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Comparison of the Properties of Cationic Alkyl- and Hydride-Rhodium(III) Complexes of the Triphosphine Bis(3-diphenylphosphinopropyl)phenylphosphine

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Treatment of RhCl(ttp) (ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$) with alkylcarbonium ions and protons (e.g., CH_3^+, $C_2H_5^+$, H^+) produces cationic rhodium alkyls and hydrides which may be considered to involve oxidative addition of the electrophile to rhodium(I). Formally, CH_3^+, $C_2H_5^+$, and H^+ are transformed to CH_3^-, $C_2H_5^-$, and H^-, respectively, while Rh(I) is converted to Rh(III). Although formally similar, the hydride complexes show striking differences in chemical behavior compared to the alkyls. Whereas the five-coordinate alkyl-rhodium complexes show essentially no association with solvents such as C_2H_5OH, SO_2, or DMSO, the hydride-rhodium cation is stable only as six-coordinate complexes of the type $[RhHCl(ttp)(L)]^+$ (L = C_2H_5OH, CH_3CN, THF, CO). Another difference between $[RhCl(CH_3)(ttp)]^+$ and $[RhCl(H)(ttp)]^+$ is the relative tendency to add CH_3CN and CO, which is much stronger for the hydride cation. Structural assignments for several of the complexes are made on the basis of infrared, ^1H, and ^{31}P NMR spectroscopy and correlations with the known structures of RhCl(ttp), $[RhCl(ttp)(NO)]PF_6$, and $[RhCl(ttp)(N_2Ph)]PF_6$.

Introduction

Transition metal–alkyl and –hydride bonds are currently being investigated extensively in efforts to understand, for example, their thermodynamic stability,[2,3] their roles in homogeneous hydrogenation and hydroformylation catalysis,[4,5] and the mechanisms of insertion reactions.[6,7] Tertiary phosphine ligands are often used to increase the stability of metal–alkyl and metal–hydride complexes.[8] However, complexes containing monodentate phosphines often undergo phosphine dissociation during chemical reactions to give the "active catalyst" or to form a product that contains fewer phosphine ligands than the starting reagent.[9,10]

As a part of our studies in the areas of organometallic chemistry and homogeneous catalysis by transition metals, we planned to attempt isolation of complexes that are analogues of the proposed intermediates and/or "active species" in catalytic systems. In order to accentuate the special stabilizing effects of phosphines on heavy transition metal complexes and to minimize phosphine ligand dissociation, we decided to prepare and use the chelating triphosphine ligand $PhP(CH_2CH_2CH_2PPh_2)_2$.[11,12] Compared to a monodentate phosphine, such a polyphosphine provides simultaneously (1) more control on the coordination number, stoichiometry, and stereochemistry of the resulting complex, (2) an increased basicity (or nucleophilicity) at the metal, and (3) detailed structural and bonding information in the form of metal–phosphorus and phosphorus–phosphorus coupling constants. Some of these advantages and control are illustrated by the chemistry of cationic alkyl- and hydride–rhodium(III) complexes of $PhP(CH_2CH_2CH_2PPh_2)_2$ reported herein. A preliminary communication on some aspects of the methyl complexes has appeared.[13]

Experimental Section

Reagents and Characterization. All solvents were reagent grade and were thoroughly degassed before use. Further purification of solvents and reagents, if necessary, was performed using standard literature methods. The ligand ttp, $PhP(CH_2CH_2CH_2PPh_2)_2$,[11,12] was used as a stock benzene solution. Complexes were prepared routinely in degassed solvents and isolated under a nitrogen atmosphere; the solid complexes are generally air stable (except where noted). Conductivity measurements were made at ca. 23 °C on $\sim 10^{-3}$ M nitromethane solutions and results are given in $cm^2/(ohm\ mol)$. Proton NMR measurements were made on Varian HA-100 and Jeol MH-100 instruments with an ambient operating temperature of ~38 °C. Phosphorus-31 spectra were obtained with a Bruker XL-90 Fourier transform spectrometer using spinning 10-mm tubes, deuterium lock from the deuterated solvent, and external 85% H_3PO_4 as the reference. Elemental analyses and molecular weights were determined by Galbraith Laboratories, Knoxville, Tenn., or by M-H-W Laboratories, Garden City, Mich. Infrared spectra of the solid compounds were taken on Perkin-Elmer 337 grating and Beckman IR-9 spectrometers as Nujol mulls between KBr plates (unless otherwise specified) and are listed as cm^{-1}. Infrared spectra of dichloromethane solutions of the complexes under gas pressures up to 80 psi were obtained as described previously.[12]

