂] (Table VIII), selected least-squares planes (Table IX), and observed and calculated structure factors (Table X) (77 pages). Ordering information is given on any current masthead page.

Registry No. **1**, 96165-68-3; **2**, 96165-70-7; **3**, 96193-95-2; **4**, 96165-71-8; {Cu(etam)(ClO₄)}₂, 96165-72-9; {Cu(etae)(ClO₄)}₂, 96165-73-0; [{Cu(pta)(dmso)}(ClO₄)₂, 96193-97-4; {Cu(etah)(ClO₄)}₂, 96165-74-1; [ptad]ClO₄, 96165-76-3; [H(etad)]ClO₄, 96165-77-4.

Contribution from the Istituto Chimico G. Ciamician, Università di Bologna, 40126 Bologna, Italy,
Istituto di Chimica Generale, Università di Milano, 20133 Milano, Italy,
and Dipartimento di Chimica, Università di Napoli, 80134 Napoli, Italy

Five- vs. Four-Coordination in Platinum(II)–Olefin Complexes with Bidentate Nitrogen Ligands

VINCENZO G. ALBANO,† FRANCESCO DEMARTIN,‡ AUGUSTO DE RENZI,*§ GIANCARLO MORELLI,§ and ANTONIO SAPORITO§

Bidentate nitrogen ligands (N–N) can bind the fragment PtCl₂(olefin) to give five- or four-coordinate species. In the latter case N–N acts as a monodentate or a bridging ligand. The ¹H NMR spectra of [PtCl₂(N–N)(olefin)] complexes provide information on the metal coordination number through the chemical shift of the olefin protons. The crystal and molecular structures of the two complexes [PtCl₂(C₂H₄)(Me₂CHN═CHCH═NNMe₂)] (**1d**) (monoclinic, space group $P2_1/c$; $a = 8.710$ (1) Å, $b = 15.400$ (1) Å, $c = 10.753$ (1) Å, $\beta = 99.16$ (1)°; $Z = 4$; $R_w = 3.8\%$) and [PtCl₂(*E*-CH₃CH═CHCH₃)(Me₃CN═CHCH═NCMe₃)] (**4g**) (orthorhombic, space group $P2_12_12_1$; $a = 6.969$ (5) Å, $b = 10.675$ (7) Å, $c = 26.009$ (15) Å; $Z = 4$; $R_w = 4.6\%$) have been determined by single-crystal X-ray diffraction. An attempt to correlate the geometry of the complexes with the electronic and steric properties of the nitrogen ligands and of the coordinated olefins is presented.

Introduction

Five-coordinate species have been postulated for a long time[1] as intermediates in substitution reactions involving platinum(II) complexes, but theoretical speculations[2] seemed to exclude the possibility that stable complexes with such a coordination number could be isolated. The few five-coordinate platinum(II) complexes described until 1973 seemed to be very unusual species that could only be obtained with a particular choice of ligands.[3] However,

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†Università di Bologna.
‡Università di Milano.
§Università di Napoli.

(1) See e.g.: Basolo, F.; Pearson, R. G. "Mechanism of Inorganic Reactions"; Wiley: New York, 1967.
(2) Nyholm, R. S.; Tobe, M. L. "Essay in Coordination Chemistry"; Birkhausen Verlag: Basel, Switzerland, 1964; p 112.

Table I. ^{1}H NMR Data of the N–N Ligands^a

ligand	CH=NR	CH=NN	(CH₃)C=NR	CH₃C=NN	(CH₃)₂NN=	(CH₃)₃CN=	(CH₃)₂CHN=	(CH₃)₂CHN=
DHB (a)				2.10 s	2.63 s			
DHE (b)		7.02 s			2.93 s			
DHBIE (c)	8.00 d	7.03 d			3.03 s	1.23 s		
DHPIE (d)^b	8.00 d	6.93 d			3.00 s		3.4 m	1.17 d
DHPIP (e)^b		6.99 s		2.10 s	3.00 s		3.9 m	1.20 d
		6.68 s		2.33 s	3.17 s			
DHBIP (f)	7.90 s		2.15 s		2.70 s	1.27 s		
BIE (g)	7.97 s					1.23 s		
PIE (h)	8.00 s						3.5 m	1.25 d
BIP (i)^c	8.23 s					1.33 s		

^{a}Spectra recorded at 60 MHz in CDCl₃ solution; chemical shift in δ with Me₄Si as internal standard. ^{b}The two sets of signals are due to a restricted rotation around the C–C bond; the two isomers are in a 3:2 approximate ratio. ^{c}Chemical shifts for the aromatic protons are δ 8.47 d, 7.94 m, 7.47 m, and 7.00 m.

it has subsequently been shown[4,5] that a ligand environment comprising a π-acid species, e.g. an alkene, and a chelating nitrogen ligand, with good σ-donor properties, is apt to promote five-coordination in platinum(II) complexes. In the last few years several five-coordinate olefin complexes of platinum(II) of general formula [PtCl₂(N–N)(olefin)], where N–N is a bidentate nitrogen ligand, have been synthesized and characterized.[4]

Steric effects appear to be important in determining the formation of these compounds. In fact, results[6] concerning a series of R₂N(CH₂)ₙNR₂ ligands, with R = CH₃, show that when n increases from 2 to 4 the tendency toward formation of five-coordinate complexes decreases. The five-membered chelate ring, although involving an exceptionally small N–Pt–N angle, is much more effective in stabilizing five-coordination than the larger rings.[6] Square-planar compounds, where N–N acts as a monodentate ligand, are obtained when n = 4. Furthermore, when N–N is a N,N′-substituted 1,2-ethanediamine, and the olefin is ethylene, and increase of the steric demand of the N substituents decreases[4c] the rate of the olefin release according to the dissociation reaction

$$[PtCl_2(N-N)(olefin)] = [PtCl_2(N-N)] + olefin$$
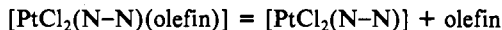
In this paper we are going to examine the influence of substitution on the N–N and/or the olefin ligands on the coordination number for a series of olefin complexes of platinum(II) with N–N ligands having trigonal N-donor atoms.

Results

All the investigated complexes were prepared by adding, at 0 °C, the stoichiometric amount of N–N (providing a 1:1 Pt:ligand ratio) to a methanol solution containing the [PtCl₃(olefin)]⁻ anion (method A) or to a suspension in methylene chloride of the binuclear species [PtCl₂(olefin)]₂ (method B). The N–N ligands are reported in Figure 1, and their ^{1}H NMR parameters are listed in Table I. For all these ligands the ethylene (**1**), the propene (**2**), and the E-2-butene (**4**) complexes were prepared. The DHB, DHBIE, BIE, and BIP complexes of 1-butene (**3**), E-3-hexene (**5**), and E-cyclooctene (**6**) were also isolated. All complexes could be recrystallized from several solvent mixtures and could be stored in the cold for weeks without decomposition. The only exception
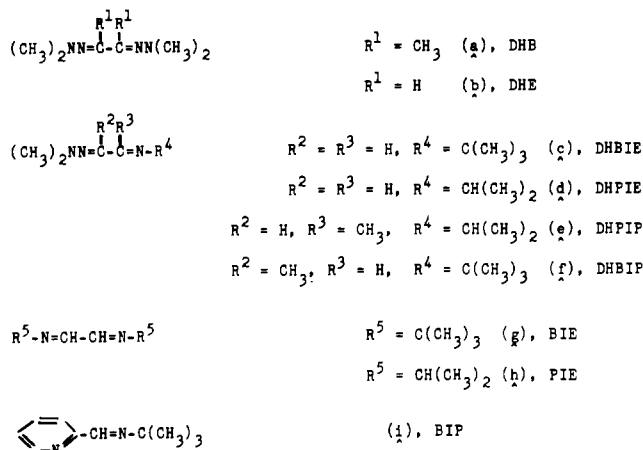

Figure 1. N–N ligands with the notations used in the text.

is the E-2-butene–DHPIP (**4e**) complex, which was not isolated in the solid state owing to extensive decomposition but was identified by ^{1}H NMR spectroscopy in the reaction medium. In addition, a slow temperature-dependent olefin loss was observed in solution for the BIP–olefin complexes, affording the [PtCl₂(BIP)] species.

