Inorganic Chemistry, Vol. 16, No. 12, 1977 **3187**

Contribution from the Chemical Research Center,
Allied Chemical Corporation, Morristown, New Jersey 07960

Preparation, Characterization, and Catalytic Reactions of Cyclooctadiene(dimethylphosphonium bis(methylide))rhodium(I) and Its Carbonyl Derivatives

ROGER A. GREY* and L. R. ANDERSON

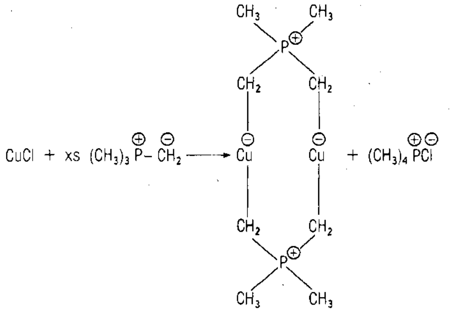
Received June 20, 1977

AIC70430N

The reaction of excess trimethylphosphonium methylide with cyclooctadienerhodium(I) chloride dimer yields cyclooctadiene(dimethylphosphonium bis(methylide))rhodium(I) (**1**) which was characterized by ^{1}H NMR, ^{31}P NMR, elemental analyses, and molecular weight. Benzene solutions of **1** under a hydrogen atmosphere were found to catalyze the hydrogenation of olefins. Treatment of **1** with carbon monoxide displaces the cyclooctadiene ligand and gives a mixture of monomeric and dimeric carbonyl derivatives, dicarbonyl(dimethylphosphonium bis(methylide))rhodium(I) (**2**) and 1,1,2,2-tetracarbonyl-bis(μ-dimethylphosphonium bis(methylide))-dirhodium(I) (**3**), respectively. **2** and **3** could not be separated, and the mixture was characterized by ^{1}H NMR, ^{31}P NMR, elemental analyses, and mass spectra data. Variable-temperature ^{1}H NMR and ^{31}P NMR data indicate that **2** and **3** are in equilibrium in solution. Benzene/methanol solutions of **2** and **3** under carbon monoxide pressure catalyze the conversion of methyl iodide to methyl acetate.

Introduction

In recent years there have been many transition-metal complexes prepared using phosphonium ylides as ligands.[1-5] For example, Schmidbaur and co-workers have shown that the reaction of metal halides with excess phosphonium ylides can undergo a transylidation that frequently results in the formation of metal dimers bridged by bis(methylide) ligands, as shown in eq 1.



(1)

They have also demonstrated that the metal–alkyl bonds of metal ylides exhibit unusual thermal stability and that the dimers can undergo transannular oxidative addition reactions.[1] Despite the large amount of work going on in this area, there have been relatively few reports of transition-metal ylide complexes as catalysts.[6]

In order to observe any unique catalysis associated with transition metals in close proximity during catalytic reactions, we have been interested in preparing dimers bridged by ligands that would not readily dissociate or cleave in the presence of substrate ligands. We therefore sought to prepare catalysts using ylides as potential nonlabile bridging ligands between two rhodium atoms. The results of our investigation are reported in this paper.

Experimental Section

The air-sensitive organometallics used in this work were handled with the exclusion of oxygen and moisture. A Vacuum Atmospheres drybox, filled with argon gas, was used for the handling and transfer of solids.

"Chromatoquality" grade solvents were used when available (Matheson Coleman and Bell). Hydrocarbon solvents were purified by prolonged treatment with sodium–potassium alloy (Na/K) under vacuum. Tetrahydrofuran and diethyl ether were first treated with $LiAlH_4$ and then distilled into a flask containing Na/K alloy and anthracene. The ethers were distilled, as required, from the blue radical anion solutions of Na/K–anthracene.

Infrared spectra were recorded with a Perkin-Elmer 457 spectrophotometer. Proton NMR spectra were recorded on Varian HA-100 and Varian T-60 instruments. Benzene was used as an internal reference.

