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# Assignment of the Ligating Nitrogen in *o,o′*-Dihydroxyazoarene Complexes of Nickel-, Palladium-, and Platinum(II) by $^1$H and $^{13}$C NMR Spectroscopy

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The $^1$H and $^{13}$C NMR spectra of the soluble square-planar *o,o′*-dihydroxyazoarene−platinum(II) complexes [Pt(L)(tba)] (L = 5,5′-dichloro-2,2′-*dih*ydroxy*azob*enzenate (dhab), (5-chloro-2-*h*ydroxy*p*henyl*a*zo)-3-oxo-*N*-phenyl*b*utanamidate (hpab), or (5-chloro-2-*h*ydroxy*p*henyl*a*zo)-2-*n*aphtholate (hpan) and tba = *t*ri*b*utyl*a*mine) and the protonated ligands have been assigned by use of homo- and heteronuclear 2D correlated NMR spectroscopy. The assignment of spectra of the analogous complexes [M(L)(py)] (M = nickel(II), palladium(II), and platinum(II) and py = *py*ridine) has been achieved by comparison of the chemical shifts. $^{13}$C chemical shifts of corresponding carbon signals of the 5-chloro-2-hydroxyphenyl group, common to all the eight complexes with hpab and hpan, are very similar to each other, and in turn these shifts are very similar to the one set of signals from the 5-chloro-2-hydroxyphenyl groups in the four complexes of the symmetrically substituted ligand dhab. These chemical shifts exhibit the same periodic change when the ligand is coordinated to different group 10 metal ions, and the signals are assumed to originate from 5-chloro-2-hydroxyphenyl groups with equal coordination environment in all the reported complexes; thus $^{13}$C NMR spectroscopy is believed to constitute an excellent way of establishing isostructurality. On the basis of the crystal structures of complexes with the unsymmetrical ligands hpab and hpan, all the reported complexes with these ligands are $N_\alpha$-isomers coordinated to the metal at the azo nitrogen attached to the 5-chloro-2-hydroxyphenyl substituent. The changes in $^{13}$C chemical shift with coordination can be used to distinguish $N_\alpha$- from $N_\beta$-isomers. Deuterium isotope effects on $^{13}$C chemical shifts in the hpab complexes with one exchangeable amine proton and in the free unsymmetrically substituted ligands (hpab)$H_2$ and (hpan)$H_2$ themselves reveal intramolecular hydrogen bonds and predominant tautomeric forms, these being possible indicators for predicting the identity of the ligating nitrogen. $^nJ_{^{195}\mathrm{Pt}-^{13}\mathrm{C}}$ couplings in the [Pt(L)(tba)] complexes have been measured at low field, and the magnitudes of these couplings are analyzed in terms of coupling paths in the two annulated five- and six-membered rings formed by the ligand and the central platinum(II) ion.

## Introduction

NMR spectroscopy is a very sensitive probe for small covalent modifications and has also been used to identify isomers of diamagnetic coordination compounds.[1,2] Among complexes of *o,o′*-dihydroxyazoarene dyes different NMR-based methods have been used to elucidate the question of $N_\alpha$−$N_\beta$-isomerism; i.e. which of the two azo nitrogens is coordinated to the metal ion. Thus with $^{15}$N-labeled ligands the large one-bond coupling to $^{195}$Pt has been used to identify the isomers.[3−5] Another approach is based on the comparison of the chemical shifts in the complexes with those of the analogous *o,o′*-dihydroxyazomethinearene complexes.[3] Generally the chemical shifts have been compared with those of the uncoordinated ligands,[6−9] and in addition differences between easily assignable signals from the substitutents at the coordinating and at the noncoordinating nitrogen in complexes of symmetrically substituted azo dyes have been compared,[4] as have signals from unsymmetrically substituted azo-dye complexes forming both $N_\alpha$- and $N_\beta$-isomers.[3,9] The latter methods all rely on comparisons with complexes of known $N_\alpha$−$N_\beta$-isomerism or on small, difficultly interpretable changes in $^1$H chemical shift. In the present study $^{13}$C chemical shifts and $^{195}$Pt−$^{13}$C couplings have proved to be powerful tools for the determination of isomerism in a series of Ni(II), Pd(II), and Pt(II) complexes with two different azo dyes. The higher solubility in chloroform of the complexes with tributylamine in the fourth coordination site relative to the analogous pyridine ligated complexes permits observations at lower field strengths and thus reduces the problems due to *C*hemical *S*hift *A*nisotropy (CSA) relaxation of the $^{195}$Pt nucleus at high field strengths.[10,11]

## Experimental Section

**Materials.** The 3 ligands and 12 metal complexes used are those shown in Figure 1, the syntheses of which are reported in a separate paper[12] together with the crystal structures of [Ni(hpab)(py)] and [Pt(hpan)(tba)] and with a study of isomorphology between the Ni(II), Pd(II), and Pt(II) complexes by X-ray powder diffraction. Deuteriochloroform (>99.5% D) ($CDCl_3$) and hexadeuteriodimethyl sulfoxide (>99.5% D) (DMSO-$d_6$) with 0.03% and 1% tetramethylsilane (TMS) for the NMR measurements and deuteriomethanol for deuteriation were from Aldrich, Weinheim, Germany.

