Inorg. Chem. **1988**, *27*, 4435–4437

CH_2Cl_2 (30 mL) solution of **5** (1 mmol). After the mixture was stirred for 15 min, addition of $NaBPh_4$ (1 mmol) in ethanol (30 mL), followed by slow concentration, gave red orange or yellow crystals, respectively, in ca. 85% yield. Full physical–chemical characterization of both complexes will be published elsewhere.[14] We anticipate here that **8** has an octahedral geometry, the rhodium atom being coordinated by the three phosphorus atoms of triphos, the two carbon atoms of the olefin, and one of the two ester carbonyl double bonds. In contrast, **7** is five-coordinated by the three phosphorus atoms of triphos and the alkyne molecule, which acts as a 4e donor.

Acknowledgment. We are indebted to the Conselleria de Educacion de la Generalitat Valenciana for a grant that made J.A.R.'s stay at Florence possible.

Registry No. **1**, 100333-94-6; **2**, 105736-81-0; **3**, 116863-68-4; **4**, 104103-47-1; **5**, 105139-41-1; *trans*-**6**, 116863-70-8; *cis*-**6**, 116946-97-5; **7**, 116863-74-2; **8**, 116863-72-0; **9**, 104103-48-2; **10**, 104103-50-6; **11**, 104119-29-1; DMAD, 762-42-5; DMMA, 624-48-6; DMFU, 624-49-7; DMSU, 106-65-0; $[(triphos)RhH(\mu\text{-}H)_2HRh(triphos)]^+$, 116887-36-6; 3,3-dimethylbut-1-ene, 558-37-2.

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^{15}N NMR Spectra of Pentaamminerhodium(III) Complexes

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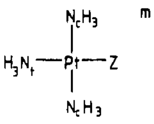
A series of pentaamminerhodium(III) complexes, $Rh(NH_3)_5Z^{n+}$, has been prepared, with 80% enrichment in ^{15}N ($Z = H_2O$, OH^-, Cl^-, Br^-, I^-, NH_3, $-ONO^-$, $-NO_2^-$, $-NCS^-$, $-SCN^-$, $-NCO^-$, CN^-). The ^1H-decoupled ^{15}N NMR spectra show two doublets (from coupling to ^{103}Rh) with approximate intensity ratio 4:1. δ_N and $^1J(Rh-N)$ are sensitive to Z, especially for the unique ammine trans to Z. Good correlations exist between δ_N in this series and δ_N in the corresponding cobalt(III) complexes $Co(NH_3)_5Z^{n+}$ and platinum(II) complexes $Pt(NH_3)_3Z^{m+}$. $J(Rh-N)$ trans to Z also correlates well with $J(Pt-N)$ trans to Z in the platinum series.

Introduction

^{15}N NMR has been used extensively to study reactions in solution of ammineplatinum complexes.[1-7] To help place the interpretation of ^{15}N NMR parameters on a firm empirical basis, we have carried out a systematic study of the effect of Z on these parameters in the series of triammineplatinum(II) complexes $Pt(NH_3)_3Z^{m+}$ (**1**) and meridional triammineplatinum(IV) complexes $Pt(NH_3)_3Z(OH)_2^{m+}$ (**2**).[8] With these series the influence of Z on the ammine ligands trans and cis to Z could be studied simultaneously. The usefulness of ^{15}N NMR in ammineplatinum systems arises from the following properties: (i) Each distinct ammine ligand gives a separate sharp signal. (ii) δ_N and the coupling constant between ^{15}N and the metal nucleus both depend in a predictable way on the ligands cis and trans to ammine (especially trans). (iii) The spectrum is not complicated by coupling between nonequivalent ^{15}N nuclei from ammine ligands cis to each other.



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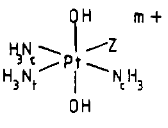

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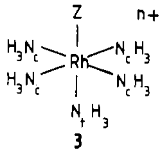
Table I. ^{15}N NMR Data for Pentaamminerhodium(III) Complexes $Rh(NH_3)_5Z^{n+}$ (**3**)

	NH_3 trans to Z (N_t)		NH_3 cis to Z (N_c)	
Z	δ_{N_t}	$J(Rh-N_t)$, Hz	δ_{N_c}	$J(Rh-N_c)$, Hz
H_2O	-77.33	17.3	-57.81	13.9
OH^-	-68.54	13.9	-57.46	14.2
Cl^-	-66.14	15.4	-57.93	13.4
Br^-	-60.53	14.9	-59.84	13.4
I^-	-50.02	13.4	-63.17	13.4
NH_3	-59.83	14.2	-59.83	14.2
$-ONO^-$	-73.24	15.1	-56.31	14.2
$-NO_2^-$	-60.41	12.2	-52.91	14.4
$-NCS^-$	-66.45	16.1	-59.26	13.7
$-SCN^-$	-52.42	13.7	-58.08	13.7
$-NCO^-$	-67.28	15.1	-58.86	13.2
CN^-	-42.32	10.3	-62.66	13.2