Elemental analyses and molecular weight determinations were in good agreement with the general formula [PtCl₂(N–N)(olefin)] for all complexes, except **4h**, which is binuclear and has the formula [Pt₂Cl₄(E-CH₃CH=CHCH₃)₂(PIE)]. Conductivity measurements ruled out ionic species.

Infrared spectra showed for all compounds a single intense absorption band centered at 340 cm⁻¹, which is typical for two chlorine atoms mutually trans.[7]

Two different coordination geometries can be conceived for the [PtCl₂(N–N)(olefin)] species, since N–N can behave as a monodentate ligand in a square-planar complex or as a bidentate ligand in a trigonal-bipyramidal five-coordinate compound:
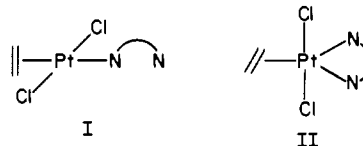

In the absence of X-ray structural determinations, several spectroscopic methods can provide information on the metal coordination number. It was observed,[4c] for instance, that five-coordinate Pt(II)–olefin complexes show in their electronic spectra two absorption bands centered near 32 000 and 27 000 cm⁻¹ that are considered[8] characteristic of trigonal-bipyramidal species. In our case this method proved to be unsuccessful, since the pattern of the electronic spectra appeared to be much more related to the

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(4) (a) Maresca, L.; Natile, G.; Cattalini, L. *Inorg. Chim. Acta* **1975**, *14*, 79. (b) Maresca, L.; Natile, G.; Calligaris, M.; Delise, P.; Randaccio, L. *J. Chem. Soc., Dalton Trans.* **1976**, 2386. (c) De Renzi, A.; Panunzi, A.; Saporito, A.; Vitagliano, A. *Gazz. Chim. Ital.* **1977**, *107*, 549. (d) De Renzi, A.; Di Blasio, B.; Saporito, A.; Scalone, M.; Vitagliano, A. *Inorg. Chem.* **1980**, *19*, 960. (e) Van der Poel, H.; Van Koten, G.; Van Stein, G. C. *J. Chem. Soc., Dalton Trans.* **1981**, 2164. (f) Van der Poel, H.; Van Koten, G.; Kokkes, M.; Stam, C. H. *Inorg. Chem.* **1981**, *20*, 2941. (g) Van der Poel, H.; Van Koten, G. *Ibid.* **1981**, *20*, 2950.

(5) (a) Clark, H. C.; Manzer, L. E. *Inorg. Chem.* **1974**, *13*, 1966. (b) Manzer, L. E. *Ibid.* **1976**, *15*, 2354.

(6) Maresca, L.; Natile, G.; Cattalini, L. *J. Chem. Soc., Dalton Trans.* **1979**, 1140.

(7) See ref 3b, pp 242–243.

(8) Norgett, H. J.; Thornley, J. H. M.; Venanzi, L. M. *J. Chem. Soc. A* **1967**, 540.

Table II. ^{1}H NMR Data of the [PtCl$_2$(N–N)(olefin)] Complexes[a]

com-plex	olefin $\rangle\!=\!\langle$ [c]	others	CH=NR	CH=NN	(CH$_3$)C=NR	(CH$_3$)C=NN	(CH$_3$)$_2$-NN=	(CH$_3$)$_3$-CN=	(CH$_3$)$_2$-CHN	(CH$_3$)$_2$-CHN
1a[d]	3.44 (69) s					2.47 s	3.08 s			
1b	4.20 (66) s			7.64 (26) s			3.81 s			
1c	4.64 (58) s		8.27 (85) d	8.11 bd			3.30 s	1.67 s		
1d	4.72 (60) s		8.13 (95) d	7.83 d			3.27 s		4.25 m	1.55 d
1e	4.07 (72) s			7.79 s	2.23 s		3.42 s		4.25 m	1.63 d
1f	3.46 (72) s		8.42 (40) s			2.46 s	3.13 s	1.64 s		
1g	3.55 (70) s		8.71 (36) s					1.69 s		
1h[e]	3.62 (76) s		8.58 (40) s						4.25 m	1.63 d
1i[e]	3.57 (69) s		8.88 (36) s					1.72 s		
2a[d]	4.05 m, 3.54 m, 3.50 m	1.21 (45) d				2.48 s, 2.42 s	3.10 s, 3.05 s			
2b	5.61 m, 4.61 m, 4.56 m	1.82 (38) d		8.07 (30) s			3.18 s			
2c	5.57 m, 4.56 m, 4.53 m	1.83 (35) d	8.19 (85)[f]	8.21[f]			3.27 s	1.66 s		
2d	5.64 m, 4.60 m, 4.57 m	1.88 (34) d	8.07 (92) d	7.94 d			3.27 s		4.22 m	1.55 d
2e	5.45 m, 4.50 m, 4.48 m	1.77 (35) d		8.49 s	2.39 s		3.27 s		4.32 m	1.67 d
2f	4.19 m, 3.58 m, 3.53 m	1.22 (45) d	8.42 (38) s			2.44 bd	3.12 s, 3.10 s	1.64 s		
2g	4.80 m, 4.01 m, 3.98 m	1.45 (48) d	8.78 (36) s					1.62 s		
2h	5.18 m, 4.29 m, 4.26 m	1.67 (45) d	8.70 (42) s						4.20 m	1.54 d
2i	4.33 m, 3.60 m, 3.57 m	1.33 (45) d	8.83 (35) s					1.70 s		
3a	4.00 m, 3.50 m, 3.47 m	1.9 m; 1.16 t				2.05 s, 2.43 s	3.10 s, 3.04 s			
3c	5.36 m, 4.57 m, 4.49 m	2.2 m, 1.9 m; 1.31 t	8.20 (80)[f]	8.23[f]			3.26 s	1.66 s		
3g	4.85 m, 4.14 m, 4.10 m	2.1 m, 1.9 m; 1.23 t	8.81 (36) s					1.60 s		
3i	4.26 m, 3.57 m, 3.54 m	1.9 m; 1.31 bt	8.85 (32) s					1.74 s		
4a[d]	4.05 (95) bq	1.21 (60) bd				2.45 s	3.05 s			
4b	5.39 (56) bq	1.80 (28) bd		8.07 (24) s			3.15 s			
4c	5.28 (60) bq	1.81 (26) bd	8.12 (82) d	8.27 d			3.27 s	1.65 s		
4d	5.32 (56) bq	1.80 (28) bd	8.00 (84)[f]	8.05[f]			3.24 s		4.17 m	1.53[i]
4e[g]	5.3 (62) b	1.73 (u) d, 1.77 (u) bd		8.64 s	2.38 s		3.23 s		4.22 m	1.62 d
4f	4.70 (68) bq	1.46 (40) bd	8.85 (24) s			2.52 s	3.11 s	1.53 s		
4g[e]	5.31 (64) bq	1.77 (32) bd	8.91 (40) s					1.55 s		
4h[h]	5.49 (60) bq	1.83 (u) bd	9.60 (84) s						4.74 m	1.66[i]
4i	4.54 (70) bq, 4.37 (65) bq	1.37 (40) d, 1.45 (40) d	8.95 (27) s					1.68 s		
5a	4.00 (100) m	1.9 m; 1.10 t				2.42 s	3.04 s			
5c	5.14 (60) m	1.8 m, 2.1 m; 1.24 t, 1.22 t	8.17 (90)[f]	8.19[f]			3.25 s	1.66 s		
5g	5.21 (52) m	1.9 m, 2.2 m; 1.24 t, 1.21 t	8.80 (40) s					1.55 s		
5i	4.40 (68) m, 4.24 (65) m	1.6 m, 2.0 m; 1.26 t, 1.15 t	8.92 (28) s					1.67 s		
6a	4.08 (72) m	2.1–1.7				2.45 s	3.06 s			
6c	5.17 (60) m	2.4–1.9	8.25 (82)[f]	8.27[f]			3.25 s	1.65 s		
6g	5.16 (58) m	2.4–1.9	8.74 (36) s					1.68 s		
6i	4.35 (70) m, 4.10 (68) m	2.3–1.9	8.80 (32) s					1.73 s		