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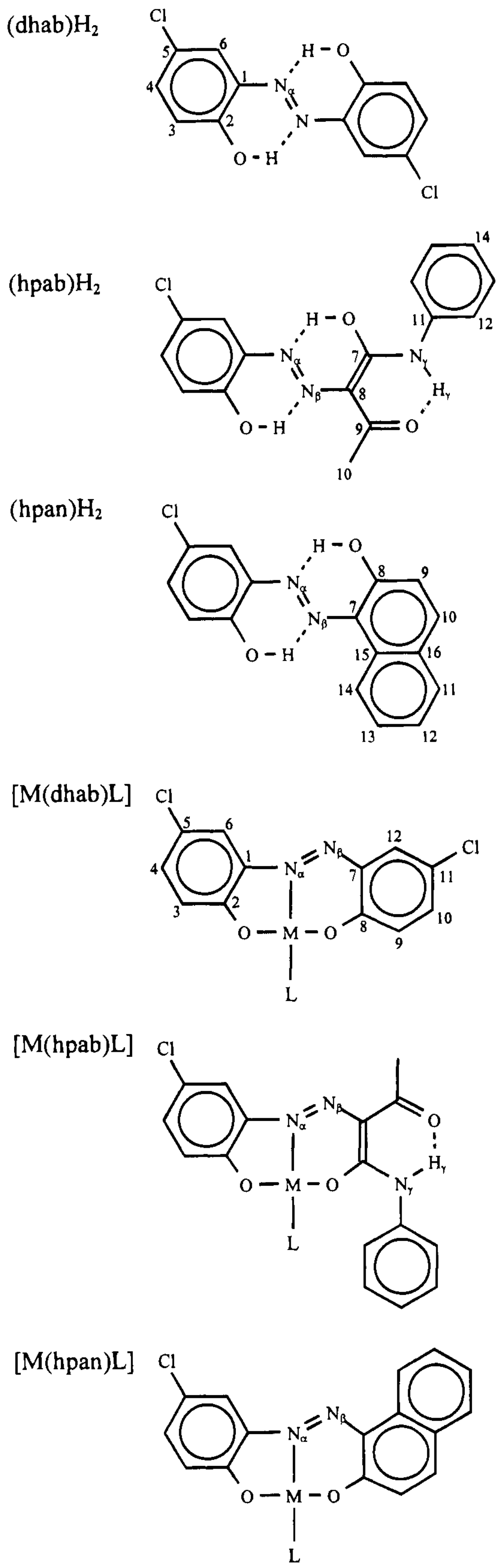

**Figure 1.** Structural formulas with numerals for NMR signal assignment. M = Ni(II), Pd(II), or Pt(II) and L = py or M = Pt(II) and L = tba.

**Deuterium Substitution.** Approximately 60% deuterium substitution of the unsymmetrically substituted ligands was achieved by refluxing 33.2 mg and 29.9 mg (0.1 mmol) of the two ligands (hpab)$H_2$ and (hpan)$H_2$, respectively, in 10 mL of a 1:3 mixture of $CH_3OH$/$CH_3OD$ for 7 days, after which the solvent was distilled off and the sample dried at 100 °C. In the case of (hpab)$H_2$, 49 mg of 37% (0.5 mmol) hydrochloric acid was added before addition of the ligand to avoid a base-catalyzed deuterium substitution of the acetyl hydrogens at C10. Deuterium substitution of the NH protons in the [M(hpab)(py)] and [Pt(hpab)(tba)] complexes was achieved by stirring 20 mg in 1 mL of a 1:4 mixture of $CH_3OH$/$CH_3OD$ at 50 °C for 3 days in a closed test tube, after which the solvent of the [M(hpab)(py)] suspensions was decanted off and the sample dried at 100 °C. The [Pt(hpab)(tba)] suspension was evaporated to dryness.

**$^1H$ and $^{13}C$ NMR Spectroscopy.** $^1H$ and $^{13}C$ NMR measurements were performed on a Bruker AC250 spectrometer operating at 250 and 62 MHz. The $^1H$ and $^{13}C$ spectra of 0.10 M solutions in DMSO-$d_6$ of the ligands $LH_2$ and of 0.10 M solutions in $CDCl_3$ of the (tributylamine)platinum complexes [Pt(L)(tba)] were recorded using a 5 mm $^1H$ and $^{13}C$ dual probe for both one- and two-dimensional spectra. $^1H$ and $^{13}C$ spectra of the saturated solutions in $CDCl_3$ of the nine [M(L)(py)] complexes were measured in a 10 mm broadband probe. TMS was used as internal reference in the one-dimensional spectra, and all two-dimensional spectra were sweep width optimized for the aromatic region in both dimensions except for the COLOC spectra of the ligands and [Pt(hpab)(tba)], where the hydroxyl and amine proton resonances were included.

$^1H-^1H$-correlated spectra of the ligands and the [Pt(L)(py)] and [Pt(L)(tba)] complexes with enhancement of long-range effects were recorded using a COSY pulse sequence with D2 = 50 ms.[13] A total of 16 transients were used in each of 128 increments with zero-filling in f1 and sine-bell apodization applied in both dimensions prior to transformation. $^1H-^{13}C$-correlated spectra with $^1H$ refocusing and decoupling were recorded using a heteronuclear COSY pulse sequence with D2 = 2 × D3 = 3.13 ms.[14-16] A total of 64 transients were used in each of 64 increments with 5 Hz line broadening in f2 and sine-bell apodization and zero-filling in the f1 dimensions prior to transformation.

$^1H-^{13}C$-correlated spectra with enhancement of long-range effects and $^1H$ refocusing and decoupling were recorded using the COLOC pulse sequence with D2 = 2 × D3 = 64.9 ms.[17] A total of 256 transients were used in each of 256 increments with 5 Hz line broadening in f2 and sine-bell apodization and zero-filling in the f1 dimensions prior to transformation. The total measuring time for one series of all three two-dimensional spectra was less than 12 h.

$^1H$ and $^{13}C$ spectra of the tributylamine−platinum complexes in $CDCl_3$ (0.10 M) with observable $^{195}Pt$-couplings were measured in 10 mm tubes both on a JEOL JNM-FX 100 spectrometer operating at 100 and 25 MHz, respectively, and on a JEOL-90 spectrometer operating at 90 and 23 MHz.

**Assignments.** NMR assignment was straightforward for the proton spectra using the homonuclear COSY spectra of the ligands, [Pt(L)(py)], and the more soluble [Pt(L)(tba)] complexes. The only ambiguities were caused by the signal multiplicity in H9 and H10 in the 2-naphthol substituent, both resonances seen as coupled doublets, and H11, H12, H13, and H14 in the same spectra, where H11 and H12 can be interchanged with H14 and H13, respectively. This problem was solved by comparison with the low-field chemical shift of H14 in analogous compounds and by the inter-ring five-bond long-range coupling between H10 and H14 being significantly larger in various 1,2-disubstituted naphthalenes than the four-bond coupling between H10 and H11,[18-20] thus giving rise to larger cross-peaks in the $^1H-^1H$ COSY spectra.

