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Nuclear Magnetic Resonance Studies of Planar Low-Spin Complexes of Cobalt(II) with Schiff Bases. *N,N'*-Ethylenebis(salicylideneiminato)cobalt(II) in Noncoordinating Solvents

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Abstract: Isotropic proton NMR shifts have been measured for low-spin salicylaldehyde Schiff base complexes of cobalt(II) in $CDCl_3$. The isotropic shifts are shown to arise from both dipolar and contact interaction of comparable magnitude. This appreciable contact contribution is attributable to spin delocalization involving $M \leftarrow L$ π charge transfer out of the highest filled π MO. From the mode of the interaction between the cobalt ion and the ligand, it is concluded that the cobalt(II) complexes have an electronic ground state with the unpaired electron in the d_{yz} orbital.

The electronic structure of the *N,N'*-ethylenebis(salicylideneiminato)cobalt(II) complex, Co(salen), has been widely investigated by electronic spectroscopy,[1] ESR spectroscopy,[1,2] and other methods.[3] It is known that in coordinating solvents, such as pyridine, piperidine, etc., the complex forms a five-coordinate, square pyramidal species with the solvent molecules, and it possesses an electronic ground state having an unpaired electron in the d_{z^2} level.[1b,c,2b,4] In

Table I. Isotropic Proton NMR Shifts (ppm)

Complex	3	4	5	6	8
Co(salen)	*a*	−7.05	+38.36	−0.96	
Co(3-Me(salen))	(−36.11)[b]	−7.31	*a*	−1.25	
Co(4-Me(salen))	*a*	(+12.04)[b]	+36.27	−1.87	
Co(5-Me(salen))	*a*	−6.28	(−22.81)[b]	−1.31	
Co(salibn)	*a*	−6.85	+34.27	−1.51	(−22.60)[b]

[a] Not observed. [b] Value for the methyl protons.

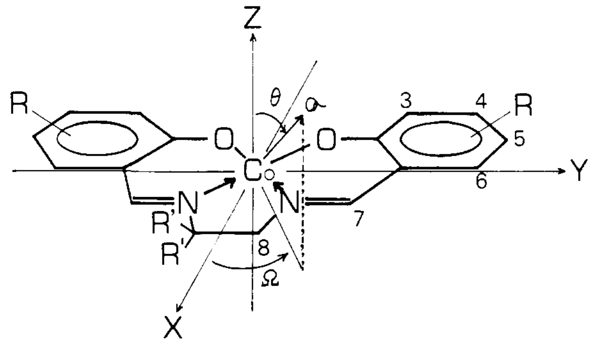

Figure 1. Schematic illustration of salicylaldehyde Schiff base complexes of cobalt(II) and definition of the coordinate system fixed in the molecule: R = H, R′ = H, Co(salen); R = Me, R′ = H, Co(Me(salen)); R = H, R′ = Me, Co(salibn).

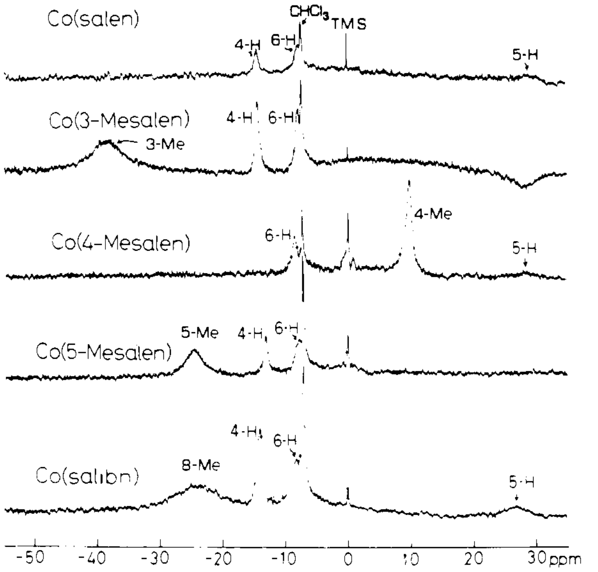

Figure 2. Proton NMR spectra of Co(salen), Co(Me(salen)), and Co(salibn) in $CDCl_3$ at 39°.