Preparation of $(C_8H_{12})Rh(CH_2)_2P(CH_3)_2$ (1). An H-shaped tube containing a filter disk in the horizontal arm was charged with cyclooctadienerhodium(I) chloride dimer (900 mg, 1.82 mmol) and dissolved in 100 mL of benzene in vacuo. At room temperature, trimethylphosphonium methylide (2 g, 22 mmol) was distilled into this solution. The reaction mixture was allowed to stir at room temperature for 1 week. The white precipitate which formed was separated by filtration and the precipitate was washed with two portions (40 mL) of benzene. The solvent was removed from the filtrate in vacuo and the remaining yellow material was washed with 30 mL of methanol, giving **1** in 82% yield (890 mg, 2.9 mmol). Recrystallization by slow evaporation of saturated benzene solutions afforded analytically pure $(C_8H_{12})Rh(CH_2)_2P(CH_3)_2$ (**1**). Anal. Calcd for $(C_{12}H_{22}RhP)$: C, 48.01; H, 7.39; Rh, 34.28; P, 10.32. Found: C, 48.32; H, 7.36; Rh, 34.10; P, 10.40. IR spectrum (Nujol mull): 3000 (m), 2900 (s), 2810 (s), 1595 (s), 1485 (m), 1460 (m), 1420 (m), 1385 (m), 1330 (m), 1292 (s), 1240 (m), 1180 (m), 1060 (s), 1025 (s), 990 (m), 980 (m), 925 (m), 918 (m), 852 (m), 810 (s), 790 (m), 772 (m), 762 (s), 740 (s), 510 (w), 495 (w), 480 (w) cm^{-1}. High-resolution mass measurement: calcd 300.0503, found 300.0507.

Preparation of $(CO)_2Rh(CH_2)_2P(CH_3)_2$ (2) and $(CO)_2Rh[\mu\text{-}(CH_2)_2P(CH_3)_2]_2Rh(CO)_2$ (3). A single tube reactor was charged with crystalline $(C_8H_{12})Rh(CH_2)_2P(CH_3)_2$ (**1**) (600 mg, 2 mmol) and evacuated, and 60 mL of benzene was added in vacuo (this amount of solvent was not sufficient to dissolve more than 200 mg of **1**). The yellow mixture was then allowed to stir under a carbon monoxide atmosphere. There was an immediate color change of the solution from yellow to red. After 1 h the reaction mixture became a homogeneous cherry red solution. The solvent was removed in vacuo yielding the red solids **2** and **3**. All attempts to prepare crystalline materials by recrystallization failed.

A mixture of analytically pure **2** and **3** can be obtained by reacting crystalline **1** with an atmosphere of carbon monoxide in the absence of solvent. After several hours the displaced cyclooctadiene is then removed by pumping in vacuo. Anal. Calcd for $(C_6H_{10}RhPO_2)_n$: C, 29.05; H, 4.06; Rh, 41.49; P, 12.48; O, 12.92. Found: C, 28.57; H, 4.25; Rh, 41.78; P, 12.91; O, 12.49 by difference. IR spectrum (Nujol mull): 2920 (s), 2860 (s), 2035 (s), 2020 (m), 1950 (s), 1935 (s), 1465 (m), 1380 (m), 935 (m), 900 (m), 500 (w) cm^{-1}.

Catalytic Hydrogenation of Olefins. A single tube reactor was charged with $(C_8H_{12})Rh(CH_2)_2P(CH_3)_2$ (**1**) (30 mg, 0.1 mmol) and evacuated; the compound was dissolved in 30 mL of benzene. To this yellow solution, 1-hexene (673 mg, 8 mmol) was added in vacuo. The reaction mixture was pressurized to 762 mm of hydrogen pressure and allowed to stir at 28 °C for 20 h. Gas chromatographic analysis of the reaction mixture showed complete hydrogenation to hexane.

Catalytic Preparation of Methyl Acetate. A glass pressure tube was charged with a mixture of **2** and **3** (20 mg), 2.4 mL of methanol (59 mmol), 10 mL of benzene, and 1.2 mL (19 mmol) of methyl iodide, giving an orange reaction mixture. The reaction mixture was pressurized to 105 psi of carbon monoxide and heated to 100 °C. The

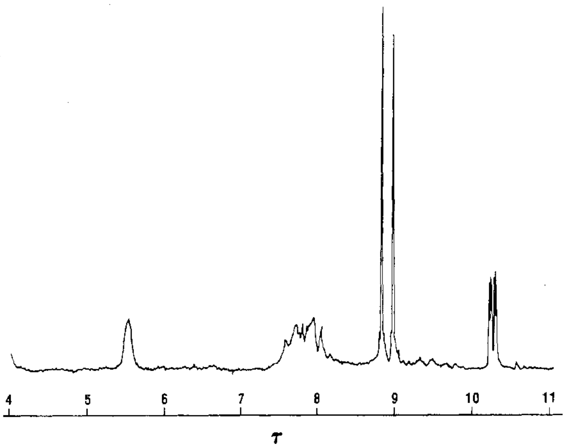
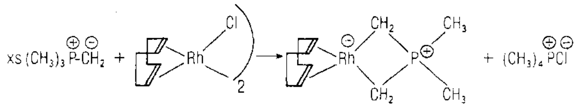