The changes in analogous $^1H$ chemical shifts, when substituting py for tba in the platinum complexes, are very small (<0.15 ppm) for all three coordinated ligands. The variation among [Pt(L)(py)], [Pd(L)(py)], and [Ni(L)(py)] is a strictly periodical change in signal position (Tables 1−3). The assignment was facilitated by the easily recognizable signal patterns. The distinction between the similar spin systems of

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**Table 1.** $^1H$ and $^{13}C$ Chemical Shifts Assignments and Values of (dhab)$H_2$, [Ni(dhab)(py)], [Pd(dhab)(py)], [Pt(dhab)(py)], and [Pt(dhab)(tba)] in ppm vs TMS

| | (dhab)$H_2$[a] | | [Ni(dhab)(py)][b] | | [Pd(dhab)(py)][b] | | [Pt(dhab)(py)][b] | | [Pt(dhab)(tba)][c] | |
|---|---|---|---|---|---|---|---|---|---|---|
| signal | $^1H$ | $^{13}C$ | $^1H$ | $^{13}C$ | $^1H$ | $^{13}C$ | $^1H$ | $^{13}C$ | $^1H$ | $^{13}C$ |
| 1 | | 139.0 | | 146.9 | | 147.0 | | 147.0 | | 146.7 |
| 2 | 11.02 | 154.5 | | 164.5 | | 166.9 | | 167.2 | | 167.7 |
| 3 | 7.10 | 119.9 | 6.79 | 117.9 | 6.99 | 119.4 | 7.18 | 118.3 | 7.09 | 118.3 |
| 4 | 7.43 | 132.9 | 7.14 | 129.4 | 7.21 | 131.6 | 7.27 | 130.8 | 7.24 | 130.4 |
| 5 | | 123.9 | | 121.5 | | 121.5 | | 121.9 | | 121.1 |
| 6 | 7.97 | 119.2 | 8.03 | 116.6 | 8.08 | 117.2 | 8.29 | 118.4 | 8.26 | 116.7 |
| 7 | | | | 140.5 | | 140.6 | | 141.8 | | 141.6 |
| 8 | | | | 149.2 | | 150.1 | | 148.6 | | 148.3 |
| 9 | | | 7.02 | 121.9 | 7.23 | 122.1 | 7.30 | 122.9 | 7.16 | 123.1 |
| 10 | | | 7.22 | 132.6 | 7.33 | 134.0 | 7.50 | 132.3 | 7.45 | 131.6 |
| 11 | | | | 122.2 | | 121.6 | | 122.9 | | 122.1 |
| 12 | | | 7.85 | 131.7 | 7.96 | 132.3 | 8.17 | 131.3 | 8.12 | 131.0 |
| 1'[e] | 8.62[d] | 149.9 | 8.69 | 149.8 | 8.96 | 149.3 | 9.19 | 149.8 | 3.13 | 56.6 |
| 2' | 7.28 | 123.7 | 7.47 | 124.5 | 7.56 | 125.2 | 7.62 | 125.4 | 1.18 | 26.7 |
| 3' | 7.68 | 135.9 | 7.88 | 138.8 | 7.96 | 139.2 | 8.02 | 139.3 | 1.34 | 20.5 |
| 4' | | | | | | | | | 0.94 | 13.9 |

[a] 0.1 M in DMSO-$d_6$ at 310 K. [b] Saturated in $CDCl_3$ at 300 K. [c] 0.1 M in $CDCl_3$ at 300 K. [d] 0.1 M py in $CDCl_3$ at 300 K. [e] The primes refer to the chemical shifts from py and tba.

**Table 2.** $^1H$ and $^{13}C$ Chemical Shift Assignments and Values of (hpab)$H_2$, [Ni(hpab)(py)], [Pd(hpab)(py)], [Pt(hpab)(py)], and [Pt(hpab)(tba)] in ppm vs TMS

| | (hpab)$H_2$[a] | | [Ni(hpab)(py)][b] | | [Pd(hpab)(py)][b] | | [Pt(hpab)(py)][b] | | [Pt(hpab)(tba)][c] | |
|---|---|---|---|---|---|---|---|---|---|---|
| signal | $^1H$ | $^{13}C$ | $^1H$ | $^{13}C$ | $^1H$ | $^{13}C$ | $^1H$ | $^{13}C$ | $^1H$ | $^{13}C$ |
| 1 | | 130.6 | | 147.7 | | 147.6 | | 146.8 | | 146.7 |
| 2 | 10.65 | 145.0 | | 161.4 | | 163.6 | | 164.8 | | 165.4 |
| 3 | 6.96 | 117.0 | 6.61 | 116.0 | 6.73 | 117.3 | 6.86 | 116.5 | 6.87 | 116.4 |
| 4 | 6.99 | 124.6 | 6.86 | 127.5 | 6.89 | 128.1 | 6.94 | 127.5 | 6.96 | 127.4 |
| 5 | | 123.8 | | 120.4 | | 120.6 | | 121.0 | | 120.3 |
| 6 | 7.51 | 113.7 | 7.54 | 114.8 | 7.51 | 115.6 | 7.61 | 115.5 | 7.73 | 115.4 |
| 7 | 11.27 | 161.8 | | 153.6 | | 153.6 | | 151.9 | | 152.1 |
| 8 | | 126.8 | | 121.7 | | 121.7 | | 123.4 | | 123.1 |
| 9 | | 198.7 | | 197.9 | | 198.5 | | 199.3 | | 199.1 |
| 10 | 2.52 | 25.9 | 2.59 | 26.6 | 2.58 | 27.5 | 2.61 | 27.4 | 2.71 | 27.4 |
| 11 | | 136.9 | | 136.7 | | 137.2 | | 137.4 | | 137.2 |
| 12 | 7.64 | 120.3 | *d* | 122.5 | *d* | 122.9 | *d* | 122.7 | *d* | 123.9 |
| 13 | 7.37 | 128.9 | *d* | 128.8 | *d* | 128.8 | *d* | 128.9 | *d* | 128.9 |
| 14 | 7.16 | 124.4 | *d* | 124.2 | *d* | 125.3 | *d* | 125.1 | *d* | 125.5 |
| NH | 14.28 | | 12.65 | | 13.13 | | 13.15 | | 13.06 | |
| 1'[e] | | | 8.40 | 150.1 | 8.56 | 149.3 | 8.74 | 149.6 | 2.83 | 56.5 |
| 2' | | | 7.29 | 125.3 | *d* | 124.9 | *d* | 125.0 | 1.80 | 26.5 |
| 3' | | | 7.80 | 138.7 | 7.83 | 138.8 | 7.86 | 138.6 | 1.23 | 20.3 |
| 4' | | | | | | | | | 0.88 | 13.9 |

[a] 0.1 M in DMSO-$d_6$ at 310 K. [b] Saturated in $CDCl_3$ at 300 K. [c] 0.1 M in $CDCl_3$ at 300 K. [d] $^1H$ Chemical shifts have not been determined accurately. [e] The primes refer to the chemical shifts from py and tba.