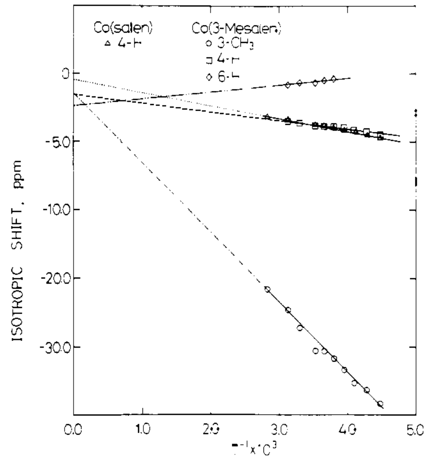

Figure 3. Plot of isotropic shift vs. reciprocal temperature for Co(salen) and Co(3-Me(salen)) in $CDCl_3$.

noncoordinating solvents or matrices, such as chloroform, toluene, or Ni(salen) matrix, the complex takes a planar form. However, its electronic ground state is still ambiguous, although many proposals have been made.[1b,c,2b-f,5] Some proposed electronic configurations with an unpaired electron in the d_{z^2} level for the ground state of the Co(salen),[1b,c,2b,d] and others preferred those with an unpaired electron in the d_{yz} level.[2c,f] In a recent ESR study made in our laboratory,[6] the latter was shown to more likely be as the ground state of planar Co(salen). Although ESR has been utilized most extensively in investigations of Co(salen), the NMR technique seemed most useful to determine the half-filled orbital in the ground state electronic configuration of the complex. The present investigation was undertaken in order to obtain conclusive evidence for the unpaired electron orbital in the ground state electronic configuration of the four-coordinated low-spin Co(salen) by means of NMR.

Experimental Section

Co(salen), Co(Me(salen)), and Co(salibn) (see Figure 1) were prepared according to previously reported methods.[7] Methyl substituted salicylaldehydes used in the preparation were obtained from the corresponding phenols by the Duff reaction.[8]

The sample solutions for NMR measurements were prepared by dissolving 0.7–3 mg of the cobalt(II) complexes into 0.3–0.5 ml of degassed $CDCl_3$ in a vacuum line. Proton NMR spectra at ambient temperature (39°) were recorded by means of a Jeol C-60 HL spectrometer. Temperature dependence of the NMR spectra was measured by use of a Jeol JNM PS 100 spectrometer equipped with a variable temperature probe and a temperature controller. TMS was used as an internal reference. Isotropic shifts are referenced against the corresponding free ligands and are reported in parts per million.

Results

The proton NMR spectra for Co(salen), Co(Me(salen)), and Co(salibn) in $CDCl_3$ are illustrated in Figure 2, and the isotropic shifts obtained are listed in Table I. Signal assignments were made on the basis of methyl substitution at three of the four ring positions. The signals due to the protons at the 3 position, azomethine protons and methylene protons, were not found in the range of ±300 ppm from TMS, though the signals due to the methyl protons substituted at these positions were detected. The failure to observe the signals is probably due to large shifts out of the range of observation or large line broadening caused by strong electron spin–nuclear spin interaction. In the NMR spectrum of Co(3-Me(salen)) (Figure 2), a signal due to the proton at position 5 was not clearly observed, because of the overlap with the out-of-phase signal of one due to the methyl protons at position 3. Temperature dependence of the isotropic shifts for Co(salen) and Co(3-Me(salen)) is shown in Figure 3. For the protons at 5 and 6 positions, reliable data of temperature dependence could not be obtained because of low intensities due to the large line broadening and of the overlap with a $CHCl_3$ signal.

Table II. Separation of Dipolar and Contact Shifts and Hyperfine Coupling Constants of Ligand Protons

Position	Obsd shift (ppm)	Calcd dipolar shift (ppm)		Resultant contact shift (ppm)		a_N (G)	
		a	*b*	*a*	*b*	*a*	*b*
3 Me[c]	−36.11	−25.78	−16.13	−10.33	−19.98	+0.122	+0.235
4 H[d]	−7.05	−0.47	−0.28	−6.58	−6,77	+0.078	+0.080
Me[c]	+12.04	+0.57	+0.37	+11.47	+11.67	−0.135	−0.137
5 H[d]	+38.36	+6.02	+3.79	+32.34	+34.57	−0.382	−0.407
Me[c]	−22.81	+3.82	+2.41	−26.63	−25.22	+0.315	+0.298
6 H[d]	−0.96	+13.90	+8.74	−14.86	−9.70	+0.175	+0.114

[a] Values calculated by the use of *g* values for Co(salen) in Ni(salen) matrix. [b] Values calculated by the use of *g* values for Co(salen) in CH_2Cl_2 solution. [c] Values for the methyl protons in the respective methyl derivatives of Co(salen). [d] Values for the ligand protons of Co(salen).