Figure 1. The 100-MHz pulsed ^{1}H NMR spectrum of $(C_8H_{12})Rh(CH_2)_2P(CH_3)_2$ (1) at 35 °C.

reaction mixture became a homogeneous yellow; it was allowed to react at 100 °C for 24 h. A GC analysis of the reaction mixture shows methyl acetate at ~50% conversion.

Results and Discussion

$(C_8H_{12})Rh(CH_2)_2P(CH_3)_2$ (1). Cyclooctadiene(dimethylphosphonium bis(methylide))rhodium(I) (**1**) was prepared by treating a benzene solution of cyclooctadienerhodium(I) chloride dimer with excess trimethylphosphonium methylide (see eq 2) in vacuo and stirring at room temperature for 1 week. The expected tetramethylphosphonium chloride (eq 2) precipitated and was separated by filtration. This salt was identified by comparing its IR and NMR spectra with an authentic sample prepared by treating trimethylphosphine with methyl chloride. The yellow material (**1**) was isolated from the benzene solution by removal of the solvent in vacuo and washing the precipitate with methanol. Crystals of **1** were obtained by slow evaporation of saturated benzene solutions.



(2)

1

The 100-MHz ^{1}H NMR[7] of **1** in benzene-d$_6$ is shown in Figure 1.[8] The doublet of doublets centered at τ 10.5 was assigned to the methylene protons attached to the phosphorus and rhodium (J_{P-H} = 7 Hz, J_{Rh-H} = 2 Hz). The protons of the methyl groups attached to the phosphorus appeared as a doublet (J_{P-H} = 15 Hz) centered at τ 8.9. The broad absorption centered at τ 5.5 was assigned to the olefinic protons of the coordinated cyclooctadiene. The complex series of resonances centered at τ 7.8 were assigned to the aliphatic protons of the cyclooctadiene.

At 35 °C the proton-decoupled ^{31}P NMR spectra of **1** in benzene-d_6 solvent showed no evidence for rhodium–phosphorus coupling and appeared as a singlet at −3.6 ppm,[9] even though rhodium–phosphorus coupling is observed in the carbonyl derivatives discussed below. This observation is somewhat puzzling since the rhodium–proton and phosphorus–proton couplings are observed in the proton spectrum. This result is attributed to an unknown exchange phenomenon of the bis(methylide) ligands in solution.

The elemental analyses and mass spectral data (*m/e* 300) confirmed the molecular formulation as $C_{12}H_{22}PRh$. The ^{1}H NMR, IR, and elemental analyses are consistent with both a monomeric and dimeric structure for **1**; but, on the basis of the mass spectrum, compound **1** is assigned the monomeric formulation as shown in eq 2. However, since compound **1** had to be heated to 125 °C in order to obtain a mass spectrum, the possibility still remains that **1** is a dimer at room temperature but fragments to a monomer before volatilizing. The crystal structure of compound **1** is currently being determined in order to establish whether the solid-state structure is in agreement with the observed mass spectrum.

Although compound **1** is only slightly air sensitive as a solid, solutions of it quickly decompose in air. Benzene, tetrahydrofuran, and methylene chloride solutions of **1** under a nitrogen atmosphere are stable indefinitely, but **1** rapidly decomposes in chloroform solution under strictly anaerobic conditions.

Benzene solutions of **1** (10^{-3} M) under a hydrogen atmosphere (1 atm) at 30 °C catalyzed the complete hydrogenation of 1-hexene (0.1 M) to hexane. Gas chromatographic analysis of a hydrogenation reaction at 16% completion showed no detectable isomerization of 1-hexene to internal olefins. While following the consumption of hydrogen during the hydrogenation, an induction period was observed. It was inferred from this that the active catalyst is probably being formed by first hydrogenating the complexed cyclooctadiene. It was observed that, when the hydrogenation of the 1-hexene was complete, the catalyst decomposed. However, the catalyst will not decompose under hydrogen as long as excess ligand such as olefin or phosphine is present. Apparently, after the cyclooctadiene is hydrogenated, the bis(methylide) ligand alone is not sufficient to stabilize the rhodium atom without the presence of additional ligands. When 2 equiv of triphenylphosphine is present during the hydrogenation of 1-hexene, the rate of reduction is slowed down three- to fourfold. This result is believed to be due to the triphenylphosphine effectively competing with the olefin for coordination sites.