**Table 3.** $^1H$ and $^1C$ Chemical Shift Assignments and Values of (hpan)$H_2$, [Ni(hpan)(py)], [Pd(hpan)(py)], [Pt(hpan)(py)], and [Pt(hpan)(tba)] in ppm vs TMS

| | (hpan)$H_2$[a] | | [Ni(hpan)(py)][b] | | [Pd(hpan)(py)][b] | | [Pt(hpan)(py)][b] | | [Pt(hpan)(tba)][c] | |
|---|---|---|---|---|---|---|---|---|---|---|
| signal | $^1H$ | $^{13}C$ | $^1H$ | $^{13}C$ | $^1H$ | $^{13}C$ | $^1H$ | $^{13}C$ | $^1H$ | $^{13}C$ |
| 1 | | 130.0 | | 147.8 | | 148.0 | | 147.8 | | 147.6 |
| 2 | 10.83 | 146.9 | | 163.0 | | 165.4 | | 166.0 | | 166.5 |
| 3 | 7.02 | 117.5 | 6.81 | 117.3 | 7.04 | 118.9 | 7.21 | 118.0 | 7.12 | 118.0 |
| 4 | 7.17 | 126.7 | 7.09 | 129.8 | 7.20 | 130.6 | 7.28 | 129.3 | 7.22 | 128.9 |
| 5 | | 124.2 | | 121.0 | | 121.3 | | 121.6 | | 120.8 |
| 6 | 7.89 | 114.9 | 8.15 | 116.1 | 8.26 | 116.8 | 8.46 | 116.6 | 8.43 | 116.5 |
| 7 | | 132.2 | | 132.5 | | 134.1 | | 134.0 | | 133.8 |
| 8 | 16.13 | 174.5 | | 150.7 | | 151.3 | | 149.2 | | 148.6 |
| 9 | 6.78 | 125.3 | 7.14 | 124.5 | 7.41 | 123.4 | 7.45 | 124.6 | 7.30 | 124.2 |
| 10 | 7.88 | 140.9 | 7.70 | 138.6 | 7.81 | 135.1 | 7.94 | 133.1 | 7.87 | 132.3 |
| 11 | 7.71 | 128.8 | 7.67 | 127.8 | 7.73 | 127.7 | 7.79 | 127.7 | 7.73 | 127.6 |
| 12 | 7.43 | 126.2 | 7.40 | 124.5 | 7.42 | 124.3 | 7.45 | 124.6 | 7.37 | 124.3 |
| 13 | 7.59 | 129.2 | 7.63 | 127.8 | 7.66 | 127.9 | 7.73 | 127.5 | 7.68 | 127.3 |
| 14 | 8.48 | 121.5 | 8.67 | 122.6 | 8.81 | 122.8 | 8.93 | 123.8 | 8.87 | 123.5 |
| 15 | | 132.6 | | 132.5 | | 132.3 | | 134.0 | | 133.8 |
| 16 | | 127.6 | | 127.8 | | 127.7 | | 128.5 | | 128.4 |
| 1'[e] | 2.38[d] | 54.1 | 8.75 | 149.9 | 9.06 | 149.4 | 9.25 | 149.9 | 3.16 | 56.7 |
| 2' | 1.41 | 29.5 | 7.49 | 124.5 | 7.58 | 125.2 | 7.62 | 125.4 | 1.90 | 26.7 |
| 3' | 1.29 | 20.9 | 7.88 | 138.6 | 7.97 | 139.1 | 7.99 | 139.1 | 1.37 | 20.5 |
| 4' | 0.91 | 14.1 | | | | | | | 0.93 | 13.9 |

[a] 0.1 M in DMSO-$d_6$ at 310 K. [b] Saturated in $CDCl_3$ at 300 K. [c] 0.1 M in $CDCl_3$ at 300 K. [d] 0.1 M tba in $CDCl_3$ at 300 K. [e] The primes refer to the chemical shifts from py and tba.

the two rings in the dhab complexes can be achieved by comparison with $^1H$ chemical shifts of hpan and hpab complexes.

The exchangeable hydrogens of the ligands were assigned by inspection of the $^1H$ traces in the COLOC spectra, which showed distinct cross-peaks between H10,C8; $NH_\gamma$,C8; $NH_\gamma$,C12; $N_\alpha H$,C8; and $N_\alpha H$,C1 in (hpab)$H_2$ and between H8,C7 and H8,C2 in (hpan)$H_2$. The hydroxy hydrogens from the 5-chloro-2-hydroxyphenyl groups are comparable in all three ligands and can thus also be identified by the

**Table 4.** Deuterium Isotope Effects on $^{13}$C Chemical Shifts in ppb, Where $\Delta[H(D)^{13}C] = \delta[C(H)] - \delta[C(D)]^a$

| $\delta_{^{13}C}$ signal | (hpab)$H_2$ | (hpan)$H_2$ | [Ni(hpab)(py)] | [Pd(hpab)(py)] | [Pt(hpab)(py)] | [Pt(hpab)(tba)] |
|---|---|---|---|---|---|---|
| 1 | 58<br>127 | 61 | | | | |
| 2 | 190<br>53 | 192$^b$<br>27$^b$ | | | | 21 |
| 3 | 84 | ~34$^b$ | | | | |
| 4 | | 165 | | | | |
| 5 | −69 | *b* | | | | |
| 6 | 36 | 88 | | | | |
| 7 | 102<br>80 | −138 | 130 | 128 | 142 | 145 |
| 8 | ~30<br>~13 | −377 | 35 | 44 | | 38 |
| 9 | 59<br>18 | −108 | 35 | 51 | 44 | 33 |
| 10 | ~15<br>~8 | | −52 | −54 | −57 | −62 |
| 11 | 100<br>18 | −61 | 104 | 118 | 111 | 124 |
| 12 | 101<br>12 | | 113 | 101 | 104 | 95 |
| 13 | ~9 | | | | | |
| 14 | | −71 | | | | |
| 15 | | −54 | | | | |
| 16 | | −40 | | | | |

[a] ~ indicates approximate value and uncertain sign. [b] Broad signal with resolved or partly resolved deuterium couplings.

chemical shift in the symmetrical (dhab)$H_2$. The hydroxy hydrogen signal in (dhab)$H_2$ is relatively broad. This is probably due to weak hydrogen bonds and thus exchange with solvent water or is subject to tautomeric or conformational exchange. This suggestion is supported by the inability to measure hydrogen−deuterium isotope effects when dissolved in DMSO-$d_6$, possibly due to signal averaging.