[a] Spectra recorded at 270 MHz in CDCl$_3$ solution; chemical shifts are with Me$_4$Si as internal standard; J_{PtH} coupling constants, in brackets, are in Hz. Legend for multiplicity: s = singlet; d = doublet; q = quartet; m = multiplet; b = broad. [b] Average values of the chemical shifts of the aromatic protons in 1i–6i complexes are δ 9.2 d ($^3J_{Pt-H}$ = 20–25 Hz), 8.0 m, 7.8 m, and 7.65 m. [c] Coupling constants of the olefinic protons in the propene and 1-butene complexes are in the range 70–80 Hz for complexes 2a, 2f–2i, 3a, and 3i and in the range 60–65 Hz for the complexes 2b–2e, 3c, and 3g. [d] See: De Renzi, A.; Panunzi, A.; Saporito, A.; Scalone, M.; Vitagliano, A. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 535. [e] See ref 4f. [f] AB quartet. [g] The spectrum was recorded on the crude reaction mixture that contains at least two components, probably a mononuclear and a binuclear Pt complex. Figures refer to the most abundant mononuclear species. [h] Binuclear complex of formula [Pt$_2$Cl$_4$(E-CH$_3$CH=CHCH$_3$)$_2$(PIE)]. [i] Complex multiplet, see text.

type of the N–N ligand than to the geometry of the complex.[9] A recent study[10] of the photoelectron spectra of a series of four- and five-coordinate platinum(II)–olefin complexes showed that in the latter case higher Pt 4f binding energy values are generally observed, thus indicating a higher π back-donation. However, since the effect is modest, the available data are not sufficient and an unambiguous assignment of the coordination number with

this technique is not feasible. At present ^{1}H NMR spectroscopy is the most straightforward way to discriminate between the two situations. A substantial upfield shift (>1 ppm) has been reported[4] in previous papers for the olefinic proton resonances in five-coordinate in comparison with square-planar complexes containing monodentate ligands with N donor atoms similar to those in N–N. In addition, significantly larger (>10 Hz, as an average) Pt–H coupling constants are reported[4] for the five-coordinate species.[11]

(9) An unequivocal of the coordination geometry can be carried out by comparison of circular dichroism spectra of Pt(II) complexes containing enantiotopically coordinated prochiral olefins: De Renzi, A., to be submitted for publication.

(10) Morelli, G.; Polzonetti, G.; Sessa, V. *Polyhedron*, in press.

(11) The features of the ^{1}H NMR spectra indicate a larger metal-to-olefin π back-donation in five-coordinate species and agree with XPS results (see text) and with the lack of reactivity of the coordinated alkene toward nucelophiles.[4c]

The relevant features of the ^{1}H NMR spectra of all the investigated complexes are reported in Table II. Some of the listed compounds were described previously, and their features are included for comparison.

^{1}H NMR Studies. Ethylene Complexes. The olefin proton resonances show that the ethylene complexes (**1a–1i**) can be separated in three groups. Complexes **1a**, **1f**, **1g**, **1h**, and **1i** display chemical shifts (of the olefin protons) between δ 3.4 and 3.6 ($^2J_{Pt-H}$ = ca. 70 Hz) and should be five-coordinate, according to the previous observations. The data for complexes **1c** and **1d** ($\delta_{C_2H_4}$ 4.6 and 4.7, respectively, $^2J_{Pt-H}$ = ca. 60 Hz) suggest a square-planar geometry with monodentate N–N trans to the olefin. In such a case two different isomers could be formed for each of the two complexes since both ligands **c** and **d** have chemically inequivalent nitrogen donors (($CH_3)_2NN$= and R^4N=). The spectra show only one signal for each set of chemically equivalent protons. In particular, the two methyne protons adjacent to the sp^2 hybridized nitrogens give rise to two distinct doublets, of which only one is Pt coupled. The spectral pattern is substantially unaffected[12] by temperature changes until –90 °C. Although these data do not exclude the possible equilibrium **1c′**, **1d′** ⇌ **1c″**, **1d″**,
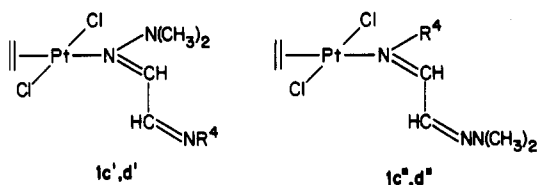
they indicate that it should be very fast on the ^{1}H NMR time scale and clearly shifted toward one isomer. However, a precise structural assignment is not trivial, since the chemical shifts of the two methyne protons in the complexes **1c** and **1d** both differ from those observed in the free ligands **c** and **d**. As an example, the free ligand **c** shows two doublets centered at δ 8.00 (CH=NR^4) and 7.03 (CH=NN(CH$_3$)$_2$), while the complex **1c** presents a Pt-coupled doublet at δ 8.27 ($^3J_{Pt-H}$ = 95 Hz) and another doublet at δ 8.11. Whatever the correct assignment of these two signals, a large downfield shift is observed for the resonance due to the CH=NN(CH$_3$)$_2$ proton. Previous studies[13] on the coordination mode of diimines of the type RN=CHCH=NR (R = alkyl group) to d^8 ions, in particular Pd(II), have shown that when these ligands bind in a monodentate fashion, the favored conformation of the coordinated diimine is all trans in a plane normal to the metal coordination plane. This arrangement brings the methyne hydrogen near the uncoordinated nitrogen just beneath the metal atom and is responsible[14] for the remarkable downfield shift of its resonance in the ^{1}H NMR spectrum. On these grounds, the reasonable hypothesis that the ligands **c** and **d** coordinate to platinum(II) in **1c** and **1d** through the iminic nitrogen can be made. This hypothesis has been confirmed by the X-ray structural investigation on **1d** (vide infra). Finally, the data reported in Table II indicate a particular behavior for the two complexes **1b** and **1e**. The $\delta_{C_2H_4}$ and $^2J_{Pt-H}$ values are between the two typical ranges for four- and five-coordinate complexes. The magnetic equivalence of the halves of the N–N ligand **b** is not sufficient to rule out a four-coordinate species. In fact, the same type of spectrum could be obtained by fast head-to-tail inversion of monodentate N–N in a square-planar complex. Nevertheless, the high-field shift of the olefinic proton resonance that is observed at low temperature (i.e.: $\delta_{C_2H_4}$ = 3.80 for **1b** at –27 °C) is indicative of a fluxional behavior. This result suggests that the intermediate values of the ^{1}H NMR parameters are due to fast interconversion of the two geometries:
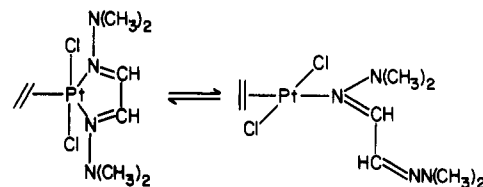
A similar finding and a similar explanation were presented[8] for the ethylene–Pt(II) complex with (CH$_3$)$_2$N(CH$_2$)$_3$N(CH$_3$)$_2$. It is noteworthy that in the solid state complex **1b** is found[15] to have a trigonal-bipyramidal geometry but lacks the expected C_{2v} symmetry because of the buckling of the N–N loop.