Under the same conditions as the 1-hexene hydrogenation, **1** has been used to catalyze the hydrogenation of other olefins such as 2-hexene and cyclohexene. The α,β-unsaturated ester, methyl acrylate, however, could not be hydrogenated under these conditions.

$(CO)_2Rh(CH_2)_2P(CH_3)_2$ (2) and $(CO)_2Rh[\mu-(CH_2)_2P(CH_3)_2]_2Rh(CO)_2$ (3). Treatment of a yellow benzene solution of **1** with 1 atm of carbon monoxide liberates cyclooctadiene and generates a red solution containing monomeric **2** and dimeric **3** carbonyl derivatives. The formation of carbonyls occurs equally well in the solid state. The crystalline **1** can be treated with carbon monoxide in the absence of solvent to give **2** and **3** with the liberation of liquid cyclooctadiene, which is later removed under vacuum. Since **2** and **3** are soluble in cyclooctadiene, cyclooctadiene functions as a solvent which is formed in situ. Attempts to isolate **2** and **3** separately were unsuccessful, and as a result, the characterization data were obtained from the mixture.

The mass spectral data exhibited parent mass peaks for both the monomer (*m/e* 248) and the dimer (*m/e* 496) as well as *m/e* values corresponding to successive losses of carbon monoxide. Elemental analyses confirmed the empirical formula as $C_6H_{10}PRhO_2$. The IR spectrum (Nujol mull) showed carbonyl absorptions at 2035, 2202, 1950, and 1935 cm^{-1}. No absorptions corresponding to bridging carbon monoxide or acyl carbon monoxide were present.

The proton-decoupled ^{31}P NMR spectrum of the mixture of **2** and **3** in toluene (d_8) at 35 °C is shown in Figure 2. The triplet, centered at −29.11 ppm (J_{Rh-P} = 1.5 Hz), relative area 10, is assigned to the dimer which has two rhodium atoms coupled to the phosphorus atoms. The doublet, centered at −27.2 ppm (J_{Rh-P} = 24.9 Hz), relative area 2.3, is assigned to the monomer which has only one rhodium atom coupled to the phosphorus atom. The large difference in coupling constants is believed to be due to the difference in bond angles and concomitant ring strain that the phosphorus atoms have in the four-membered ring of the monomer vs. the eight-

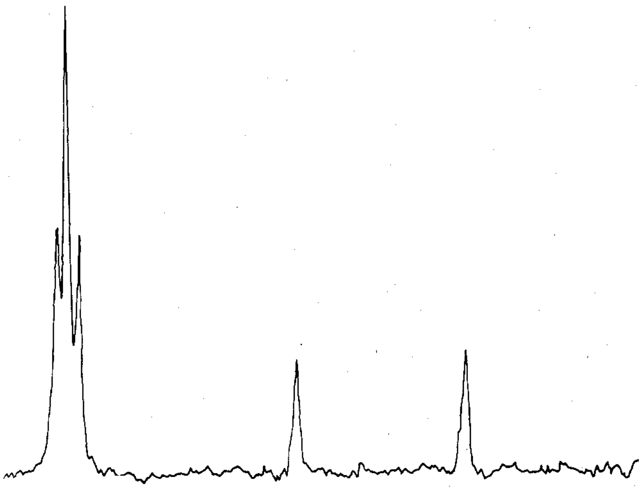
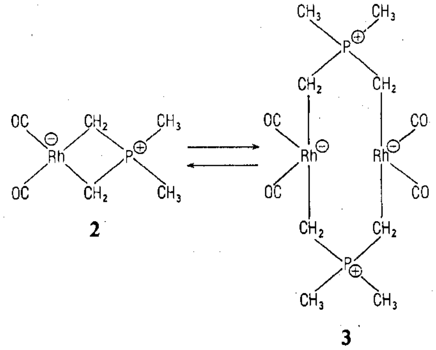


Figure 2. The proton-decoupled ^{31}P NMR spectrum of $(CO)_2Rh(CH_2)_2P(CH_3)_2$ (**2**) and $(CO)_2Rh[\mu\text{-}(CH_2)_2P(CH_3)_2]_2Rh(CO)_2$ (**3**) at 35 °C.

membered ring of the dimer. In the ^{31}P NMR spectrum at 60 °C the chemical shifts remain the same; however, the relative areas change to 10 and 6.8 for the dimer and monomer, respectively, indicating that on heating, monomer formation is increased. On cooling to 35 °C, the original spectrum returns, thus demonstrating the reversibility of the reaction and indicating equilibrium 3.