Despite the successful application of ^{15}N NMR spectroscopy with ^{15}N-enriched ammine ligands to the chemistry of ammine complexes of platinum, we are not aware of any attempts to apply this technique to the study of ammine complexes of other metals. To assess its potential in the investigation of the chemistry of ammine complexes of rhodium(III), we have now prepared a series of pentaamminerhodium(III) complexes, $Rh(NH_3)_5Z^{n+}$ (**3**), in which there is 80% enrichment of the ammine ligands with ^{15}N ($I = {}^1/_2$), and obtained their ^{15}N NMR spectra. The only naturally occurring isotope of rhodium is ^{103}Rh ($I = {}^1/_2$). We are aware of only one report on the ^{14}N chemical shift of $Rh(NH_3)_6^{3+}$.[9] Nitrogen shifts are now available for a number of pentaamminecobalt(III) complexes,[10] and it is of interest to compare trends for the rhodium complexes with those in that series.



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0020-1669/88/1327-4435$01.50/0

Experimental Section

Starting Materials. Ammonium sulfate, 80% enriched in ^{15}N was purchased from Novachem (Melbourne). To convert it to ammonium chloride, the stoichiometric quantity of barium chloride in aqueous solution was added. The precipitated $BaSO_4$ was filtered off, and the filtrate, with washings, was evaporated to dryness on a steam bath. "$RhCl_3 \cdot 3H_2O$" was purchased from Johnson-Matthey Ltd.

Preparation of Pentaamminerhodium(III) Complexes. Most of the preparations were based on procedures given in the literature. These were sometimes modified to minimize the amount of ammonia (or ammonium salt) used or to improve product quality or yield where possible. In most cases, preparative procedures were optimized by using complexes containing nitrogen with natural isotopic composition and then used to prepare ^{15}N-enriched materials. All solid compounds isolated were characterized by microanalysis and IR and visible-UV spectroscopy. Where details of the preparations differ from those previously published, we have given details in the supplementary material, along with Table II, which gives microanalytical data for these complexes.

NMR Spectra. All ^{15}N NMR spectra were ^{1}H-decoupled. They were run at 10.09 MHz on a JEOL FX-100 FT spectrometer with an external ^{7}Li lock. For compounds that were sufficiently soluble, spectra were run on solutions containing approximately 0.1 g of the compound in 2 mL of water (H_2O). For more sparingly soluble compounds, the solution was saturated. Spectra were run by using 10-μs pulses (22° tilt of magnetization vector) 3 s apart, with spectrum width 2000 Hz and 8K data points, in the double-precision mode. The number of scans ranged from 500 for more soluble compounds to 17000 (overnight run) for sparingly soluble compounds. Shifts are positive to lower shielding and are referenced relative to the $^{15}NH_4^+$ signal from 5 M $^{15}NH_4{}^{15}NO_3$ in 2 M HNO_3 in a coaxial capillary.

Results

^{15}N NMR data for pentaammine complexes are presented in Table I.

The ^{15}N NMR spectrum of $Rh(NH_3)_6^{3+}$ (67% enriched in ^{15}N) showed a sharp doublet, due to coupling with ^{103}Rh. Except for $Rh(NH_3)_5(NO_2)^{2+}$ with ^{15}N-enriched nitrite (see below) each of the pentaammine complexes $Rh(NH_3)_5Z^{n+}$ (3) showed two doublets, with intensity ratio 4:1, corresponding to ammine ligands cis (N_c) and trans (N_t) to Z, respectively. There is no resolvable coupling between nonequivalent ^{15}N nuclei that are mutually cis (as previously observed for platinum complexes[1,2,8]) or between ^{15}N nuclei and ^{14}N nuclei cis or trans. $[Rh(NH_3)_5(ONO_2)](NO_3)_2$ in water gave the same ^{15}N spectrum as $[Rh(NH_3)_5(H_2O)](ClO_4)_3$. The ^{15}N spectrum of $Rh(NH_3)_5(^{14}NO_2)^{2+}$ also showed two doublets. The ^{15}N spectrum of $Rh(NH_3)_5(^{15}NO_2)^{2+}$ showed, as expected, additional complexity in the ammine region. The ammine ligands cis to nitrite gave a doublet, but the ammine ligand trans to nitrite gave a doublet of doublets owing to coupling to the nitrite ^{15}N nucleus as well as to ^{103}Rh ($J(^{15}N\text{-}Rh\text{-}^{15}N) = 7.3$ Hz). When 0.1 g of chrome alum was added to the solution (to provide faster relaxation of the nitrite nucleus), a doublet of doublets due to coordinated nitrite was observed at +435.4 ppm. Since this eliminates nuclear Overhauser enhancement, all peaks appeared as absorptions. One doublet coupling, 7.3 Hz, corresponded to coupling with the trans ammine, and the other, 18.3 Hz, to coupling with ^{103}Rh. For the O-bound nitrito isomer complex $Rh(NH_3)_5(\text{-}O^{15}NO)^{2+}$ no coupling with nitrite ^{15}N was observed in the spectrum of the ammine ^{15}N nuclei. This linkage isomer does not persist for long periods in solution, and the ^{15}N signal due to coordinated nitrite was not observed.