Monosubstituted Olefin Complexes. Complexes containing a monosubstituted olefin, such as propene (**2**) and 1-butene (**3**), were obtained. The complexes of **2** were synthesized with all the nine investigated N–N ligands. By application of the reasoning discussed above for the ethylene complexes to the ^{1}H NMR data of the propene compounds **2a–2i**, it appears reasonable to ascribe a trigonal-bipyramidal geometry only to **2a**, **2f**, and **2i** ($\delta_{=CH}$ 4–4.3, $\delta_{=CH_2}$ 3.5–3.6, $^2J_{Pt-H}$ = 75–80 Hz). For these complexes a significant upfield shift of the =CCH$_3$ proton signals is also observed ($\delta_{=CCH_3}$ 1.2–1.3). In addition, it has been reported[4f] that the barrier to the rotation of the olefin around the Pt–alkene bond is slightly higher in five- than in four-coordinate olefin complexes. In fact, a distinct doubling of the ligand proton resonances is present in the ^{1}H NMR spectrum of **2a** recorded at room temperature. No such doubling is observed for complexes **2f** and **2i**, in spite of the presence of chemically nonequivalent nitrogens in the ligand, but the broadening of the olefin proton resonances points to a restricted rotation of the coordinated propene. All signals in fact double at –50 °C. Complexes **2b**, **2c**, **2d**, and **2e** are four-coordinate species, as indicated by the chemical shifts of the olefinic protons ($\delta_{=CH}$ 5.5–5.6, $\delta_{=CH_2}$ 4.5–4.6, δ_{CH_3} 1.8–1.9). Note that ligand **b**, which provides ethylene complex **1b** with a fluxional behavior in solution (vide supra), affords a four-coordinate propene-containing compound. The symmetry of the ^{1}H NMR spectrum of **2b** can be easily explained on the basis of a fast head-to-tail inversion of the monodentate ligand. In the case of the other three complexes **2c**, **2d**, and **2e**, which contain N–N ligand with chemically different donor atoms, the coordination to the metal of the iminic nitrogen can be inferred, as discussed for the analogous ethylene complexes.

A clear assignment of the metal coordination number cannot be made for **2g** and **2h** since the ^{1}H NMR spectra recorded at room temperature show olefinic proton parameters that are intermediate between those of the four- and the five-coordination. However, the upfield shift of the olefinic protons at –50 °C points to a fluxional behavior, as in the case of **1b**. For the 1-butene complexes **3a**, **3c**, **3g**, and **3i**, conclusions similar to those reported for the corresponding propene compounds can be easily reached.

Disubstituted Olefin Complexes. The ^{1}H NMR parameters concerning complexes of *E*-2-butene (**4**), *E*-3-hexene (**5**), and *E*-cyclooctene (**6**) show a decreased tendency to form five-coordinate species. In fact, if the data referring to the nine *E*-2-butene complexes **4a–4i** are examined, only **4a** and **4i** are to be safely considered five-coordinate, the doubling of the olefinic proton signals in the latter compound being attributed to a restricted rotation around the Pt–olefin bond. Also complex **4f** should be five-coordinate, although a fluxional behavior cannot be excluded, owing to the values of the chemical shifts of the olefin resonances. A square-planar arrangement with N–N acting as a monodentate ligand toward the platinum atom is present in all the other cases (**4b–4d**, **4g**, **4h**). We note that this geometry is the only one possible for **4h**, which is binuclear with the N–N ligand bridging two platinum atoms. In this case a very large downfield shift is observed for the methyne proton ($\delta_{=NCH}$ 9.60 vs. 8.00 for the free ligand).

This finding agrees well with the predicted[13,14] large downfield

(12) The most significant difference observed is the doubling of the NN(C-H$_3$)$_2$ single signal that occurs at temperatures below –25 °C. This finding can be attributed to a restricted rotation around the N–N bond.

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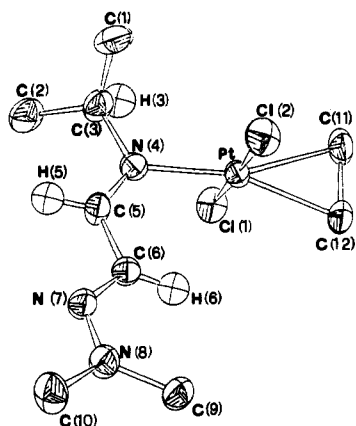
Figure 2. ORTEP drawing of the molecule of *trans*-[PtCl$_2$(C$_2$H$_4$)-(Me$_2$HCN==CHCH==NNMe$_2$)] (**1d**), approximately projected in the plane of the organic ligands.

shift of the resonance of a hydrogen in the steric arrangement shown:
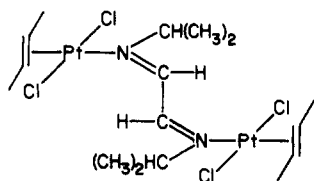
Binuclear complex **4h** is not involved in any fluxional equilibrium. As a consequence the shift of the methyne proton can be observed at room temperature. Another feature in the ^{1}H NMR spectrum of **4h** is the resonance of the methyl protons. Four doublets are observed. This can be attributed to the nonequivalence of the two methyl groups of the isopropyl group and to the presence of binuclear compounds in which the two coordinated *E*-2-butene molecules have the same or opposite absolute configurations.

Complex **4g** was previously[4f] prepared and characterized by ^{1}H and ^{13}C NMR spectra. The ^{1}H NMR parameters reported for this complex[4f] are coincident with those measured during this study. The symmetry of the proton NMR spectrum of **4g** is not sufficient in order to prove that **g** is chelated to the metal center. On the other hand, the NMR spectrum of **4g** does not change significantly even at −60 °C. In addition, the chemical shifts of coordinated **g** are unaffected by the presence of free **g**. However, structural determination by X-ray diffraction (vide infra) unequivocally shows that **4g** is square planar, thus confirming that the chemical shift of the olefinic protons actually is diagnostic of the coordination geometry. According to the ^{1}H NMR spectra, both five-coordinate (with N−N = **a** or **i**) and square-planar complexes (with N−N = **c** or **g**) are formed for the other two symmetrically *E*-substituted olefins (*E*-3-hexene and *E*-cyclooctene).

X-ray Structural Determination. Description of the Structure of *trans*-[PtCl$_2$(η^2-C$_2$H$_4$)((CH$_3$)$_2$HCN==CHCH==NN(CH$_3$)$_2$)] (**1d**). The structure of **1d** will be described here without comparison with **4g**. A comparative discussion of features of interest is postponed to the next section. The molecule, depicted in Figure 2, possesses the expected square-planar geometry with the two chlorine and the two organic ligands mutually trans to each other. The main outcome of the structure determination is that the bonding mode of the bidentate **d** ligand has been ascertained. The ethylene is symmetrically coordinated with an average Pt−C distance of 2.173 (7) Å and a C==C length of 1.40 (1) Å.