(3)

The 100-MHz ^1H NMR spectrum of **2** and **3** (see Figure 3) in toluene-d_8 at 35 °C revealed two sets of absorptions for methylene protons coupled to rhodium and phosphorus and two sets of absorptions for the protons of the methyl groups attached to the phosphorus. The assignments of monomer and dimer absorptions in the ^1H NMR were made by comparing the relative areas of the two sets of proton absorptions at 35 and 60 °C to the relative areas of the triplet and doublet in the ^{31}P NMR spectra at 35 and 60 °C. The set of absorptions in the ^1H NMR that increased in intensity on heating were assigned to the monomer since in the ^{31}P NMR spectrum the doublet, corresponding to the monomer, increased in intensity on heating. The set of absorptions in ^1H NMR that decreased in intensity on heating were assigned to the dimer since in the ^{31}P NMR spectrum the triplet, corresponding to the dimer, decreased in intensity. Therefore, the doublet of doublets centered at τ 9.34 (J_{P-H} = 16 Hz, J_{Rh-H} = 4 Hz), relative area 1.52, and the doublet centered at τ 9.08 (J_{P-H} = 11 Hz), relative area 2.28, were assigned to the dimer. The doublet of doublets centered at τ 10.45 (J_{P-H} = 6 Hz, J_{Rh-H} = 2 Hz), relative area 0.48, and the doublet centered at τ 9.41 (J_{P-H} = 12 Hz), relative area 0.72, were assigned to the monomer. Uncoordinated cyclooctadiene showed absorptions at τ 4.55, relative area 2, for the olefinic protons and at τ 7.92, relative area 4, for the aliphatic protons. The variable-temperature ^1H NMR data also show that the relative ratio of the two compounds changes reversibly as a function of temperature.[10]

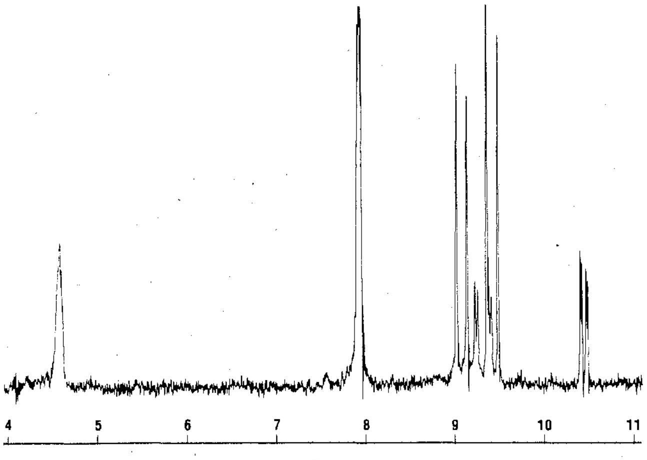


Figure 3. The 100-MHz ^1H NMR spectrum of $(CO)_2Rh(CH_2)_2P(CH_3)_2$ (**2**), $(CO)_2Rh[\mu\text{-}(CH_2)_2P(CH_3)_2]_2Rh(CO)_2$ (**3**), and cyclooctadiene at 55 °C.

The NMR data revealed no evidence for carbon monoxide insertion into the rhodium bis(methylide)alkyl bonds, even in carbon monoxide saturated solution.