Discussion

From Table I, it is evident that both δ_N and J(Rh-N) for ammine trans to Z (N_t) in $Rh(NH_3)_5Z^{n+}$ (3) are more sensitive to Z than for the ammine ligands cis to Z (N_c). Comparison of the data with typical trans influence series[11] shows that there is a general trend for $J(Rh\text{-}N_t)$ to decrease and for the nitrogen nucleus to become less shielded as the trans influence of Z increases. However, the correlation between the two parameters is only moderate (correlation coefficient $R = -0.83$).

As mentioned above, Bramley et al. have published recently a compilation of nitrogen chemical shifts for pentaamminecobalt(III) complexes, largely derived from ^{14}N spectra.[10] As illustrated in Figure 1, there is a good linear correlation between the shifts for the cobalt and rhodium complexes, including ammine ligands both trans and cis to Z. This figure also shows that there is a good correlation between the shifts for the rhodium complexes and those for the platinum(II) complexes $Pt(NH_3)_3Z^{m+}$. We have noted the inverse linear correlation (similar to that observed for hydride shifts) between δ_N trans to Z and δ_{Pt} in the platinum complexes.[8] Bramley et al.[10] have described the similar correlation between δ_N and δ_{Co} in the pentaamminecobalt(III) series, which they, in turn, correlated with the ratio Δ/B, where Δ is the ligand field d orbital splitting and B is a Racah parameter (a measure of interelectron repulsion, whose magnitude decreases as covalency increases in the metal-ligand bonds). This proposal is in accord with our discussion of the origins of variations in ^{195}Pt shifts[8] (necessarily more qualitative in the absence of accepted values of Δ and B for platinum(II) complexes). The remarkable correlation between the nitrogen shifts in the three series of complexes (two octahedral and one square planar, with metals in three different rows of the periodic table) therefore represents indirectly a correlation between the metal shifts in the three series. ^{103}Rh shifts are not available, but it can be confidently predicted that they would correlate with the ^{59}Co and ^{195}Pt shifts in their respective series and with the ^{15}N shifts in the pentaamminerhodium series.

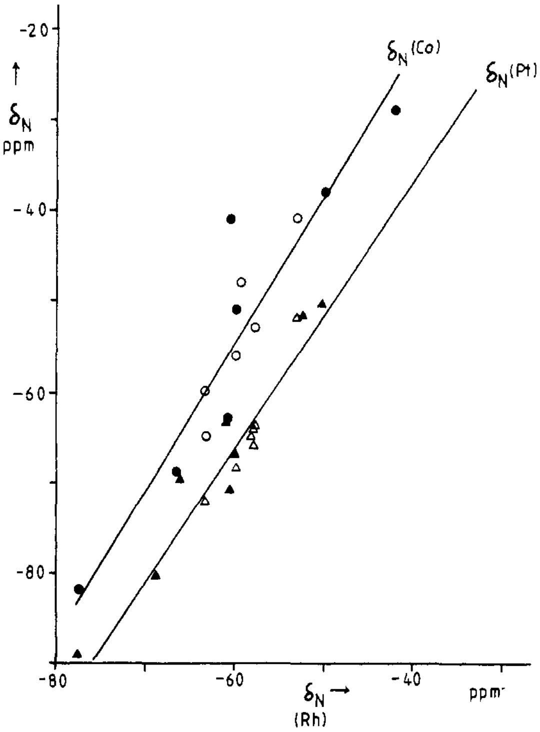

Figure 1. Plot against δ_N in the series $Rh(NH_3)_5Z^{n+}$: δ_N in the series $Co(NH_3)_5Z^{n+}$, for (●) ammine trans to Z (N_t) and (○) ammine cis to Z (N_c) (line shown is line of best fit, $\delta_N(Co) = 1.635[\delta_N(Rh)] + 43.5$ ($R = 0.924$)); δ_N in the series $Pt(NH_3)_3Z^{m+}$, for (▲) ammine trans to Z (N_t) and (△) ammine cis to Z (N_c) (line shown is line of best fit, $\delta_N(Pt) = 1.454[\delta_N(Rh)] + 20.8$ ($R = 0.958$)).