The double-bond plane, defined by C(11), C(12), and Pt, is orthogonal to the coordination plane, defined by Pt, Cl(1), Cl(2), and N(4) (91°), but the ligand is displaced slightly downwards (see Figure 2), the distances of C(11) and C(12) from the coordination plane being +0.66 and −0.75 Å, respectively. The two chlorine atoms show strictly equivalent bond lengths (2.293 (2) Å) and very small deviation from linearity. The Cl(1)−Pt−Cl(2)
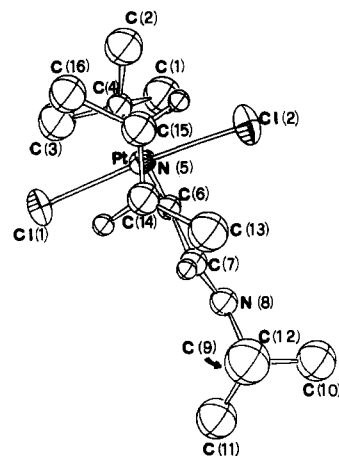
Figure 3. ORTEP drawing of the molecule of *trans*-[PtCl$_2$(*E*-CH$_3$CH==CHCH$_3$)(Me$_3$CN==CHCH==NCMe$_3$)] (**4g**). The view is almost orthogonal to that of the molecule in Figure 2.

angle is 178.1 (1)°. The ligand **d** is coordinated through the iminic nitrogen with a Pt−N length of 2.031 (5) Å. The molecule is planar and adopts an all-trans conformation (average deviation from the plane 0.07 Å). Only the hydrogen and methyl groups bonded to the tetrahedrally hybridized C(3) atom are in out-of-plane positions. A system of delocalized π orbitals extends through the ligand, forcing the chain to planarity (see bond values in Table V) and keeping H(6) in contact with the platinum (2.9 Å). The angle between the plane of the ligand **d** and the plane of coordination is 69.4° and is probably dictated by nonbonded contacts. The molecule of **1d** is asymmetric in the crystal, but it may gain a mirror plane in the absence of the packing forces.

Description of the Structure of (+)-*trans*-[PtCl$_2$(*E*-CH$_3$CH==CHCH$_3$)((CH$_3$)$_3$CN==CHCH==NC(CH$_3$)$_3$)] ((+)-**4g**).[16] The molecule of **4g**, shown in Figure 3, possesses a trans-planar geometry very similar to that of **1d**, the important difference arising from the presence of the two chiral centers in the coordinated *E*-2-butene (C(14) and C(15)) that have *S* absolute configuration (see Experimental Section).

The *E*-2-butene is symmetrically coordinated to the platinum with Pt−C distances of 2.16 (2) Å. The double-bond length, C(14)==C(15), is 1.38 (3) Å, and the C−Me average value is 1.54 (6) Å. The dihedral angle C(13)−C(14)==C(15)−C(16) is 26.9° and measures the bending of the methyl groups away from the platinum atom. These bond values are in the range of those found in a host of platinum−olefin complexes. We cite as an example the species *cis*-[PtCl$_2$(*E*-CH$_3$CH==CHCH$_3$)(NH$_2$CHCH$_3$Ph)]:[17] C==C = 1.36 (6), Pt−C = 2.16 (5), C−Me = 1.53 (6) Å; C−C==C−C dihedral angle 30 (5)°. The double-bond plane, defined as in **1d**, is twisted by 107.3 (5)° with respect to the coordination plane. Although deviations from the minimum energy orthogonal orientation[18] are commonly observed, the present deviation is remarkable and, if compared to the almost ideal value in **1d** of 91°, can be attributed to nonbonded contacts. The olefinic carbon atoms C(14) and C(15) are not equidistant from the coordination plane, being +0.58 and −0.74 Å, respectively. The effect is present in **1d** as well and is another consequence of nonbonded contacts.

The chlorine atoms show equivalent distances from platinum with average 2.290 (4) Å, almost equal to the value in **1d**. The Cl−Pt−Cl angle is 174.3 (2)°; the deviation from linearity is toward

(16) The structure of the complex **4g** has been determined on the dextrorotatory enantiomer ([α]^{25}$_D$ +59°, c 1.1, CHCl$_3$) that was synthesized as reported in the Experimental Section. Thus, the absolute configuration of the chiral olefinic ligand has been determined and related in a parallel investigation to the chiroptical properties of four- and five-coordinate complexes.

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Scheme I

PtCl₂(olefin) + N–N ⟶
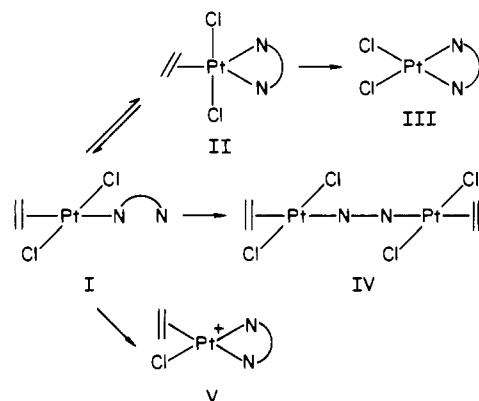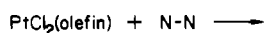
N(5). The potentially bidentate **g** ligand is actually monodentate and adopts a planar geometry of the chain atoms with C_{2h} idealized symmetry, i.e. *trans* conformation at the central C—C bond and anti configuration at the C=N double bonds. The angle between the ligand plane and the coordination plane (82.6°) is to be compared with the value in **1d** (69.4°). The Pt–N distance (2.07 (1) Å) is normal if compared to that of **1d** (2.031 (5) Å) and to the value in *trans*-[PtCl₂(NH₃)₂][19] (2.05 (4) Å) but is significantly shorter than the value in [(PtCl₂(PBu₃))₂(BIE)][20] (2.21 Å). These differences are probably due to different electronic effects of the ligands in trans positions. The two C=N double bonds (1.26 and 1.28 (2) Å) compare well with the value in the aforementioned[20] complex (1.27 (3) Å)8 and in **1d** (1.284 (7) and 1.300 (7) Å), the shorter value in both molecules is associated with the coordinated nitrogen. The central C(6)–C(7) distance (1.46 (2) Å) is indicative of conjugation between the double bonds. The shortening of the corresponding carbon–carbon bond in **1d** is even more significant (1.423 (8) Å). A hydrogen–platinum contact as short as 2.6 Å is present in this molecule, similar to that found in **1d** (2.9 Å). This difference cannot be commented upon because the hydrogen positioning was idealized (see Experimental Section). A more complete comparison of the available bond parameters in the α-diimine ligands can be found in ref 20.

Discussion

The addition of a bidentate nitrogen ligand to the fragment PtCl₂(olefin) can in principle afford a variety of products. Scheme I lists the possible products (excluding reactions on coordinated ligands), assuming the first reaction step in every case is the formation of a Pt–N bond trans to the olefin.

All five products (I–V) can be isolated[4a,c,5,21,22] when the olefin is ethylene and N–N is a diamine of the type RR′N(CH₂)ₙNRR′ (R, R′ = H, alkyl group). The cationic complexes (V) are obtained[23] upon elimination of the halide by a suitable reagent, e.g. AgBF₄. The type of product that is actually obtained depends on the nature of R and R′ and on the value of *n*, but a satisfactory discrimination between steric and electronic effects has not yet been achieved. In particular, these factors deserve a detailed discussion when the transformation of a type I complex to a five-coordinate species is considered.

The N–N ligands and the olefin examined in this work have mainly the general formula Z¹N=CZ²CZ³=NZ⁴ (Z¹, Z⁴ = NMe₂, CHMe₂, CMe₃; Z², Z³ = H, Me) and Z⁵CH=CHZ⁶ (Z⁵, Z⁶ = H, alkyl group). The only exceptions are the ligand **i** and the olefin **6**, but similar atom sequences can be recognized. In Table VII the metal coordination numbers of the complexes that have been obtained are reported.