Benzene solutions of **2** and **3** were found to react with methyl iodide to produce a rapid color change from red to orange. We were unable to isolate any stable compounds from these orange solutions since they decomposed in the absence of excess carbon monoxide. However, benzene solutions (100 °C) of **2** and **3** in the presence of methanol and carbon monoxide pressure (100 psi) can catalytically convert methyl iodide into methyl acetate. Unfortunately, **2** and **3** have been found to be completely inactive for the hydroformylation of olefins or diolefins.[11]

Conclusions

We have described the synthesis, characterization, and chemical and catalytic properties of $(C_8H_{12})Rh(CH_2)_2P(CH_3)_2$ (**1**), $(CO)_2Rh(CH_2)_2P(CH_3)_2$ (**2**), and $(CO)_2Rh[\mu\text{-}(CH_2)_2P(CH_3)_2]_2Rh(CO)_2$ (**3**). Compound **1** has been found to be useful as a hydrogenation catalyst of olefins, and **2** and **3** have been used as a catalyst for the conversion of methyl iodide into methyl acetate. These are the first reported examples of these types of catalyses with well-characterized ylide complexes.

The monomer–dimer equilibrium which has been observed between **2** and **3** illustrates that our original hypothesis that bridging bis(methylide) ligands would be able to hold transition metals in close proximity during catalytic reactions is not necessarily correct in this case since the dimer cleaves to the monomer so readily. Therefore, it may be either the monomer or the dimer that is the actual catalytic species in a catalytic reaction.

Acknowledgment. The authors wish to thank Mrs. Andrea Wallo and Mr. Stephen Horensky for technical assistance. We also wish to thank Mr. Michael Albright of JEOL analytical instruments for the ^{31}P NMR spectra and Dr. Ronald L. Lapinski and Dr. Henry J. Yue of Allied Chemical for the 100-MHz ^1H NMR spectra.

Registry No. **1**, 64314-98-3; **2**, 64314-97-2; **3**, 64314-96-1; $[(C_8H_{12})RhCl]_2$, 12092-47-6; $(CH_3)_3P^+\text{–}CH_2^-$, 29218-61-9; CO, 630-08-0.

References and Notes

(1) H. Schmidbaur, *Acc. Chem. Res.*, **8**, 62 (1975), and references therein.
(2) E. Kurras, U. Rosenthal, H. Mennenga, G. Oehne, and G. Engelhardt, *Z. Chem.*, **14**, 160 (1974); *J. Organomet. Chem.*, **84**, C13 (1975).
(3) L. E. Manzer, *Inorg. Chem.*, **15**, 2567 (1976).
(4) W. C. Kaska, D. K. Mitchell, R. F. Reichelderfer, and W. D. Korte, *J. Am. Chem. Soc.*, **96**, 2847 (1974).
(5) D. L. Reger and E. C. Culbertson, *J. Organomet. Chem.*, **131**, 297 (1977).

(6) Other ylide complexes have been found to be useful for ethylene polymerization catalysts: U.S. Patents 2 998 416 (1961) and 3 686 159 (1972).
(7) All proton chemical shifts are reported with respect to Me_4Si.
(8) Due to the low solubility of **1** in any nonreactive solvent, a pulsed NMR technique was necessary to obtain this spectrum. The authors wish to thank Dr. George Gray of Varian Associates for obtaining this spectrum.
(9) The ^{31}P chemical shifts are downfield with respect to external 85% H_3PO_4.
(10) The details of these variable temperature ^1H NMR studies will be reported elsewhere.
(11) Hydroformylations of ethylene, 1-hexene, and butadiene were attempted in benzene solution at 100 °C and pressures of CO/H_2 (1:1) up to 1200 psi. At temperatures of 150 °C and above hydroformylation did occur, but at these temperatures the catalyst decomposed to give rhodium metal.

Contribution from the Department of Chemistry,
Hunter College of the City University of New York, New York, New York 10021

Natural Abundance Nitrogen-15 Nuclear Magnetic Resonance Spectroscopy of Some Rhodium(III) Complexes

K. S. BOSE and E. H. ABBOTT*

Received April 13, 1977 AIC70262Z

The natural abundance nitrogen-15 NMR spectra of the rhodium(III) complexes of several alkyldiamine and aza aromatic ligands are reported. Spectra were obtained in several hours for the first class of compounds but required ca. 15 h for the latter group. Spectra could not be observed for a number of other complexes. The resonances of the complexes are found ca. 20 ppm upfield from those of the free ligand in the alkyldiamine case but are ca. 100 ppm above the aza aromatic ligands. This is attributed to shifts arising from the influence of low-lying excited states for the aza aromatic ligands themselves rather than any special property of their complexes. When comparison is made between the chemical shift of the complex and that of the protonated ligand, a rather constant difference of ca. 30 ppm is observed. No correlation of shift with position of the ligands in the spectrochemical series is observed. It is suggested that the upfield shift generally observed is a consequence of nonbonded magnetic interactions. Coupling constants between nitrogen-15 and rhodium-103 are observed and correlate simply with the s character of the bonding electron on nitrogen with $J = 18$ Hz for sp^2 and $J = 14$ Hz for sp^3. Diastereoisomerism is detectable in the tris complex of 1,2-diaminopropane, and rather rigid, different ligand conformations are observed for the tris(1,3-diaminopropane) case.

