

(ca. 5%) isotopic impurity in $(\mu\text{-D})_2\text{Os}_3(\text{CO})_{10}$.¹ The usefulness of vibrational data of this type lies in the decoupling which must occur between the motions of equivalent, or very similar, molecular groupings. The vibrations of the isotopically dilute $(\mu\text{-H})(\mu\text{-D})\text{Os}_3(\text{CO})_{10}$ species will be subject to neither the correlation-field (factor-group) coupling which may occur in the crystal nor the intramolecular coupling between two similar H (or D) atoms of the isotopically pure species.

The infrared spectrum of $(\mu\text{-D})_2\text{Os}_3(\text{CO})_{10}$ contains two weak, but well-defined, absorptions in the Os-H stretching region, with the lower frequency band (1222 cm^{-1}) being 4-5 times more intense than that at higher frequency (1242 cm^{-1}). Two bands are also observed in the Os_2H rocking region, at 710.0 cm^{-1} and 701.5 cm^{-1} , whereas $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ absorbs at 730 cm^{-1} .

Interpretation of these observations leads to two conclusions. (i) The two μ -bridging hydrido atoms in $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$ are symmetrically disposed with respect to Os-H bond length and Os-H-Os bond angle but are nonetheless inequivalent, as evidenced by the dissimilarity of the Os_2H rocking frequencies associated with the two protons. This description differs from the results of neutron² and combined X-ray/neutron³ diffraction studies only in the disparity of the two Os-H-Os angles determined in the former work.² (ii) The symmetric Os-H stretching mode is at higher wavenumber than the antisymmetric mode in $(\mu\text{-H})(\mu\text{-D})\text{Os}_3(\text{CO})_{10}$ if, as is generally assumed,^{4,5} the infrared intensity associated with the antisymmetric mode is the greater.

The second conclusion provides an insight into the accuracy of the model proposed to describe the vibrations of μ -bridging hydride ligands in metal cluster complexes,⁵ in that the Os-H stretching frequencies of the isotopically dilute $(\mu\text{-H})(\mu\text{-D})\text{Os}_3(\text{CO})_{10}$ species, on that model, lead to a calculated interbond angle of 89° , $4-5^\circ$ less than that determined by neutron diffraction.^{2,3} The limitations of this model have been outlined with respect to high-angle hydrido bridges,⁵ but the data described here permit an assessment of the predictive accuracy of the model in the case of lower angle systems. In the simple treatment presented by Howard et al.,⁵ the metal-hydride stretching frequencies are related to the interbond angle, θ , by expression 1. It is, however, apparent from the plot of

$$\nu_{\text{asym}}/\nu_{\text{sym}} = \tan(\theta/2) \quad (1)$$

$\nu_{\text{asym}}/\nu_{\text{sym}}$ vs. $\tan(\theta/2)$ in ref 5 that there is a systematic deviation from this relationship. When the interaction force constant associated with the stretching of the two M-H bonds, f_{rr} , is incorporated into eq 1, one obtains expression 2 in which

$$\nu_{\text{asym}}/\nu_{\text{sym}} = [(k_r - f_{rr})/(k_r + f_{rr})]^{1/2} \tan(\theta/2) \quad (2)$$

k_r is the primary M-H stretching force constant. The direction of the deviation between the experimental data and eq 1 is consistent with a small, positive value of f_{rr} . In the case of $(\mu\text{-H})_2\text{Os}_3(\text{CO})_{10}$, we may derive values of $+90\text{ N m}^{-1}$ and $+5\text{ N m}^{-1}$ for k_r and f_{rr} , respectively,⁶ utilizing the Os-H stretching frequencies of the $(\mu\text{-H})(\mu\text{-D})\text{Os}_3(\text{CO})_{10}$ species and the mean value of θ determined by Orpen et al.³ (92.9°).

While the predictive value of the simple model remains valid, it would appear that the M-H-M angles estimated in this way will be underestimated by at least $4-5^\circ$. This implication will

be examined in more detail when spectroscopic data from a wider selection of metal hydrido cluster complexes have been obtained.

Use of vibrational data from isotopic "impurities", of the type discussed here, might be expected to prove worthwhile in the study of other metal cluster complexes containing more than one μ -bridging hydrido ligand such as $(\mu\text{-H})_3\text{Mn}_3(\text{CO})_{12}$ ^{7,8} or in cases where the presence of inequivalent bridged-hydride locations is suspected.