The factors that influence the coordination geometry of these complexes are as follows: (i) the different σ-donor properties of the nitrogen atoms in the N–N ligands, which are higher for N(imine) than for N(hydrazone), as indicated by the coordination mode of ligands **c**, and **d**; (ii) the different π-acceptor abilities of the olefin, which decrease[24] on going from ethylene to monosubstituted to disubstituted alkenes; (iii) the tendency of Z¹N=CZ²CZ³=NZ⁴ ligands to assume an all-trans conformation in a plane normal to the metal coordination plane, when the type I complex is formed. Starting from this last point, a premise supported by X-ray structural determinations on **1d**, **4g**, and other strictly related complexes,[20] it follows that this arrangement brings the Z substituent on the carbon adjacent to the uncoordinated nitrogen near the platinum atom. Therefore, when Z = Me, this positioning is sterically forbidden and a type II five-coordinate complex is obtained, irrespective of the nature of the N donor atoms and of the olefin. In fact, such coordination is present in all the olefin complexes with the ligands **a** and **f**. When Z = H, an exceedingly short Pt–H contact could still arise[4c] (as observed with ligand **i**), in which case a five-coordinate species is still obtained for all the olefins. When steric factors do not interfere, a five-coordinate compound can form from a type I species through a rotation around the C–C bond of the ligand, leaving the uncoordinated nitrogen in a suitable position for chelation. In this case the actual I ⇌ II conversion depends on factors i and ii. In fact it requires both good σ-donor properties of the N–N ligand and good π-acceptor ability of the olefin. Thus, with the diimine ligands **g** and **h** the ethylene complex is five-coordinate, while four-coordinate species are favored on decreasing the π backdonation toward the olefin. The use of N–N ligands in which one or both of the nitrogen atoms have reduced σ-donor properties, such as **c**, **d**, and **e** or **b**, respectively, results generally in the formation of type I species. Only the ethylene complexes exhibit, in some cases, fluxional behavior in solution.

Conclusions

The reported data confirm that ¹H NMR spectroscopy is the most suitable method to ascertain the metal coordination number in platinum(II)–olefin complexes. In addition, the chemical shifts of the olefinic protons are so markedly dependent on this feature that a possible dynamic equilibrium between a four- and a five-coordinate species (types I and II in Scheme I) is easily recognized by room-temperature measurements. The formation of five-coordinate [PtCl₂(N–N)(olefin)] complexes is very sensitive to both the σ-donor and π-acceptor properties of the N–N and the olefinic ligands, respectively. The tendency of N–N toward chelation increases with increasing σ-donor properties of the N–N ligand π-acceptor properties of the olefin. Five-coordination is also favored by the presence of alkyl substituents on the carbon atoms of the N–N ligands. In fact, such substituents favor the cis conformation of the coordinated ligand. As a result five-coordination of Pt is favored in comparison with four-coordination. We note that, when very good σ-donor N–N ligands are used, like N,N′-substituted 1,2-ethanediamine,five-coordinate olefin complexes are formed, even with substituted ethenes.[4c] In that case, however, decomposition (olefin loss) of the five-coordinate complex occurs in solution. It is interesting to compare these data with the observed instability in solution of the five-coordinate [PtCl₂(BIP)(olefin)] complexes, in which the chelation of N–N is forced only by steric factors, the pyridine nitrogen being a weak σ donor.

Experimental Section

¹H NMR spectra were recorded on a Varian T-60A spectrometer for the N–N ligands and on a Bruker WH 270-MHz spectrometer for the Pt(II) complexes; CDCl₃ was used as solvent and tetramethylsilane as an internal reference. Melting points were determined on a Kofler hot-stage apparatus. UV–vis spectra were obtained on a Perkin-Elmer 320 spectrophotometer in ethanol solution. IR spectra were recorded on a Perkin-Elmer 457 spectrophotometer as Nujol mulls. Molecular weight

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Table III. Crystal Data and Intensity Collection Parameters

	1d	4g
formula	$C_9H_{19}Cl_2N_3Pt$	$C_{14}H_{28}Cl_2N_2Pt$
M_r	435.3	490.4
cryst syst	monoclinic	orthorhombic
space group	$P2_1/c$	$P2_12_12_1$
a/Å	8.710 (1)	6.969 (5)
b/Å	15.400 (1)	10.675 (7)
c/Å	10.753 (1)	26.009 (15)
β/deg	99.16 (1)	
U/Å^3	1424	1935
Z	4	4
D_{calcd}, g cm^{-3}	2.03	1.68
μ(Mo Kα)/cm^{-1}	103.14	75.98
min transmission factor	0.724	0.723
cryst dimens/mm	0.14 × 0.17 × 0.25	0.10 × 0.16 × 0.31
scan mode	$\omega/2\theta$	ω
θ range/deg	2–27	3–25
octants of rec space explored	$h,k,\pm l$	$\pm h,k,l$
measd reflcns	3424	3647
obsd unique reflcns ($I > 3\sigma(I)$)	2258	2214
final R and R_w indices	0.027, 0.038	0.040, 0.046
ω-scan width/deg	0.7 + 0.35 tan θ	0.9 + 0.35 tan θ
prescan speed/deg min^{-1}	6.6	10
prescan acceptance $\sigma(I)/I$	0.5	0.5
max scan time/s	100	100
requested $\sigma(I)/I$	0.01	0.02

Table IV. Positional Parameters for *trans*-[PtCl$_2$(C$_2$H$_4$)(Me$_2$CHN=CHCH=NNMe$_2$)] (1d) with Their Standard Deviations in Parentheses

atom	x	y	z
Pt	−0.26916 (3)	0.04352 (2)	−0.11515 (2)
Cl(1)	−0.1743 (3)	0.0807 (1)	0.0889 (2)
Cl(2)	−0.3698 (3)	0.0100 (1)	−0.3199 (2)
N(4)	−0.2423 (6)	0.1687 (4)	−0.1674 (5)
N(7)	0.0464 (7)	0.1736 (4)	−0.3607 (5)
N(8)	0.1455 (7)	0.1288 (4)	−0.4119 (6)
C(1)	−0.506 (1)	0.2235 (7)	−0.216 (1)
C(2)	−0.300 (1)	0.3207 (6)	−0.1018 (8)
C(3)	−0.355 (1)	0.2324 (5)	−0.1279 (7)
C(5)	−0.1422 (9)	0.1940 (4)	−0.2354 (6)
C(6)	−0.0294 (8)	0.1395 (4)	−0.2780 (6)
C(9)	0.181 (1)	0.0395 (5)	−0.3849 (8)
C(10)	0.214 (1)	0.1716 (5)	−0.5089 (7)
C(11)	−0.370 (1)	−0.0734 (5)	−0.0499 (9)
C(12)	−0.218 (1)	−0.0924 (5)	−0.0701 (9)

determinations and elemental analyses were made in part by Analytische Laboratorien, Elbach, West Germany. Solvents and reagents were of AnalaR grade. N–N ligands were synthesized and stored under nitrogen. Platinum complexes were obtained and stored in air.

Materials. The N–N ligands a,[25] b,[25] g,[26] h,[26] and i[48] were synthesized and characterized as previously described. The ligands c and d were prepared by condensing the dimethylhydrazone (CH$_3$)$_2$NN=CHCHO[27] with *tert*-butylamine and isopropylamine, respectively, according to a known[26] procedure. Ligand e was obtained by condensing[28] isopropylamine with the dimethylhydrazone (CH$_3$)$_2$NN=CHCOCH$_3$.[29] Ligand f was synthesized by condensing[25] *N,N*-dimethylhydrazine with (C-H$_3$)$_3$CN=CHCOCH$_3$, prepared according to a known method.[30] [PtCl$_2$(olefin)]$_2$ complexes were obtained by olefin exchange[31] starting from [PtCl$_2$(C$_2$H$_4$)]$_2$. K$^+$[PtCl$_3$(olefin)]$^-$ compounds were isolated as yellow crystalline solids by dissolving the corresponding binuclear complexes in the minimum amount of aqueous KCl and concentrating in vacuo the filtered solution.