The $^{13}$C assignments of the primary carbons in the ligands and the tributylamine complexes were established using $^1$H−$^{13}$C-correlated spectra.

The quaternary carbons of the [Pt(L)(tba)] complexes were assigned from the long-range enhanced heteronuclear correlated spectra and generally confirm the $^1$H and primary carbon assignments mentioned above, as the visible cross-peaks originate exclusively from one-, two-, and three-bond couplings. The cross-peak patterns observed from the 5-chloro-2-hydroxyphenyl groups are similar for the three platinum(II) complexes. The cross-peaks are due to the following couplings; most $^1J(Cx,Hx)$ and the two-bond couplings between C1,H6; C2,H3; C5,H6; and C5,H4 and all the possible three-bond couplings except between C6 and H4. This pattern is in accordance with expectations as two-bond carbon−hydrogen couplings are small in benzene, except when the carbon is substituted with an electronegative substituent.

In the assignment of the $^{13}$C spectra of the series of [M(L)(py)] complexes, the small chemical shift differences, and the higher intensity of the primary carbon signals due to NOE effects, facilitated signal recognition.

In the hpab complexes the C7 and C8 signals are unequivocally and independently assigned by the two- and three-bond hydrogen-deuterium isotope effect (see Table 4). The isotope effects confirm the $^{13}$C signal assignments of the ligands, taking into account the intramolecular hydrogen bonds. The $^1$H and $^{13}$C chemical shifts and assignments and $^{13}$C−H(D) isotope substitution effects of the ligands and their complexes are shown in Tables 1−4.

The observations of platinum satellites due to carbon−platinum couplings are hampered by chemical shift anisotropy relaxation. This prevents observation at 5.88 T and higher fields, whereas the couplings can be observed at 2.35 T. The symmetrically positioned $^{195}$Pt satellites at 2.35 T are marked in pairs with asterisks or crosses in the $^{13}$C NMR spectrum of [Pt(hpan)(tba)] in Figure 2a. For comparison the illustration includes spectra at both fields and the magnitudes of carbon−platinum couplings are given in Figure 3. A very large platinum−proton coupling is also observed in [Pt(hpab)(tba)], and this four-bond coupling of 22 Hz to the NH proton is unusual. Platinum couplings to aromatic protons are not resolved.

## Results and Discussion

**Chemical Shifts.** When comparing the $^{13}$C chemical shifts of the 5-chloro-2-hydroxyphenyl groups in the complexes with the *same* ligand (Tables 1−3), but with different group 10 metals (see Figure 4 for C1, C2, C7, and C8), we observe a periodic shift when ascending the periods from nickel to platinum. The ranges in chemical shifts, of less than 3.4 ppm (4.0 ppm when including the [Pt(L)(tba)] complexes), are attributed to the differences in complex bond character (an inductive effect) and electric field effects (effects mediated through space) rather than different conformational or coordination geometries. However, comparison of the $^{13}$C chemical shifts of the corresponding C1 and C7 signals in the [M(dhab)L] complexes shows differences between 5.1 and 6.4 ppm. The differences between the corresponding C2 and C8 in these complexes are between 15.3 and 19.4 ppm. These $^{13}$C chemical shifts originate from the five-membered chelate ring containing C1 and C2 (Figure 1) and from the different six-membered chelate ring formed with the central metal ion, containing C7 and C8 and both nitrogens of the azo group. For complexes with *different* ligands, the $^{13}$C chemical shifts of the 5-chloro-2-hydroxyphenyl group in the [M(hpab)(L)] and [M(hpan)(L)] complexes (Tables 2 and 3, signals 1−6) are almost identical to one of the two sets in the [M(dhab)(L)] complexes (Table 1, signals 1−6).

On the basis of the X-ray structure of [Ni(hpab)(py)] and [Pt(hpan)(tba)][12] and the almost identical $^{13}$C chemical shift of the 5-chloro-2-hydroxyphenyl groups in all the complexes, we conclude that both unsymmetrically substituted ligands, (hpab)$H_2$ and (hpan)$H_2$, form $N_\alpha$-isomers with no change in coordination geometry when coordinated to the different group 10 metal ions. Likewise, with a ligand not very different from hpan containing a nitro group in the 4-position instead of the chloro substituent in hpan, the same coordination geometry was found in the chromium(III) complex of (2-hydroxy-4-nitrophenylazo)-2-naphthol,[21] which is coordinated at the nitrogen with the 2-hydroxy-4-nitrophenyl substituent. In addition to determining the coordinating nitrogen in the unsymmetrically substituted hpab and hpan complexes, we can unequivocally assign signals 1−6 in the dhab complexes (Table 1) as originating from the

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(21) Grieb, R. Inaugural Dissertation, Universität Zürich, 1967.