Discussion

Analysis of NMR Isotropic Shifts. The observed isotropic shifts, $(\Delta H/H)^{\mathrm{iso}}$, are divided into contact and dipolar contributions

$$(\Delta H/H)^{\mathrm{iso}} = (\Delta H/H)^{\mathrm{dip}} + (\Delta H/H)^{\mathrm{con}} \qquad (1)$$

For a complex with only one thermally populated multiplet with an effective spin S', the dipolar shift, $(\Delta H/H)^{\mathrm{dip}}$, and the contact shift, $(\Delta H/H)^{\mathrm{con}}$, are expressed by the following equations, which obey the Curie law.[9]

$$(\Delta H/H)^{\mathrm{dip}} = \frac{\beta^2 S'(S'+1)}{18kTR^3}\{(2g_{zz}^2 - g_{xx}^2 - g_{yy}^2) \times (1 - 3\cos^2\theta) + 3(g_{yy}^2 - g_{xx}^2)\sin^2\theta\cos 2\Omega\} \qquad (2)$$

$$(\Delta H/H)^{\mathrm{con}} = -\frac{a_N \beta S'(S'+1)}{9\hbar\gamma_N g_e kT}(g_{xx}g_{s_{xx}} + g_{yy}g_{s_{yy}} + g_{zz}g_{s_{zz}}) \qquad (3)$$

where R is the distance from the metal ion to the ligand nucleus, θ is the angle between the z axis and the vector, σ, joining the metal and ligand nucleus, Ω is the angle between the x axis and projection of σ in the xy plane, and $g_{s_{ii}}$ is the spin contribution to g_{ii} values. When splittings between the ground state and excited states are smaller than kT, the second-order Zeeman (SOZ) term should be further taken into account to the both dipolar and contact shifts.[9] In the present work, the variable temperature NMR data suggest that the SOZ term may make some contribution to the isotropic shifts (vide infra). However, as detailed analysis of the SOZ term was not warranted in the absence of reliable data on magnetic susceptibilities or the excited states, the observed itropic shifts were analyzed based on eq 2 and 3. The g values necessary to calculate the dipolar term were taken from ESR data. It is known from ESR that low spin Co(salen) in noncoordinating solvents has rhombic anisotropy,[1,2b-d,6,10] that is $g_1 \simeq g_2 < g_3$. By a single-crystal study,[2c] the g_1, g_2, and g_3 are assigned to g_{yy}, g_{zz}, and g_{xx}, respectively. Here the coordinate axes are chosen as is shown in Figure 1. The g values obtained for Co(salen) in various noncoordinating matrices are in the range of 3.17–3.81 for g_{xx}, 1.66–1.93 for g_{yy}, and 1.74–1.96 for g_{zz}. However, as the reliable analysis of ESR for Co(salen) in $CDCl_3$ was impossible,[6,10] the calculation of the dipolar term was carried out for the two cases with use of g values obtained in the Ni(salen) matrix ($g_{xx} = 3.805$, $g_{yy} = 1.66$, $g_{zz} = 1.74$)[2c] and in CH_2Cl_2 solution ($g_{xx} = 3.32$, $g_{yy} = 1.91$, $g_{zz} = 1.96$).[10] The g values in Ni(salen) matrix show the largest anisotropy among the known data. Hence the dipolar shifts calculated are the largest to be expected, and vice versa for the case of CH_2Cl_2 solvent system. The geometric factor for the calculation of the dipolar shifts was taken from X-ray structural data.[11] The contact shifts were obtained from the observed isotropic shifts and the calculated dipolar shifts as a difference between them. Table II shows the resultant dipolar and contact shifts, together with the hyperfine coupling constants, a_N, calculated by eq 3.