Synthesis of [PtCl$_2$(N–N)(olefin)] Complexes. Two methods (A and

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Table V. Positional Parameters for *trans*-[PtCl$_2$(*E*-MeCH=CHMe)(Me$_3$CN=CHCH=NCMe$_3$)] (4g) with Their Standard Deviations in Parentheses

atom	x	y	z
Pt	0.02318 (7)	−0.16581 (6)	−0.37665 (2)
Cl(1)	−0.2101 (7)	−0.2717 (6)	−0.4210 (2)
Cl(2)	0.2333 (7)	−0.0455 (6)	−0.3305 (2)
N(5)	−0.177 (2)	−0.129 (1)	−0.3197 (4)
N(8)	−0.325 (2)	0.171 (2)	−0.3564 (5)
C(1)	−0.027 (4)	−0.295 (2)	−0.2685 (9)
C(2)	−0.379 (4)	−0.300 (3)	−0.289 (1)
C(3)	−0.246 (3)	−0.147 (3)	−0.227 (1)
C(4)	−0.209 (2)	−0.222 (2)	−0.2768 (6)
C(6)	−0.270 (2)	−0.026 (2)	−0.3205 (6)
C(7)	−0.246 (2)	0.066 (2)	−0.3614 (6)
C(9)	−0.308 (3)	0.269 (2)	−0.3967 (9)
C(10)	−0.511 (4)	0.293 (3)	−0.419 (1)
C(11)	−0.248 (5)	0.381 (4)	−0.369 (1)
C(12)	−0.158 (6)	0.228 (5)	−0.439 (2)
C(13)	0.263 (3)	−0.030 (3)	−0.4576 (9)
C(14)	0.181 (3)	−0.155 (2)	−0.4482 (7)
C(15)	0.272 (3)	−0.238 (2)	−0.4161 (8)
C(16)	0.247 (3)	−0.385 (2)	−0.4229 (9)

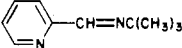**Table VI.** Bond Distances (Å) and Relevant Angles (deg)

trans-[PtCl$_2$(C$_2$H$_4$)(Me$_2$HCN=CHCH=NNMe$_2$)] (1d)

Pt–Cl(1)	2.291 (2)	C(6)–N(7)	1.300 (7)
Pt–Cl(2)	2.295 (2)	N(7)–N(8)	1.293 (7)
Pt–C(11)	2.169 (7)	N(8)–C(9)	1.431 (8)
Pt–C(12)	2.177 (7)	N(8)–C(10)	1.440 (8)
C(11)–C(12)	1.405 (9)	C(3)–C(1)	1.50 (1)
Pt–N(4)	2.031 (5)	C(3)–C(2)	1.45 (1)
N(4)–C(3)	1.495 (8)	Pt···H(6)	2.9
N(4)–C(5)	1.284 (7)	Cl(1)···H(6)	4.0
C(5)–C(6)	1.423 (8)	Cl(2)···H(6)	3.3
Cl(1)–Pt–Cl(2)	178.1 (1)	N(4)–C(3)–C(2)	117.4 (6)
Cl(1)–Pt–N(4)	89.3 (1)	N(4)–C(5)–C(6)	124.8 (5)
Cl(2)–Pt–N(4)	89.5 (1)	C(5)–C(6)—N(7)	115.8 (5)
C(11)–Pt–C(12)	37.7 (3)	C(6)–N(7)–N(8)	121.5 (5)
Pt–N(4)–C(3)	115.8 (4)	N(7)–N(8)–C(10)	116.5 (5)
Pt–N(4)–C(5)	124.4 (4)	N(7)–N(8)–C(9)	124.4 (5)
C(3)–N(4)–C(5)	119.8 (5)	C(9)–N(8)–C(10)	118.9 (6)
N(4)–C(3)–C(1)	108.0 (5)		

trans-[PtCl$_2$(*E*-MeCH=CHMe)(Me$_3$CN=CHCH=NCMe$_3$)] (4g)

Pt–Cl(1)	2.292 (4)	C(7)–N(8)	1.26 (2)
Pt–Cl(2)	2.288 (4)	N(8)–C(9)	1.49 (2)
Pt–C(14)	2.16 (2)	C(4)–C(1)	1.50 (3)
Pt–C(15)	2.16 (2)	C(4)–C(2)	1.48 (3)
C(14)–C(15)	1.38 (3)	C(4)–C(3)	1.55 (3)
C(14)–C(13)	1.47 (3)	C(9)–C(10)	1.55 (3)
C(15)–C(16)	1.59 (3)	C(9)–C(11)	1.46 (4)
Pt–N(5)	2.07 (1)	C(9)–C(12)	1.58 (4)
N(5)–C(4)	1.51 (2)	Pt···H(7)	2.6
N(5)–C(6)	1.28 (2)	Cl(1)···H(7)	3.5
C(6)–C(7)	1.46 (2)	Cl(2)···H(7)	3.4
Cl(1)Pt–Cl(2)	174.3 (2)	C(7)–N(8)–C(9)	121.7 (14)
Cl(1)–Pt–N(5)	88.7 (3)	N(5)–C(4)–C(1)	108.7 (13)
Cl(2)–Pt–N(5)	87.1 (3)	N(5)–C(4)–C(2)	109.5 (14)
C(14)–Pt–C(15)	37.1 (7)	N(5)–C(4)–C(3)	108.0 (14)
Pt–N(5)–C(4)	120.4 (9)	N(8)–C(9)–C(10)	108.5 (18)
Pt–N(5)–C(6)	119.6 (10)	N(8)–C(9)–C(11)	104.3 (22)
C(4)–N(5)–C(6)	120.0 (11)	N(8)–C(9)–C(12)	110.1 (23)
N(5)–C(6)–C(7)	122.0 (13)	C(13)–C(14)–C(15)	120.5 (18)
C(6)–C(7)–N(8)	118.2 (14)	C(14)–C(15)–C(16)	121.4 (20)

B) were used, the first giving usually purer products and higher yields when the resulting complex is five-coordinate since it precipitates from the reaction medium. The methods are described in detail for the syntheses of 1e and 4c.

Method A. A 1.12-g (3-mmol) amount of K$^+$[PtCl$_3$(C$_2$H$_4$)]$^-$·H$_2$O dissolved in 20 mL of MeOH was treated with 0.465 g (3 mmol) of DHPIP at 0 °C. After 10 min of standing, the reaction mixture was concentrated and cooled at −15 °C. The precipitated crystalline product was filtered off and recrystallized from CH$_2$Cl$_2$/MeOH. 1e was obtained as yellow needles (1.07 g, 80% yield) having mp 125 °C dec. The UV–vis spectrum showed maxima at 320 (ϵ = 17 200) and 250 nm (ϵ = 2800).

Table VII. Metal Coordination Number for $PtCl_2(N-N)(olefin)$ Complexes

	olefin		
	c=c	＼c=c	＼c=c＼
ligand	1	2,3	4–6
$(CH_3)_2NN=C(CH_3)C(CH_3)=NN(CH_3)_2$ (a)	5	5	5
$(CH_3)_2NN=C(H)C(H)=NN(CH_3)_2$ (b)	4, 5^a	4	4
$(CH_3)_2NN=C(H)C(H)=NC(CH_3)_3$ (c)	4	4	4
$(CH_3)_2NN=C(H)C(H)=NCH(CH_3)_2$ (d)			
$(CH_3)_2NN=C(H)C(CH_3)=NCH(CH_3)_2$ (e)	4, 5^a	4	4
$(CH_3)_2NNC(CH_3)C(H)=NC(CH_3)_2$ (f)	5	5	5
$(CH_3)_3CN=C(H)C(H)=NC(CH_3)_3$ (g)	5	4, 5^a	4
$(CH_3)_2CHN=C(H)C(H)=NCH(CH_3)_2$ (h)			
[pyridyl-CH=NC(CH₃)₃] (i)	5	5	5

^{a} Fluxional behavior in solution; see text.

Anal. Calcd for $C_{10}H_{21}Cl_2N_3Pt$: C, 26.7; H, 4.70; N, 9.35; mol wt, 449.3. Found: C, 27.0; H, 4.65; N, 9.2; mol wt (osmometric, CHCl₃), 446.