The much smaller magnitude of the Rh-N coupling constants compared with that of the Pt-N coupling constants previously reported[8] is due in part to the small magnitude of the magnetogyric ratio for ^{103}Rh, but the magnitude of the reduced coupling constant[11] for $Rh(NH_3)_6^{3+}$ (3.71×10^{21} N A^{-2} m^{-3}) is still significantly less than the reduced Pt-N coupling constant in $Pt(NH_3)_4^{2+}$ (1.10×10^{22} N A^{-2} m^{-3}). There is a good correlation between $J(Pt\text{-}N_t)$ in the platinum series and $J(Rh\text{-}N_t)$ in the rhodium series ($R = 0.965$) (Figure 2). The smaller variations in $J(Rh\text{-}N_c)$ do not correlate as well with $J(Pt\text{-}N_c)$ in corresponding platinum complexes ($R = 0.835$).

We have interpreted our coupling constant data for the platinum(II) series in terms of the $Pt\text{-}N_t$ coupling constant being

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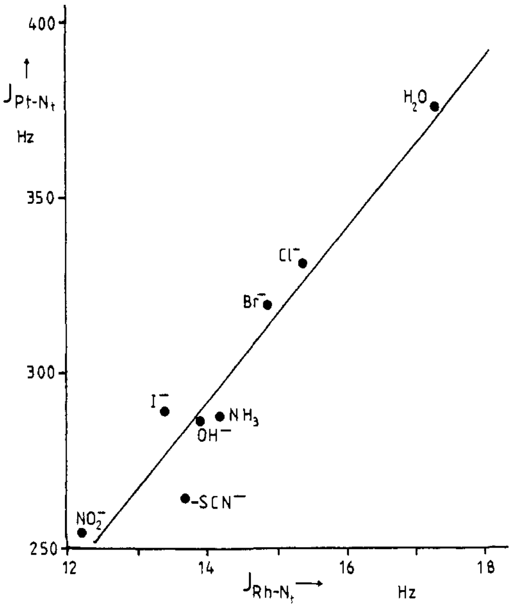

Figure 2. Plot of J(Pt–N$_t$) in the series Pt(NH$_3$)$_3$Z^{m+} (**1**) against J(Rh–N$_t$) in the series Rh(NH$_3$)$_5$Z^{n+} (**3**). The line shown is the line of best fit, J(Pt–N$_t$) = 25.07[J(Rh–N$_t$)] – 59.7.

sensitive primarily to the effect of Z on the platinum 6s contribution to the Pt–N$_t$ bond,[8] an approach that has previously successfully rationalized the variations in one-bond coupling constants between ^{195}Pt and ^{1}H, ^{31}P, and ^{13}C.[12-15] Basch et al.[16] have since studied the bonding in the hypothetical molecule *cis*-Pt(NH$_3$)$_2$(CH$_2$OH)(OCH$_3$) (a model for the ascorbic acid C,O-chelate complex). They concluded that the platinum 5d$_{x^2-y^2}$ orbital made the largest contribution to the Pt–N bonds and that this contribution was dramatically reduced in the Pt–N bond trans to carbon. Our qualitative discussion of NMR parameters is in accord with their findings. If the metal s orbital makes only a relatively small contribution to the metal–nitrogen bonds, and coupling constants are sensitive primarily to this contribution, care must be taken to avoid facile attempts to use these coupling constants alone as a measure of bond strength.

From the correlations noted above, it is clear that NMR parameters for N$_t$ in the rhodium complexes are affected by Z in a way similar to those for N$_t$ in the platinum complexes, and conditions i–iii given as desirable in the Introduction do apply. The usual method for characterizing rhodium(III) compounds in solution is by visible–UV spectroscopy, and this method must continue to be useful. However, the broadness of the peaks can make it difficult to be certain about the presence of minor components in a solution, especially if the different ligands present occupy similar positions in the spectrochemical series. The ^{15}N NMR lines are very sharp, and there is little probability that two different species would have identical chemical shifts and Rh–N coupling constants for all of the ammine ligands present. Even relatively minor components of a mixture may be detected and characterized.