Spin Delocalization on the Ligand. The contact shifts for Co(salen) and its methyl derivatives show alternation at adjacent protons. Such an alternation of contact shifts is most common in π delocalization systems. However, there are cases in which such an alternation is well explained by the σ delocalization mechanism,[12] and hence it does not seem that there is a simple diagnosis for spin delocalization mechanisms. However, it seems valuable to compare the present result with the following two cases: (a) a pyridine diadduct of bis(salicylaldehydato)nickel(II) complex, $Ni(sal)_2 \cdot 2py$, and (b) bis(*N*-isopropylsalicylaldiminato)nickel(II) complex. Both of them have analogous structures to Co(salen), but the nickel(II) complexes have metal ground states different from each other. The former has two unpaired electrons in the $d_{x^2-y^2}$ and d_{z^2} orbitals and σ delocalization is expected to make appreciable contribution to the contact shifts. The latter is known to have two t_2 unpaired electrons, and the contact shifts have been shown to be dominated by π delocalization.[13]

From the NMR data reported by Schwarzhans,[14] the contact shifts for $Ni(sal)_2 \cdot 2py$ were found to be +0.44, −18.88, −1.19, and +6.45 ppm for the protons at the 3, 4, 5, and 6 positions of the salicylaldehydato ligand, respectively. In general, σ delocalization causes downfield shift of proton NMR, which attenuate in magnitude with the number of interconvening bonds, and in some cases it causes large downfield shifts for protons on a zigzag route from a spin site.[13b,15] The large downfield shift observed for the 4 position in $Ni(sal)_2 \cdot 2py$ is apparently due to this stereospecific spin transfer through σ orbitals, showing existence of appreciable σ delocalization in $Ni(sal)_2 \cdot 2py$. It should be noted that the pattern of the contact shifts for Co(salen) and its methyl derivatives differs from that seen for $Ni(sal)_2 \cdot 2py$.

In contrast to the above result, the contact shifts for Co(salen) and its methyl derivatives resemble well those reported for bis(*N*-isopropylsalicylaldiminato)nickel(II) complex and its methyl derivatives[13] in relative magnitude and sign, though the contact shift for the 6 position in Co(salen) is much larger than that in the nickel(II) complexes. Better proportionality is seen between the contact shifts for Co(salen) and the spin density distribution for the salicylaldiminato π cation calculated by the valence bond method;[13a] the proportionality is shown by the ratio of the calculated and experimental spin densities in Table III (vide infra). In view of these facts it seems reasonable to conclude that π delocalization far outweighs σ delocalization in the planar low-spin Co(salen) and its methyl derivatives.

Table III lists the spin densities calculated by the McConnell relation[17] for ring protons, $a_H = Q_{CH}\rho_C$, and the similar relation for methyl protons, $a_{Me} = Q_{Me}\rho_C$, as-

Table III. Comparison of Spin Densities for Co(salen), ρ_{expl}, with Those Calculated for the Salicylaldiminato π Cation, ρ_{calcd}

Position	ρ_{expl}[a]	ρ_{calcd} VB method[b]	ρ_{calcd} McLachlan[c] method	$\rho_{\text{calcd}}/\rho_{\text{expl}}$[d]
3	(+0.0087)	+0.3477	+0,2546	(40.0)
4	−0.0035 (−0.0051)	−0.1972	−0.0612	54.8 (38.7)
5	+0.0181 (+0.0110)	+0.3897	+0.3127	21.5 (35.4)
6	−0.0051	−0.2190	+0.1270	42.9

[a] Obtained from a_N values based on g values in the CH_2Cl_2 solvent system. The vlaues in parentheses are obtained from a_N for methyl protons and others from a_N for ring protons. [b] Taken from ref 13a. [c] The following parameters were used. $\delta\alpha_N = 2.0\beta$, $\delta\alpha_0 = 2{,}8\beta$, $\beta_{N\text{-}7} = 0.9\beta$, $\beta_{O\text{-}2} = 0.8\beta$, and $\lambda = 1.0$. [d] The spin densities by the VB method were used for ρ_{calcd}. The values in parentheses are based on ρ_{expl} obtained using methyl protons.

suming the values for Q_{CH} and Q_{Me} to be −22.5 and +27 G, respectively. The spin densities obtained are compared to those for the salicylaldiminato π cation in the table. From the fact that the spin densities for Co(salen) are proportional to those for the salicylaldiminato π cation, it is deduced that there is transfer of β spin from the highest bonding π MO of the ligand to the metal, retaining excess α spin on the ligand. It may be worthwhile to note that the mode of the spin delocalization is also anticipated from the viewpoint of the MO theory. That is, the lowest vacant π orbital has a node on the plane including the axis of the $d\pi$ orbital of the cobalt(II) ion. However, the highest bonding π orbital does not have a node in the plane, and hence it is more preferable for the $p\pi$–$d\pi$ interaction than the lowest vacant π orbital. From the observed spin density distribution, the total unpaired electron densities delocalized on the ligand are estimated to be about 1–4% of that in the cobalt(II) ion.