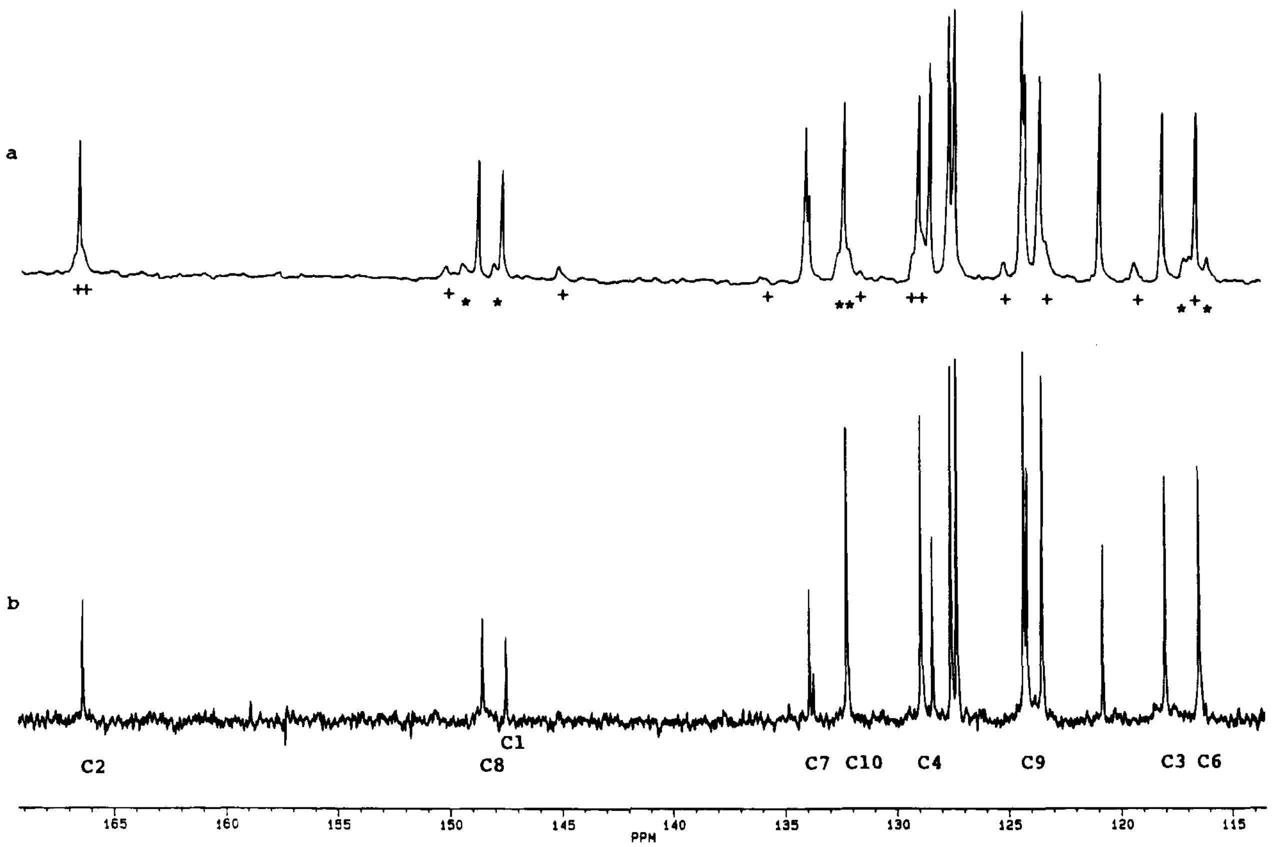

**Figure 2.** $^{13}C$ spectra (a) at 2.35 T and (b) at 5.88 T of the aromatic region of [Pt(hpan)(tba)] in $CDCl_3$. + and * indicate $^{195}Pt$ satellites.

5-chloro-2-hydroxyphenyl substituent attached to the coordinating nitrogen.

We conclude that $^{13}C$ chemical shifts are sensitive probes for isostructurality between group 10 metal complexes of this type.

Significant changes in $^{13}C$ chemical shifts of the quaternary carbons of the ligands are observed due to complexation. Both C1 and C2 in the five-membered chelate ring show large *downfield* shifts on complexation, between 8.0 and 18.0 ppm at C1 and 13.2 and 20.4 at C2 (see Tables 1–3 and Figure 4). For comparison, the change in chemical shift on complexation for the quaternary C7 and C8 in the six-membered chelate ring, formed with the central metal ion, is upfield at C8 (C7 in the hpab complexes; see Figure 1) between 4.4 and 25.9 ppm but varies between −2.6 and 5.1 ppm at C7 (C8 in the hpab complexes). The large spread in the C7 and C8 behavior is probably due to the fact that widely different azo substituents are compared. Our chemical shift data for complexation of the 5-chloro-2-hydroxyphenyl group in the five-membered chelate ring are in agreement with the data obtained for a cobalt complex of (5-chloro-2-hydroxyphenylhydrazo)-3-oxo-*N*-phenylbutanamide,[6] but our chemical shift data are less consistent with other observations.[5] In palladium- and platinum(II) complexes of substituted 2,2′-dihydroxyazobenzenes, relatively large upfield shifts were observed at the aromatic carbon ortho to the carbon attached to the coordinating azo nitrogen and meta to the carbon with the hydroxy substituent (at C6 between 12.8 and 15.7 ppm[5]). In the present work we do not observe a similar upfield shift on complexation but an effect between −2.6 and 1.9 ppm on C6. However, the upfield shift reported in ref 6 was based on a C6 chemical shift of 129.6 ppm in the uncomplexed ligand. Chemical shifts for very similar ligands from this study and from Lyčka *et al.*[6] gave 119.2, 113.7, 114.9, 114.7, and 109.6 ppm, respectively, the first three with a chloro substituent in

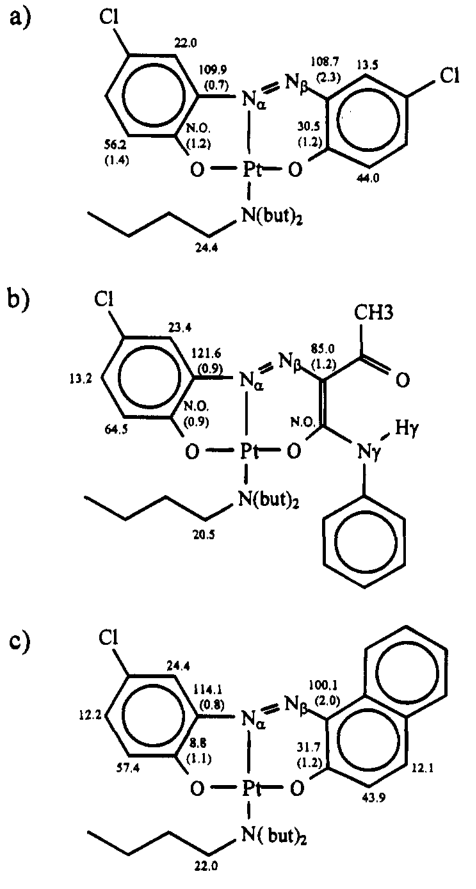

**Figure 3.** Structural formulas with $^{n}J_{^{195}Pt-^{13}C}$ couplings and $^{n}J_{^{103}Rh-^{13}C}$ in Hz: (a) [Pt(dhab)(tba)]; (b) [Pt(hpab)(tba)]; (c) [Pt(hpan)(tba)]. $^{n}J_{^{103}Rh-^{13}C}$ are shown in parentheses, and N.O. means not observed. For the sake of simplicity tba has been given with only one butyl group and the other two are designated as "but".