Method B. To a suspension of 1.29 g (2 mmol) of $[PtCl_2(E\text{-}CH_3CH=CHCH_3)]_2$ in CH_2Cl_2 was added DHBIE (0.62 g, 4 mmol) with stirring at 0 °C. The complex suddenly dissolved, and the solution was filtered after 5 min. The solution was concentrated to a few milliliters, and *n*-pentane was added until clouding occurred A yellow crystalline compound formed at −5 °C on standing (1.33 g, 70% yield) having mp 120–130 °C dec. The UV–vis spectrum showed maxima at 330 (ϵ = 28 400) and 250 nm (ϵ = 3000). Anal. Calcd for $C_{12}H_{25}Cl_2N_3Pt$: C, 30.2; H, 5.28; N, 8.80; mol wt, 477.35. Found: C, 31.0; H, 5.1; N, 8.5; mol wt (osmometric, CHCl₃), 475.

Synthesis of $(+)$-[PtCl₂(BIE)(E-CH₃CH=CHCH₃)] ($(+)$-4g). (i) Tetraphenylphosphonium trichloro $(S,S$-E-2-butene)platinate(II) was prepared by treating $(+)$-dichloro(E-2-butene)((S)-2-methylbenzene-methanamine)platinum(II) ($[\alpha]^{25}{}_D$ +45°, c 1.08, CH_2Cl_2)[31] (1.33 g, 3 mmol) dissolved in 10 mL of acetone with 1.5 mL of concentrated HCl at −15 °C. To this solution was added PPh₄Cl (1.15 g, 3 mmol) dissolved in 5 mL of H_2O. A yellow crystalline product precipitates (1.95 g, 94% yield) with $[\alpha]^{25}{}_D$ +56° (c 1.05, CHCl₃). The product was not recrystallized since the ¹H NMR spectrum agreed with its formulation. (ii) Tetraphenylphosphonium trichloro($S,S,$-E-2-butene)platinate(II) (0.70 g, 1 mmol) was dissolved in the minimum amount of MeOH at 0 °C, and BIE (0.17 g, 1 mmol) dissolved in methanol was added. The solution was concentrated to a few milliliters and stored in the refrigerator. A yellow crystalline product (0.33 g, 68% yield) was obtained with $[\alpha]^{25}{}_D$ +59° (c 1.18 CHCl₃). The ¹H NMR spectrum of this product is identical with that of racemic 4g; mp 120–130 °C dec. The UV–vis spectrum showed maxima at 275 (ϵ = 2950) and 265 nm (ϵ = 3600). Anal. Calcd for $C_{14}H_{28}Cl_2N_2Pt$: C, 34.3; H, 5.75; N, 5.71; mol wt, 490.4. Found: C, 34.0; H, 5.7, N, 5.9; mol wt (osmometric, CHCl₃), 486.

X-ray Structural Determinations. The crystal data for 1d and 4g are summarized in Table III together with some experimental details. The diffraction intensities were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer with Mo Kα radiation (λ = 0.710 73 Å) and reduced to F_0 values corrected for crystal decay and absorption. The latter correction was performed by an empirical method based on a set of ψ scans of reflections having χ values near 90°.[32] Both structures were

solved by conventional Patterson and Fourier methods and refined by full-matrix least squares, the minimized function being $\sum w(F_0 - K|F_c|)^2$. Weights assigned to individual observations were $w = 1/\sigma^2(F_0)$, where $\sigma(F_0) = \sigma(F_0^2)/2F_0$, $\sigma(F_0^2) = (\sigma^2(I) + (iI)^2)^{1/2}/Lp$ and i is an "ignorance factor" equal to 0.03. The Enraf-Nonius SPD package of crystallographic programs was used with the analytical scattering factors, corrected for the real and imaginary components of anomalous dispersion, taken from ref 33. Thermal vibrations were treated anisotropically for all the non-hydrogen atoms in 1d and for platinum and chlorine alone in 4g because some thermal parameters did not behave well during refinement. Most hydrogen atoms were detected in the Δ*F* synthesis in 1d but none in 4g. In both structures the hydrogen atoms were placed in calculated positions (C–H distance 0.95 Å) wherever their positioning was not ambiguous and their contribution to the structure factors was computed.

As compound 4g crystallizes in the polar space group $P2_12_12_1$ and therefore the crystals contain molecules of the same chirality, the determination of the absolute configuration of the chiral centers in the coordinated E-2-butene was attempted and turned out to be successful. The choice of the correct enantiomer was made by comparing the results of the refinements of two structure models related by inversion. The rejected enantiomer led to significantly higher agreement indices: 0.051 and 0.060 for R and R_w, respectively, against 0.040 and 0.046 for the correct one, in which the configuration of the chiral centers is S.

The atomic coordinates of the structure models are reported in Tables IV and V for 1d and 4g, respectively. Relevant bond distances and angles are in Table VI.

Registry No. 1a, 95864-79-2; 1b (4-coordinate), 95864-80-5; 1b (5-coordinate), 94508-80-2; 1c, 95864-81-6; 1d, 95864-82-7; 1e (4-coordinate), 95864-83-8; 1e (5-coordinate), 95864-84-9; 1f, 95864-85-0; 1g, 95864-86-1; 1h, 95864-87-2; 1i, 95892-01-6; 2a, 95864-88-3; 2b, 95864-89-4; 2c, 95864-90-7; 2d, 95864-91-8; 2e, 95864-92-9; 2f, 95864-93-0; 2g (4-coordinate), 95975-93-2; 2g (5-coordinate), 95864-94-1; 2h (4-coordinate), 95864-95-2; 2h (5-coordinate), 95864-96-3; 2i, 95892-02-7; 3a, 95864-97-4; 3c, 95864-98-5; 3g (4-coordinate), 95975-94-3; 3g (5-coordinate), 95864-99-6; 3i, 95865-00-2; 4a, 95865-01-3; 4b, 95975-95-4; 4c, 95865-02-4; 4d, 95865-03-5; 4e (4-coordinate), 95865-04-6; 4e (5-coordinate), 95865-05-7; 4f, 95865-06-8; 4g, 95975-96-5; (+)-4g, 95975-97-6; 4h, 95865-14-8; 4i, 95865-07-9; 5a, 95865-08-0; 5c, 95865-09-1; 5g, 88935-10-8; 5i, 95865-10-4; 6a, 95865-11-5; 6c, 95865-12-6; 6g, 95975-98-7; 6i, 95865-13-7; a, 15677-39-1; b, 26757-28-8; c, 95864-75-8; d, 95864-76-9; e, 95864-77-0; f, 95864-78-1; g, 30834-74-3; h, 24764-90-7; i, 21478-42-2; K⁺[PtCl₃(C₂H₄)]⁻, 12012-50-9; [PtCl(E-CH₃CH=CHCH₃)]₂, 95975-99-8; [PtCl₂(BIP)], 56171-64-3; (CH₃)₂N-N=CHCHO, 62506-63-2; (CH₃)₂NN=CHCOCH₃, 65295-97-8; (C-H₃)₃CN=CHCOCH₃, 67122-50-3; tetraphenylphosphonium trichloro-(S,S-E-2-butene)platinate(II), 74432-01-2; *tert*-butylamine, 75-64-9; isopropylamine, 75-31-0; N,N-dimethylhydrazine, 540-73-8; (+)-dichloro(E-2-butene)((S)-2-methylbenzenemethanamine)platinum(II), 12126-72-6.

Supplementary Material Available: Listings of hydrogen atom coordinates, thermal parameters, and observed and calculated structure factor moduli (24 pages). Ordering information is given on any current masthead page.

(32) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968,** *24A,* 351.

(33) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Tables 2.2.B and 2.3.1.