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Registry No. $(\mu\text{-H})(\mu\text{-D})\text{Os}_3(\text{CO})_{10}$, 81293-87-0.

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INEPT ¹⁰⁹Ag NMR Evidence for Direct Pt-to-Ag Bonding in Dinuclear [[2,6-(Me₂NCH₂)₂C₆H₃][p-tolNC(H)NR]PtAgBr]

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Recently, it was shown that application of the INEPT technique (insensitive nuclei enhancement by polarization transfer^{1a}) results in a considerable intrinsic experimental time saving for the recording of ¹⁰⁹Ag NMR spectra. This allowed for the first time the study of the structure of a series of silver complexes by means of ¹⁰⁹Ag NMR.^{1b} A prerequisite for the application of the INEPT technique is the presence of a spin-spin coupling to a sensitive nucleus (e.g., ¹H^{1b}) with the insensitive nuclei to be measured. The same requirement holds equally for FT-INDOR-like experiments as recently shown for [(EtO)₃P]_nAg⁺ complexes.² However, so far Ag-H couplings have been reported for only a restricted number of silver complexes.³⁻⁸ This is due to the fact that silver complexes are very prone to intra- and intermolecular exchange processes.^{1b-9}

In the course of a study directed to the synthesis of stable heterodinuclear metal complexes, we synthesized a series of Pt-Hg and Pt-Ag complexes.¹⁰⁻¹³ For the Pt-Hg complexes two distinctly different molecular geometries have been established, containing either (a) a five-coordinate platinum with a Pt-to-Hg donor interaction (type 1) or (b) a six-coordinate platinum with a covalent Pt-Hg bond (type 2). Structures of two representative examples, determined by X-ray analysis,⁹⁻¹² are shown in Figure 1.

A series of Pt-Ag complexes [[2,6-(Me₂NCH₂)₂C₆H₃](p-tolN_YNR)PtAgBr] (Y = CH, N; tol = tolyl) had also been

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 (6) While it is possible that the value of f_{rr} is angle dependent, it would appear from the data given in ref 5 that the ratio f_{rr}/k_r is approximately constant.

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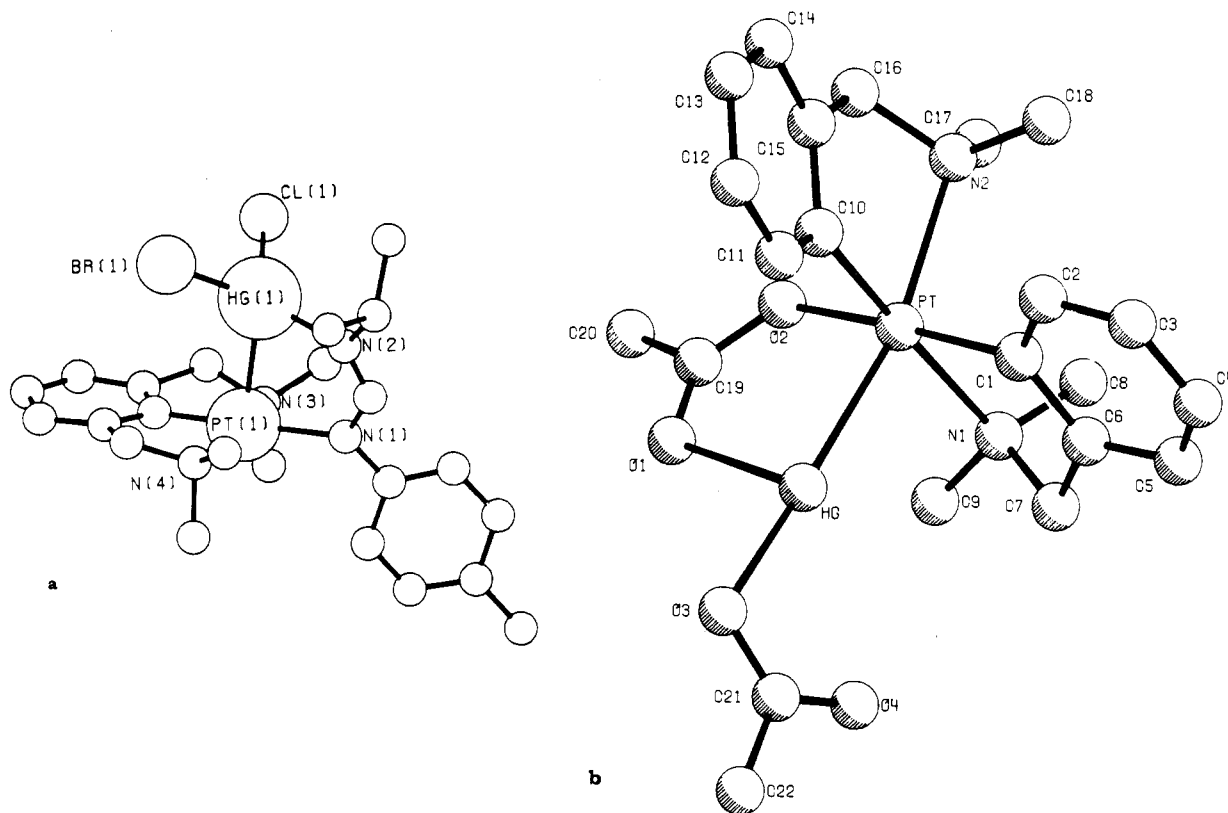