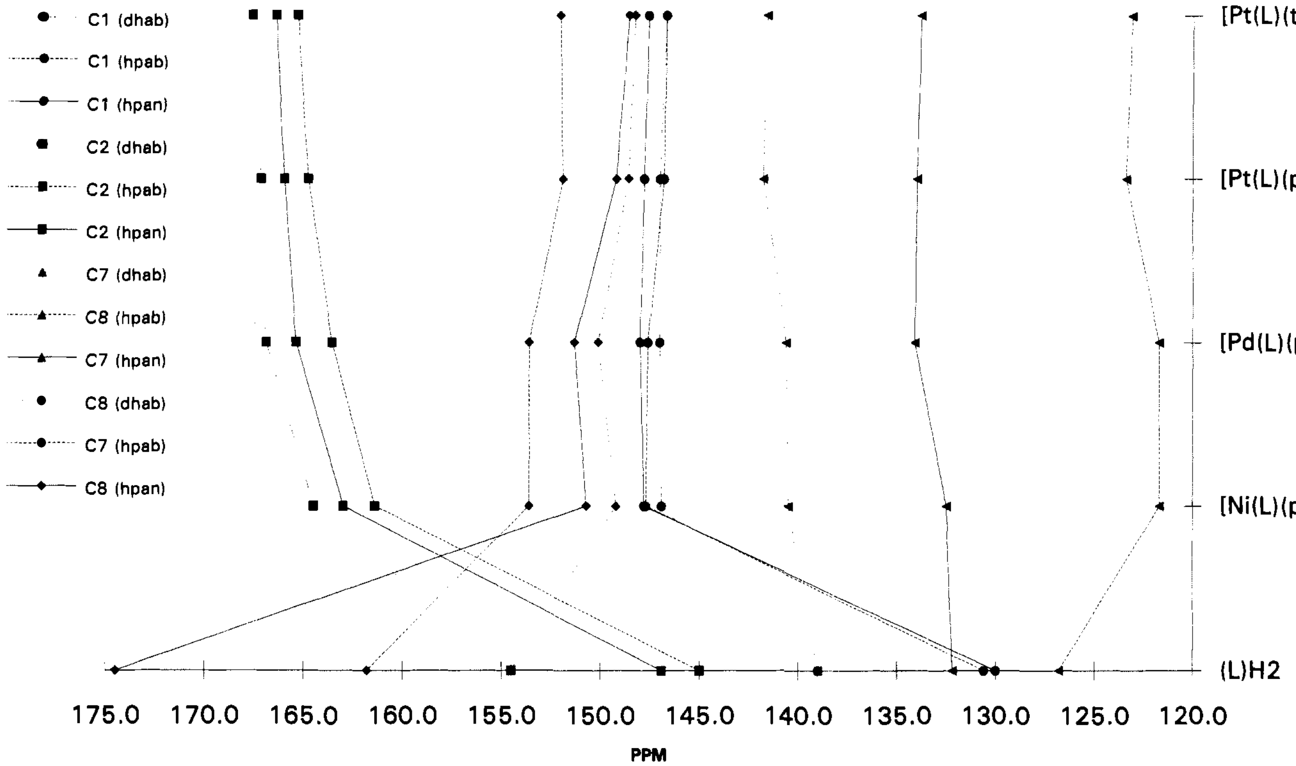

**Figure 4.** The $^{13}C$ chemical shifts of C1, C2, C7, and C8 from the uncoordinated ligands, the pyridine and tributylamine complexes. (Notice that in hpab nomenclature requires interchange of the numbering of the atoms corresponding to C7 and C8 in dhab and hpan.)

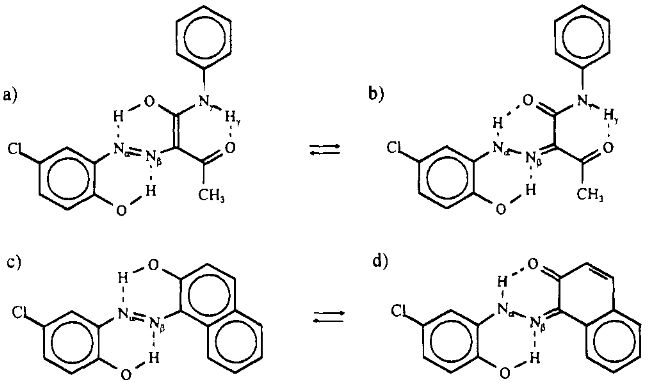

**Figure 5.** Two tautomeric forms of the unsymmetrically substituted azo dyes (a,b) $(hpab)H_2$ and (c,d) $(hpan)H_2$ in solvating media.

the 5-position, the fourth unsubstituted, and the last with a nitro group in the 5-position. We believe this incompatibility in chemical shift values between 129.6 and ~115 ppm to be the explanation for the discrepancy in findings.

The proton chemical shifts of the exchangeable hydrogens may offer an additional way of predicting the coordinating nitrogen as these hydrogen signals can be unambiguously assigned (see Assignments and Tables 1–3). In strongly solvating media like DMSO the uncoordinated dihydroxyazoarene ligands exist in an equilibrium mixture with the hydrazo tautomeric form (Figure 5), the latter having an intramolecular hydrogen bond between the intrinsicly most acidic hydrogen (neglecting the stabilization caused by the azo group) attached to the hydrazo nitrogen with the quinone oxygen forming a six-membered chelate ring[22,23] (Figure 5 b,d). In $(hpab)H_2$ the equilibrium is shifted completely toward this hydrazo tautomer (Figure 5 b).[6] The chemical shifts of the intramolecularly hydrogen-bonded hydrogens in DMSO-$d_6$ (H7 and H8 in Tables 2 and 3, respectively) are observed at lower field than the H2 hydroxy signals. The nitrogen involved in this intramolecular hydrogen bond in the uncoordinated ligands happens to be the ligating nitrogen in the metal complexes, conserving the six-membered chelate ring when coordinated to the central metal ion. This may be why it is the $^{13}C$ chemical shifts of the substituent attached to the noncoordinating nitrogen, C7 (C8 in the hpab complexes), which change the least on coordination, the ligand probably having a partial negative charge on the coordinating nitrogen both in the free ligand and in the metal complexes.