Acknowledgment. We are grateful for financial support from a University of Queensland Special Project Grant and the Australian Research Grants Scheme.

Registry No. [Rh(NH$_3$)$_5$Cl]Cl$_2$, 13820-95-6; [Rh(NH$_3$)$_5$Cl](NO$_3$)$_2$, 21264-83-5; [Rh(NH$_3$)$_5$(ONO$_2$)](NO$_3$)$_2$, 41762-28-1; [Rh(NH$_3$)$_5$Br]Br$_2$, 19682-70-3; [Rh(NH$_3$)$_5$I]I$_2$, 32088-27-0; [Rh(NH$_3$)$_5$I](NO$_3$)$_2$, 15337-81-2; [Rh(NH$_3$)$_6$](ClO$_4$)$_3$, 16786-63-3; *trans*-[Rh(NH$_3$)$_4$(SO$_3$)(CN)]·2H$_2$O, 117064-14-9; *trans*-[Rh(NH$_3$)$_4$(CN)(H$_2$O)]Cl$_2$, 116971-76-7; [Rh(NH$_3$)$_5$(CN)]Cl$_2$, 22653-47-0; [Rh(NH$_3$)$_5$(H$_2$O)](ClO$_4$)$_3$, 15611-81-1; [Rh(NH$_3$)$_5$(NCO)](ClO$_4$)$_2$, 69308-81-2; [Rh(NH$_3$)$_5$(NCS)](ClO$_4$)$_2$, 15244-72-1; [Rh(NH$_3$)$_5$(SCN)](ClO$_4$)$_2$, 15244-73-2; *trans*-Na[Rh(NH$_3$)$_4$(SO$_3$)$_2$], 117064-15-0; [Rh(^{15}NH$_3$)$_5$Cl]Cl$_2$, 116971-77-8; [Rh(^{15}NH$_3$)$_5$Cl](NO$_3$)$_2$, 116996-18-0; [Rh(^{15}NH$_3$)$_5$Br]Br$_2$, 116971-78-9; [Rh(^{15}NH$_3$)$_5$I]I$_2$, 116971-79-0; [Rh(^{15}NH$_3$)$_6$](ClO$_4$)$_3$, 116971-81-4; *trans*-[Rh(^{15}NH$_3$)$_4$(SO$_3$)(CN)]·2H$_2$O, 116971-82-5; *trans*-[Rh(^{15}NH$_3$)$_4$(CN)(H$_2$O)]Cl$_2$, 116971-83-6; [Rh(^{15}NH$_3$)$_5$(CN)]Cl$_2$, 116971-84-7; [Rh(NH$_3$)$_5$(OH)]$^{2+}$, 26214-91-5; [Rh(NH$_3$)$_5$(ONO)]$^{2+}$, 34412-16-3; [Rh(NH$_3$)$_5$(NO$_2$)]$^{2+}$, 34412-13-0; [Rh(^{15}NH$_3$)$_5$(H$_2$O)](ClO$_4$)$_3$, 116996-83-9; *trans*-Na[Rh(^{15}NH$_3$)$_4$(SO$_3$)$_2$], 116971-85-8.

Supplementary Material Available: Experimental details of compound preparation and Table II, containing microanalytical data (8 pages). Ordering information is given on any current masthead page.

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CrB$_4$ and MnB$_4$: Electronic Structures of Two Unusual Systems Containing the Tetragonal Carbon Net

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It is shown how the tetragonal carbon structure, quite energetically unfavorable for an electron count appropriate for carbon, may be stabilized by removal of electrons by a suitable metal. This observation is understandable by using a result from the method of moments. CrB$_4$ that contains a boron net of this type appears optimal not only from the viewpoint of the stability of this non-metal framework but also from that of the metal coordination. For MnB$_4$, Mn–B and Mn–Mn antibonding orbitals are occupied, the non-metal electron density is larger than for chromium, and the structure distorts as a result of coupling between the desires of metal coordination and that of the nonmetal array. For M = Fe, Co, and Ni the tetragonal carbon lattice is so destabilized as a result of the higher electron count that it may well be unstable. CrB$_4$ phases with these metals are not known.

I. Introduction

There are several metal borides and related species that may be visualized in geometric terms as arising via the insertion of a metal atom into a network of non-metal atoms. Perhaps the best known example is the structure of CaB$_6$, where Longuet-Higgins and Roberts showed[1] many years ago that the two electrons donated by the calcium atom satisfy exactly the bonding requirements of the vertex-linked boron octahedra. The structures of CaSi$_2$ and CaIn$_2$ have a similar attraction for electron counting.[2]

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