Figure 1. Molecular structure of (a) $[[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3][p\text{-tolNC}(\text{H})\text{N}-i\text{-Pr}]\text{PtHgBrCl}]^{11,12}$ and (b) $[(2\text{-Me}_2\text{NCH}_2\text{C}_6\text{H}_4)_2(\text{MeCO}_2)\text{-PtHg}(\text{O}_2\text{CMe})]^{9,11}$ containing five- and six-coordinate platinum, respectively.

synthesized, and it was considered likely that they would be isostructural with the Pt–Hg compounds of type 1.¹³ ¹⁹⁵Pt NMR spectra do not provide information concerning the presence of a Pt–Ag bond in these compounds because of considerable line broadening from either incomplete collapse of spin–spin coupling to the ¹⁴N nuclei or ¹⁹⁵Pt chemical shift anisotropy.¹⁴ However, a characteristic feature of the Pt–Ag complexes with Y = CH is the observation of ^{107,109}Ag–¹H couplings in the ¹H NMR spectra,¹³ which thereby enables the application of the INEPT technique for recording their ¹⁰⁹Ag NMR spectra.

In this paper we report the INEPT ¹⁰⁹Ag NMR results and the structural characterization of these heterodinuclear Pt–Ag compounds in solution. In particular, observation for the first

Table I. ¹H NMR Data of $[[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3][p\text{-tolNC}(\text{H})\text{NR}]\text{PtAgBr}]^a$

R	isomer ^b	rel abund	$J(\text{Ag}-\text{H}_B)^c$ Hz	$J(\text{Ag}-\text{H}_A)^d$ Hz	no. of coupling atoms
Me	I	29	17	4	4 ($\text{H}_B + 3 \text{H}_A$)
	II	71	16		1 (H_B)
Et	I	83	16	6	3 ($\text{H}_B + 2 \text{H}_A$)
	II	17	n.o.		1 (H_B)
<i>i</i> -Pr	I	99	16	10	2 ($\text{H}_B + \text{H}_A$)
	II	1	n.o.		1 (H_B)
<i>p</i> -tol ^e			14		1 (H_B)

^a In CD₂Cl₂; couplings due to ¹⁰⁷Ag (51.8%) and ¹⁰⁹Ag (48.2%) are not resolved. ^b Isomer I: N–R bonded to Ag. Isomer II: N–R bonded to Pt (see Figure 1). ^c H_B = central hydrogen atom of the bridging formamido ligand. ^d H_A = α-hydrogen atoms of the alkyl substituent R. ^e One isomer.

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time of ¹J(¹⁰⁹Ag–¹⁹⁵Pt) points to the presence of a direct Pt–Ag interaction.

Experimental Section

The synthesis of the Pt–Ag complexes $[[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3][p\text{-tolNC}(\text{H})\text{NR}]\text{PtAgBr}$ (R = Me, Et, *i*-Pr, *p*-tol) will be described in a forthcoming paper.¹³

¹H NMR spectra have been recorded by using Varian T-60 (continuous wave) and Bruker WM-250 (Fourier transform) spectrometers.