**H(D)-Isotope Effects on $^{13}C$ Chemical Shifts.** The H(D)-isotope effects of the uncomplexed ligands in DMSO-$d_6$ (Table 4) confirm that the hydrogen bonds in the unsymmetrically substituted ligands $(hpab)H_2$ and $(hpan)H_2$ are the ones involving $N_\alpha$ and H7 and H8, respectively. This is best seen from the formal three-bond isotope effect on C2 (Table 4), which in the azo tautomeric form (Figure 5a,c) is an effect across the intramolecular hydrogen bond. The large isotope effect at C8 in $(hpan)H_2$, −377 ppb, can be explained by a change in the azo–hydrazo tautomeric equilibrium upon deuteriation.[24] Deuteriation of [Pt(hpab)(tba)] and the [M(hpab)(py)] complexes lead to the isotope effects on $^{13}C$ chemical shifts as seen in Table 4. The two-bond isotope effects have been shown to be a good indicator for hydrogen bond strength.[24,25] In addition, two-bond isotope effects are influenced by subsituents on the transmission pathway. The two-bond isotope effects at C7 are clearly much smaller than the similar isotope effects observed in enamines,[26] and the variation between the complexes is small. These features can be explained by a similar inductive effect due to the metal–oxygen bond of all four complexes. This is

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in accordance with the small periodic change in $^{13}$C chemical shifts mentioned earlier.

**$^{195}$Pt$-$$^{13}$C Couplings.** Very few couplings between Pt(II) (33% $^{195}$Pt natural abundance) via oxygen or nitrogen to carbon have been published.[4,10,27] The conspicuous feature of the present data shown in Figure 3 is the large couplings observed at C1 and C7 for [Pt(dhab)(tba)] and [Pt(hpan)(tba)] and at C1 and C8 of [Pt(hpab)(tba)] and the smaller couplings at C8 combined with the absence of visible couplings at C2 of the two former and at C2 and C7 of the latter (Figure 3). The coupling at C8 of [Pt(dhab)(tba)] and Pt(hpan)(tba)] is a combination of a coupling over two bonds, $^{2}J_{\mathrm{Pt-O-C8}}$, and a coupling over four bonds, $^{4}J_{\mathrm{Pt-N-N-C-C8}}$. The latter is possibly small, as couplings over four bonds are only scarcely observed. The coupling over two bonds is therefore of a reasonable size, ~30 Hz. Three-bond couplings, $^{3}J_{\mathrm{Pt-X-C-C}}$, are fairly large as seen by the coupling at C7 (85−109 Hz) of [Pt(dhab)(tba)] and [Pt(hpan)(tba)] (C8 in [Pt(hpab)(tba)]). This coupling is a combination of two three-bond couplings. Other couplings over three bonds are observed at C3 and at C9, with the former dominating. The couplings at C1 are combinations of a two-bond, $^{2}J_{\mathrm{Pt-N-C1}}$, and a three-bond coupling, $^{3}J_{\mathrm{Pt-O-C-C1}}$. The coupling at C2 is likewise a combination of a coupling over two and three bonds but in this case $^{2}J_{\mathrm{Pt-O-C2}}$ and $^{3}J_{\mathrm{Pt-N-C-C2}}$. The logical reason for the large difference in size between the couplings fo C1 and to C2, keeping in mind that $^{2}J_{\mathrm{Pt-O-C}}$ is of the order of 30 Hz, is that $^{2}J_{\mathrm{Pt-O-C}}$ and $^{3}J_{\mathrm{Pt-N-C-C}}$ are of opposite signs, whereas $^{2}J_{\mathrm{Pt-N-C}}$ and $^{3}J_{\mathrm{Pt-O-C-C}}$ have the same sign. Three-bond couplings are normally positive; $^{2}J_{\mathrm{Pt-O-C}}$ therefore most likely is negative. Such a reversal of sign is also seen for two-bond $^{2}J_{\mathrm{C-O-C}}$ vs $^{2}J_{\mathrm{C-N-C}}$ couplings.[28]

The pattern of carbon−platinum couplings as seen in Figure 3 may be used to determine the coordinating nitrogen although more compounds will have to be studied to form a more extensive base.

Couplings to rhodium (100% $^{103}$Rh natural abundance) have been compared to couplings to platinum.[29] Despite the fact that the complexes are different, a ratio $|^{n}J_{\mathrm{Pt-C}}/^{n}J_{\mathrm{Rh-C}}|$ of 10 is usually obtained[30] (−6.8 is the ratio of the magnetic moments). Such a comparison is also possible based on the results of Figure 3. The ratio for C1 is 130−160, for C8 it is 26, and for C7 it is 45−70 (C8 in the hpab complexes). Likewise, a rhodium coupling is observed at C2. A plausible explanation for the large ratio at C1 (in other words the small coupling to rhodium) and the observation of a coupling to C2 is a reversal of the signs for two-bond couplings to rhodium compared to platinum, so that $^{2}J_{\mathrm{Rh-O-C2}}$ is of the same sign as $^{3}J_{\mathrm{Rh-N-C-C2}}$, and $^{2}J_{\mathrm{Rh-N-C1}}$ and $^{3}J_{\mathrm{Rh-O-C-C1}}$ are of opposite sign, therefore cancelling, and resulting in the relative small coupling between $^{103}$Rh and C1.

## Conclusion

The preparation of soluble square-planar platinum complexes of dhab, hpab, and hpan with tributylamine as a ligand has enabled a complete $^{1}$H and $^{13}$C NMR assignment. Negligible differences are seen between the [M(L)(py)] and [M(L)(tba)] complexes. A smooth variation in chemical shifts through the group 10 metal complexes allowed an assignment of all resonances. The isostructurality of the Ni(II), Pd(II), and Pt(II) complexes is ensured from $^{13}$C NMR spectra, and all the studied complexes with the unsymmetrically substituted ligands hpab and hpan form N$_{\alpha}$-isomers.

The trends in $^{13}$C NMR chemical shifts and Pt,C couplings are consistent with N$_{\alpha}$-coordination and can potentially be used to establish the coordination site.

**Acknowledgment.** The authors wish to thank Dr. Hanne Eggert from the H. C. Ørsted Institute, University of Copenhagen, Denmark, for recording some of the low-field $^{1}$H and $^{13}$C NMR spectra.

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