Ground State Electronic Configuration of Planar Low-Spin Co(salen). Although it has been pointed out that appreciable in-plane magnetic anisotropy for the planar Co(salen) results from a small energy difference between the d_{z^2} and d_{yz} levels,[1b,c,2b,6] it is not well-established which orbital is lower. Busetto et al.[1c] considered that an electronic configuration with an unpaired electron in the d_{z^2} orbital is the ground state of the Co(salen). On the other hand, Zelewsky et al.[2c] reported that in the ground state an unpaired electron is mainly in the d_{yz} orbital. In a recent ESR study, Kawakita et al.[6] also showed that the model of Zelewsky et al. is preferable as the ground state of the planar Co(salen).

It has been shown above that there is transfer of β spin from the highest bonding π MO of the ligand to the metal. For such a π spin-delocalization mechanism, the electronic configuration with an unpaired electron in the d_{yz} orbital is apparently more favored than that with an unpaired electron in the d_{z^2} orbital for the ground state of the cobalt(II) ion. In the model of Busetto et al., assuming the (d_{z^2}) configuration to be the lowest, they showed that the (d_{yz}) configuration also takes part in the ground state as a minor contributor (i.e., in the extent of 3%) by the spin-orbit coupling effect.[1c] In their model, the half-filled orbital in the (d_{yz}) configuration should have an unpaired electron with an opposite spin (β spin) to that of the unpaired electron in the main (d_{z^2}) configuration. Hence in their model, the M $\leftarrow$ L electron transfer would favor α spin transfer. Apparently this contradicts the observation. It can be concluded, therefore, that the electronic configuration with an unpaired electron in the d_{yz} orbital is the most likely as the ground state of the planar Co(salen).

It has been shown that the contact shifts of the planar low-spin cobalt(II) porphyrin complexes are small and have negligible contribution to the isotropic shifts.[17] This small contact interaction has been explained by La Mar et al. as being consistent with the ground state of the complexes having an unpaired electron in the d_{z^2} orbital. The significant contribution of the contact shifts in the present planar low-spin Co(salen) contrasts with the contact shifts of the cobalt(II) porphyrin complexes. This fact seems to be another support of our conclusion about the ground state electronic configuration of the complex.

Temperature Dependence of Isotropic Shifts. Deviation from the Curie law was observed for temperature dependence of the isotropic shifts (Figure 3); the plot of the isotropic shifts vs. T^{-1} is nearly linear for each proton over the range of experiment, but the extrapolated lines do not pass through the origin at $T^{-1} = 0$. Especially, the behavior of the 6 position appears to be somewhat curious. The deviations of the intercept from the origin are too large to attribute merely to inappropriate subtraction of diamagnetic contributions. In some cases it has been pointed out that changes in axial perturbation by solvent molecules with temperature cause deviation of dipolar shifts from the Curie law.[17] In the present case, however, the deviation from the Curie law is not proportional to the geometric factor in the dipolar term, suggesting that the temperature dependent axial perturbation by solvents is not a dominant effect.

On the other hand, the previous investigations by ESR have indicated that the first excited state of planar Co(salen) lies closely to the ground state; Kawakita et al.[6] and Zelewsky et al.[2c] predicted that the first excited state lies only 2 kK above the ground state. It seems likely, therefore, that the SOZ term may make some contributions to both the dipolar and contact shifts, and hence it may cause some deviation from the Curie law. Because of the absence of reliable data on the excited states or magnetic susceptibilities, detailed analysis of the SOZ contributions was not tried, though they were roughly estimated to be about 20% at most based on the data of Kawakita et al. on the excited states. By the SOZ contributions and other unknown effects, the analysis of the isotropic shifts in Table II may include some error, but the neglect of these effects in the analysis does not seem to affect our conclusion on the ground state electronic configuration of the planar low-spin Co(salen).

On the Assignment of g Tensor. In this work, we treated the largest g value as g_{xx} and the smallest one as g_{yy} according to the ESR analysis. When any other selection of g_{xx} was made, it was impossible to find a proper model which reasonably explains the resultant contact shifts. The assignment of the largest g value to g_{xx} seems most likely as was concluded from the ESR analysis. The assignment of the smallest two g values to g_{yy} or g_{zz} could not be made by means of NMR analysis, because of the small difference between the two g values.