¹⁰⁹Ag NMR spectra have been recorded on a Bruker WM-250 spectrometer (11.64 MHz ¹⁰⁹Ag) by applying the INEPT sequence $[90^\circ_{\text{H}_x}-\tau-180^\circ_{\text{H}_x}; 180^\circ_{\text{M}_x}-\tau-90^\circ_{\text{H}_y}; 90^\circ_{\text{M}_x, x-x, x-x}]$ FID¹⁸ with $\tau = (4J(\text{Ag}-\text{H}))^{-1}$, $90^\circ_{\text{H}} = 35 \mu\text{s}$, and $90^\circ_{\text{Ag}} = 50 \mu\text{s}$.^{1b} The spectra were run at 293 K by using 10-mm diameter tubes and ca. 0.1 M solutions in 4/1 CH₂Cl₂/CD₂Cl₂. CD₂Cl₂ was used for the ²H lock and AgNO₃ (2 M in D₂O) for the reference. The measurements were done in the FT mode with quadrature detection (sweep width 1500 Hz, acquisition time 1.364 s, and delay time 0.7 s). The number of scans was in the order of 5000–30 000. For the Fourier acquisition a 4K memory size was used and exponential multiplication was applied with a line-

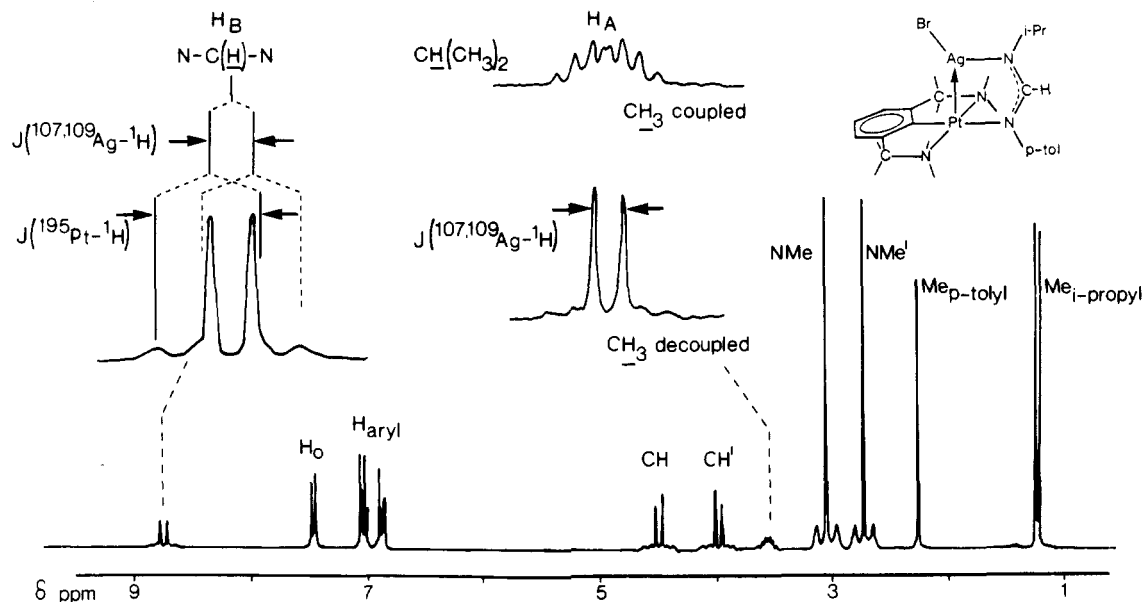


Figure 2. ^1H NMR spectrum (250 MHz) of $[[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3][p\text{-tolNC}(\text{H})\text{N-}i\text{-Pr}]\text{PtAgBr}]$ (isomer I) showing the multiplets due to coupling of hydrogen atoms with ^{195}Pt (33%) and $^{107,109}\text{Ag}$. Separate ^{107}Ag (51.8%) and ^{109}Ag (48.2%) couplings are not resolved.