Introduction

The nuclear magnetic resonance spectroscopy of nitrogen in coordination compounds is an area of considerable potential interest. Nitrogen is a constituent of many ligands which are important in coordination chemistry and biochemistry. Furthermore, unlike carbon and hydrogen, nitrogen is often bound directly to the metal ion, and its spectroscopy can be expected to be a sensitive probe of bonding, coordination geometry, electronic structure, etc. Nitrogen exists in nature as two isotopes. The most abundant one, ^{14}N, has $S = 1$, and so its resonances are often quite broad in nonzero electric field gradients. In some situations this is not a problem, and its spectroscopy has yielded important information.[1] ^{15}N, however, has $S = {}^1/_2$ and so its resonances should be sharp and should reveal spin coupling when present. This isotope, unfortunately, is characterized by a rather low abundance (0.365%) and long relaxation times. These problems have largely restricted its natural abundance study to organic molecules which are liquids or are very soluble. A few studies have been performed with organometallic or coordination compounds, but these have been restricted to ligands enriched in ^{15}N. For example, the chemical shifts of coordinated ammonia have been measured via an ENDOR method,[2] and the mode of bonding was identified in a dinitrogen complex.[3] The most thorough study of ^{15}N shifts in coordination compounds has been the work carried out using ^{15}N-enriched ethylenediaminetetraacetate (EDTA) and a series of closed-shell metal ions. In this study it was demonstrated that shifts of only a few parts per million are observed when EDTA binds such closed-shell metal ions as Ca^{2+}, Zn^{2+}, Mg^{2+}, etc. This disappointingly small shift was attributed to near cancellation of large local diamagnetic and paramagnetic effects at the nitrogen atom.

Herein we report the natural abundance nitrogen-15 spectroscopy of a series of rhodium(III) complexes. This metal ion was chosen for a variety of reasons. Its complexes are always diamagnetic and substitutionally inert, excluding ground-state paramagnetic or ligand-exchange effects from consideration. As a d^6 ion, however, it has fairly low-lying excited states whose admixture might lead to large chemical shifts and whose energies are readily varied by utilizing ligands from different parts of the spectrochemical series. Also, it exists entirely as ^{103}Rh with $S = {}^1/_2$, and so one can obtain coupling constant data.

Experimental Section

Abbreviations of ligands appear in footnote 5. The rhodium(III) compounds $Rh(en)_3Cl_3$, $Rh(pn)_3Cl_3$, and $Rh(tn)_3Cl_3$ were prepared by the method of Gatsbol[6] while $Rh(bpy)_3Cl_3$ and $Rh(phen)_3Cl_3$ were prepared by the method of McKenzie and Plowman.[7] $Rh(en)_2Cl_2Cl$ and $Rh(py)_4Cl_2Cl$ were prepared by the methods of Anderson and Basolo[8] and of Gillard and Wilkinson,[9] respectively.

The ^{15}N NMR spectra were obtained in Fourier Transform mode with JEOL PS/PFT-100 spectrometer interfaced to a JEOL EC-100 data system. Chemical shifts at 10.09 MHz were determined using a 5 kHz range and 8K memory and are measured with respect to an external ammonium chloride solution. In the case of aliphatic amine complexes, a pulse angle of about 60° and in the case of aza aromatic complexes, a pulse angle of about 25–30° was used. For all complexes H_2O was the solvent, except in the case of the pyridine complex which was dissolved in benzyl alcohol. The spectra of the bis(ethylenediamine) and tetrakis(pyridine) complexes were obtained at 50 °C to have sufficient concentration.

Results and Discussion

Table I presents the chemical shift data obtained from the present studies. It also indicates the experimental conditions necessary to obtain these spectra. The most favorable cases are those of the bidentate saturated amines, which have protonated nitrogen atoms. Spectra are easily obtained within 2–4 h at concentrations of 1–2 M. Figure 1 is the spectrum

---

* To whom correspondence should be addressed at the Department of Chemistry, Montana State University, Bozeman, Mont. 59715.