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Structure and Bonding in Octafluoro-*trans*-but-2-enebis(triphenylphosphine)platinum, $Pt[CF_3CFCFCF_3][P(C_6H_5)_3]_2$, a Compound with Unusually Long Carbon–Fluorine Bonds

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Abstract: The crystal and molecular structure of a substituted olefin complex of platinum, $Pt[CF_3CFCFCF_3][P(C_6H_5)_3]_2$, has been determined from three-dimensional X-ray diffraction data. The complex crystallizes in space group $P2_1/c$ of the monoclinic system, with four molecules in a unit cell of dimensions $a = 11.635$ (2) Å, $b = 19.213$ (4) Å, $c = 18.107$ (3) Å, $\beta = 114.39$ (2)°. The structural parameters were refined by least-squares techniques, the R factor on F converging to 5.4% for the 3841 independent reflections (measured using a four-circle diffractometer) for which $F^2 > \sigma(F^2)$ and $2\theta \le 50°$. No symmetry is crystallographically imposed upon the molecules but they have C_2 symmetry to a good approximation. Coordination around platinum is not exactly planar, the largest distortion being the displacement of one olefinic carbon atom by 0.29 (1) Å from the plane defined by the other four atoms; the dihedral angle between the PtP_2 and PtC_2 planes is 10.8 (7)°. The olefinic carbon–carbon separation is 1.429 (14) Å; this value does not differ significantly from the corresponding parameter in the analogous 4,4′-dinitro-*trans*-stilbene complex, suggesting that the separation of the olefinic carbon atoms in complexes of this type formed by acyclic olefins is not a function of the olefinic substituents. The olefinic carbon atoms are essentially equidistant from platinum, the Pt–C distances being 2.028 (12) and 2.048 (11) Å. The Pt–P bond lengths are 2.302 (3) and 2.322 (3) Å. The bonds from each olefinic carbon atom to its fluoro substituent are unusually long at 1.426 (13) and 1.437 (12) Å. The chemical shift in the ^{19}F NMR spectrum of these two fluorine nuclei is much further upfield in the complex than in the free olefin; the chemical shift of the CF_3 resonances does not change greatly upon formation of the complex, and these groups are of normal geometry in the complex. The binding energy of the Pt $4f_{7/2}$ electrons in $Pt[CF_3CFCFCF_3][P(C_6H_5)_3]_2$ is 1.0 eV higher than in the analogous 4,4′-dinitro-*trans*-stilbene complex and is close to that in $PtCl_2[P(C_6H_5)_3]_2$. These results were interpreted to mean that considerable electron density is transferred from platinum to the olefinic fluoro substituents upon formation of the complex. Since the general characteristics of fluoro substituents are such that this electron transfer would be through molecular orbitals of A symmetry, then the Dewar–Chatt–Duncanson model for the bonding in olefin–metal complexes is inappropriate.

Olefins interact to varying degrees with transition metal compounds, in some cases forming isolable complexes in which the structure and properties of the olefin moiety are modified, with the result that the reactivity of the olefin toward additional reagents is also modified. In order to design transition metal compounds that might confer unusual reactivity upon olefins, it is necessary to determine the changes in olefin geometry that occur upon interaction with a metal. The class of compounds of general formula $Pt[L][P(C_6H_5)_3]_2$, where L is an olefin, is suitable for a systematic study of the geometry of olefins in stable complexes because a wide range of olefins form such complexes[2,3] and also because steric constraints are not imposed upon the olefin by the rest of the molecule. In the first paper[4] of a series from this laboratory in which the structure and properties of selected olefin–bis(triphenylphosphine)platinum complexes are to be reported, the olefin was 4,4′-dinitro-*trans*-stilbene, chosen because it forms a very stable complex[2a] and because the substituents upon the olefin are powerfully electron withdrawing in a π-fashion. In the complex, the olefin substituents manifestly utilize their electron-withdrawing ability to the maximum extent possible, since the planes of the 4-nitrophenyl substituents are perpendicular to the plane defined by the platinum and olefinic carbon atoms, in spite of the fact that this orientation is relatively unfavorable in terms of intraolefin contacts. The separation of the olefin carbon atoms was 1.42 (2) Å in this complex, which is among the shortest observed in this type of compound. Several other complexes of this general formula have been the subject of X-ray diffraction experiments,[5-10] but relatively few of the reported structures are of high precision; the present studies were undertaken to define more clearly the relationships between the steric and electronic effects of the olefin substituents and the structure