Table II. ^{109}Ag NMR Data of $[[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3][p\text{-tolNC}(\text{H})\text{NR}]\text{PtAgBr}]^a$

R	isomer ^b	$\delta^{109}\text{Ag}$ ($J(^{109}\text{Ag}-^{195}\text{Pt})$)
Me	I	547.0 (173)
	II	543.6 (171)
Et	I	552.0 (165)
	II	538.8 (c)
<i>i</i> -Pr	I	557.3 (172)
	II	524.0 (c) ^d
<i>p</i> -tol ^e		533.9 (170)

^a In $\text{CH}_2\text{Cl}_2/\text{CD}_2\text{Cl}_2$; $\delta^{109}\text{Ag}$ relative to AgNO_3 (2 M in D_2O); $J(^{109}\text{Ag}-^{195}\text{Pt})$ in Hz within parentheses; ^{195}Pt ($I = 1/2$) 33% natural abundance. ^b Isomer I: N-R bonded to Ag. Isomer II: N-R bonded to Pt (see Figure 1). ^c Not observed. ^d Assignment not certain (see Figure 3a). ^e One isomer.

broadening factor of 1.5 Hz. A positive δ corresponds to a higher resonance frequency ("deshielding") with respect to the reference frequency.

Results and Discussion

Before describing the results of the ^{109}Ag NMR experiments, it is important to summarize some of the characteristic features of the compounds $[[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3][p\text{-tolNC}(\text{H})\text{NR}]\text{PtAgBr}]$ ($\text{R} = \text{Me}, \text{Et}, i\text{-Pr}, p\text{-tol}$) as derived from ^1H NMR data; cf. ref 13.

First of all, the Pt-Ag compounds have as the main structural feature a formamidino group bridging the Pt and Ag atoms. This was derived from the observation of coupling of the central formamidino H atom (H_B) with both Pt and Ag (^{107}Ag , $I = 1/2$, natural abundance 51.8%; ^{109}Ag , $I = 1/2$, 48.2%; ^{195}Pt , $I = 1/2$, 33%). On example is shown in Figure 2 (note the ^{195}Pt satellites which are broadened in the 250-MHz spectrum).

Secondly, the compounds for which R is an alkyl group can exist in two isomeric forms characterized by having the N-(alkyl) atom bonded to either Ag (isomer I) or Pt (isomer II), the relative isomer ratio being dependent on the alkyl group R (see Table I). Assignment of the isomeric structures was feasible on the basis of observation of coupling between Ag and the α -alkyl hydrogen atoms (H_A) for one of the two isomers. Since the ^1H NMR spectra of these mixtures are complex, we only show the spectrum of the compound with $\text{R} = i\text{-Pr}$ (Figure 2), which exists for 99% in a form with the N-*i*-Pr donor site bonded to Ag.

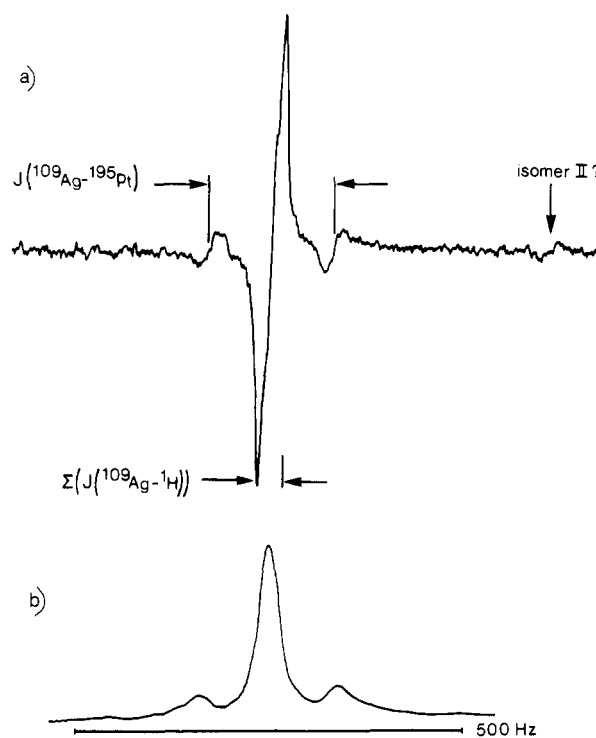


Figure 3. ^{109}Ag NMR spectra of $[[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3][p\text{-tolNC}(\text{H})\text{N-}i\text{-Pr}]\text{PtAgBr}]$: (a) INEPT spectrum; (b) integrated INEPT spectrum (for experimental conditions see text).

The ^1H NMR spectra do not provide information concerning the presence of a Pt-Ag interaction. Such information may be obtained by ^{109}Ag NMR, which can be performed with the INEPT technique since it can be seen that in each compound and isomer there is at least one Ag-H coupling present.

The proton-coupled INEPT ^{109}Ag NMR spectra of $[[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3][p\text{-tolNC}(\text{H})\text{NR}]\text{PtAgBr}]$ ($\text{R} = \text{Me}, \text{Et}, i\text{-Pr}, p\text{-tol}$) showed either one or two -1:+1 doublet resonances. Furthermore, for those resonances for which the signal-to-noise ratio was high enough, satellite doublet resonances were also observed. One example ($\text{R} = i\text{-Pr}$) is shown in Figure 3a. The chemical shifts of the main resonances lie in the range 520–560 ppm downfield with respect to 2 M AgNO_3 solution in D_2O (see Table II). The observation of

two resonances for R = Me, Et, *i*-Pr is in accordance with the presence of two isomers (*vide supra*), and the relative intensities of these resonances correspond very well with the isomer ratio as determined from the ^1H NMR spectra (see Table I). For R = *i*-Pr, a very small second resonance is observed, and this may correspond to the minor (1%) isomer, but the assignment is uncertain (see Figure 3a). The ^{109}Ag resonances with the smallest linewidth (8–10 Hz) were observed for the compounds $[[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3][p\text{-tolNC}(\text{H})\text{NR}]\text{PtAgBr}]$ with R = *p*-tol and for the main isomer with R = Me. These are the compounds in which Ag couples with only one hydrogen atom (H_B). Broader lines (15–17 Hz) were observed for the other isomers. This is almost certainly due to the fact that in these isomers Ag couples with different hydrogen atoms (H_B and H_A) and that the couplings differ in magnitude. With respect to the above it is worth noting that equal couplings should lead to multiplets with intensity ratios of $-1: +1$ (one H), $-1: 0: +1$ (two H's), $-1: -1: +1: +1$ (three H's), etc.¹⁵ For those compounds in which Ag couples with only one (R = *p*-tol, Me) or two (R = *i*-Pr) hydrogen atoms the separation between the two peaks within one doublet corresponds very well with $J(\text{Ag}-\text{H}_\text{B})$ and sum $J(\text{Ag}-\text{H}_\text{B}) + J(\text{Ag}-\text{H}_\text{A})$, respectively (^1H NMR).

On the basis of the above observations, *i.e.*, linewidth, relative intensity, and $J(^{109}\text{Ag}-\text{H})$, assignment of the resonances to the isomers having the *N-p*-tolyl group bonded either to Pt (isomer II) or the Ag (isomer I) was possible. From Table II it is clear that the two types of isomers can also be discriminated on the basis of their ^{109}Ag chemical shifts, *i.e.*, downfield for isomer I and upfield for isomer II. Furthermore, the chemical shifts change systematically as R is changed from Me to Et to *i*-Pr. Finally, the chemical shift of the compound with R = *p*-tolyl falls within the range of isomers II, and this fact is consistent with a structure in which these latter isomers contain a Ag-bonded *N-p*-tolyl moiety.

As mentioned above the main ^{109}Ag doublet resonances show satellite doublets. By integration of the normal INEPT spectrum, which, however, has the disadvantage of losing the information concerning the $J(\text{Ag}-\text{H})$ couplings, the satellite resonances become more evident (see Figure 3b). For all the compounds the separation between the two satellites amounts to about 170 Hz (see Table II) and there is no doubt that these satellites are due to coupling between ^{109}Ag and ^{195}Pt ($I = 1/2$, 33% natural abundance). Although a coupling pathway through the skeleton of the bridging formamidine ligand cannot be excluded, we propose that this coupling is a one-bond $^{109}\text{Ag}-^{195}\text{Pt}$ coupling implying the presence of a direct Pt-to-Ag interaction.

Since these are the first Pt-Ag couplings reported, it is difficult to give a rationale for the absolute values found though their magnitude can be compared to that of the $^1J(^{195}\text{Pt}-^{195}\text{Pt})$ of 332 Hz found in $[(\text{Ph}_2\text{P})_2\text{CH}_2]_2\text{Pt}_2\text{Me}_3^+$.¹⁶ The latter complex contains a square-pyramidally coordinated platinum(II) atom with a donor bond to an apically positioned (Pt(2)) atom (Pt(1)-Pt(2) = 2.769 Å). In the present Pt-Ag complexes the platinum(II) center is also expected to be square-pyramidally coordinated as established by X-ray diffraction analysis of a corresponding Pt-Hg complex $[[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3][p\text{-tolNC}(\text{H})\text{NR}]\text{PtHgBrCl}]$ (see Figure 1).¹² The latter structure shows a square-pyramidal platinum(II) center directly bonded to mercury (Pt-Hg = 2.8331 (7) Å) in the apical position.^{11,12} From that work it was concluded that the terdentate ligand system 2,6-(Me_2NCH_2)₂C₆H₃, by virtue of its fixed trans-N-donor ligand sites, enhances the nucleophilicity of the platinum center and

thus stabilizes a Pt-to-Hg donor interaction. It is therefore apparent that in all these complexes the platinum center is making use of a filled orbital, perpendicular to the basal coordination plane, which is anticipated to have low *s* character.

Conclusions

The INEPT ^{109}Ag NMR spectra of the complexes $[[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3][p\text{-tolNC}(\text{H})\text{NR}]\text{PtAgBr}]$ support the data obtained from the ^1H NMR spectra: *i.e.*, the presence of two isomers and their structural assignment, the dependence of the isomer ratio on the alkyl substituent R (Me, Et, *i*-Pr), and the presence of $J(^{107,109}\text{Ag}-^1\text{H})$ couplings. Unique information, which could not be obtained from ^{195}Pt NMR (linewidth 500 Hz), is provided by these INEPT ^{109}Ag NMR spectra: *i.e.*, observation of a $^1J(^{195}\text{Pt}-^{109}\text{Ag})$ (± 170 Hz) pointing to the presence of a direct Pt-Ag interaction.

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Registry No. $[[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3][p\text{-tolNC}(\text{H})\text{NMe}]\text{PtAgBr}]$, isomer I, 80484-86-2; $[[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3][p\text{-tolNC}(\text{H})\text{NMe}]\text{PtAgBr}]$, isomer II, 80484-95-3; $[[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3][p\text{-tolNC}(\text{H})\text{NEt}]\text{PtAgBr}]$, isomer I, 80484-87-3; $[[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3][p\text{-tolNC}(\text{H})\text{NEt}]\text{PtAgBr}]$, isomer II, 80484-96-4; $[[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3][p\text{-tolNC}(\text{H})\text{N-}i\text{-Pr}]\text{PtAgBr}]$, isomer I, 80484-88-4; $[[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3][p\text{-tolNC}(\text{H})\text{N-}i\text{-Pr}]\text{PtAgBr}]$, isomer II, 80484-97-5; $[[2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3][p\text{-tolNC}(\text{H})\text{N-}p\text{-tol}]\text{PtAgBr}]$, 80484-89-5.

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Synthesis and Characterization of Cobalt(III) Nicotinic Acid Complexes

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There has been considerable interest in transition-metal complexes that have aromatic ligands such as nicotinic acid functioning as electron-transfer mediators in oxidation-reduction reactions.¹ Nicotinic acid has two potential ligating groups (Table I), the pyridine nitrogen and the carboxylic acid oxygen. In redox reactions, pyridinecarboxylic acids facilitate electron transfer by bridging two metal ions. Recently, transition-metal complexes of nicotinic acid have again drawn attention because of their potential involvement in biological systems.²

To date, relatively little has been reported on the stereochemistry and spectral properties associated with coordinated nicotinic acid. In order to improve our understanding of the coordination chemistry of nicotinic acid, a series of Co(III) complexes of this ligand and related molecules has been synthesized and characterized by visible-UV, IR, and proton NMR spectroscopy. Several of the complexes synthesized in this study have been reported previously but were only partially characterized.

Experimental Section

Materials, Measurements, and Analyses. Reagent grade nicotinic acid and nicotinamide (Sigma), pyridine, isonicotinic acid, and methyl nicotinate (Aldrich) were used.

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