Complexes. The following complexes were prepared according to the reported procedures:[12] RhCl(ttp), RhCl(ttp)CO, $[Rh(ttp)CO]PF_6$, $[Rh(ttp)(CH_3CN)]BF_4$, $[RhHCl(ttp)(C_2H_5OH)]BF_4$, and $[RhCl(CH_3)(ttp)]FSO_3$.[13]

$[RhCl(C_2H_5)ttp]PF_6$. The complex was prepared by stirring a 50-ml benzene solution of Rh(ttp)Cl (0.6 g) with solid $(Et_3O)PF_6$ (0.6 g). After 1.5 h the yellow solid was collected on a filter and dissolved in 15 ml of CH_2Cl_2, and the resulting solution was filtered. A yellow solid crystallized after adding 50 ml of ethanol to the above CH_2Cl_2 solution and removing the CH_2Cl_2 by rotary evaporation. The product was collected on a filter, washed with ethanol and ether, and dried in vacuo; yield 0.27 g. Anal. Calcd for $[C_{38}H_{42}ClF_6P_4Rh]$: C, 52.16; H, 4.48; Cl, 4.05. Found: C, 52.39; H, 4.90; Cl, 4.33. The infrared spectrum shows the normal ionic PF_6^- peaks at 840 cm^{-1} (vs) and 553 cm^{-1} (m).

$[RhHCl(ttp)(CH_3CN)]BF_4 \cdot {}^1/_2(C_2H_5)_2O$. A 0.30-g sample of $[RhHCl(ttp)(EtOH)]BF_4$ dissolved in 3 ml of acetonitrile was treated with 15 ml of diethyl ether and the resultant solution was cooled slowly to −10 °C. Nearly white crystals separated; these were collected on a frit and dried in vacuo; yield 0.27 g, 86%. Anal. Calcd for $C_{38}H_{41}BClF_4NP_3Rh \cdot {}^1/_2(C_2H_5)_2O$: C, 55.42; H, 5.35; N, 1.52. Found: C, 55.51; H, 5.12; N, 1.52. Diagnostic infrared peaks are $\nu_{C\equiv N}$ at 2330 cm^{-1} (w) and ν_{Rh-H} at 2180 cm^{-1} (w). The proton NMR spectrum shows a triplet and a quartet at τ 8.95 and 6.65, respectively, for $(C_2H_5)_2O$, as well as a single peak at τ 8.8 for coordinated CH_3CN; Λ_M 89 in CH_3NO_2.

$[RhHCl(ttp)(CO)]PF_6$. A dichloromethane solution of $[Rh(ttp)(CO)]PF_6$ was treated with anhydrous HCl gas for 2 min. Then 15 ml of hexane was added to cause precipitation of a pale yellow solid; yield 92%. Anal. Calcd for $C_{37}H_{38}ClF_6OP_4Rh \cdot {}^1/_2CH_2Cl_2$: C, 49.09; H, 4.29; Cl, 7.73. Found: C, 48.66; H, 4.26; Cl, 7.73. Diagnostic infrared peaks are ν_{Rh-H} 2170 cm^{-1} (w) and ν_{CO} 2110 cm^{-1} (s); Λ_M 77. The 0.5 mol of dichloromethane was confirmed by proton NMR.

$[RhDCl(ttp)(CO)]PF_6$. One-tenth gram of $[Rh(ttp)(CO)]PF_6$ was dissolved in 7 ml of CH_2Cl_2 and shaken with 3 drops of 6 M DCl. The resulting pale yellow solution was shaken with ca. 5 g of Na_2SO_4 for 5 min, and then the mixture was filtered. To the filtrate was added ca. 30 ml. of hexane in 5-ml portions over a period of 15 min. The resulting pale yellow solid was collected on a filter, washed with hexane, and dried with a N_2 stream; yield 0.08 g; ν_{Rh-D} 1545 cm^{-1}.

$[RhHBr(ttp)(CO)]PF_6$ and $[RhDBr(ttp)(CO)]PF_6$. The compounds were prepared by treating $[Rh(ttp)(CO)]PF_6$, as given above for $[RhDCl(ttp)(CO)]PF_6$, with an aqueous 48% solution of HBr and DBr, respectively. Important infrared bands: ν_{Rh-H} 2170 cm^{-1}, ν_{CO} 2130 cm^{-1}; ν_{Rh-D} 1545 cm^{-1}, ν_{CO} 2130 cm^{-1}. Anal. Calcd for $[RhHBr(ttp)(CO)]PF_6 \cdot 0.8CH_2Cl_2$: C, 45.94; H, 4.04; Br, 21.03. Found: C, 45.76; H, 4.45; Br, 20.60. The 0.8 mol of CH_2Cl_2 was confirmed by proton NMR.

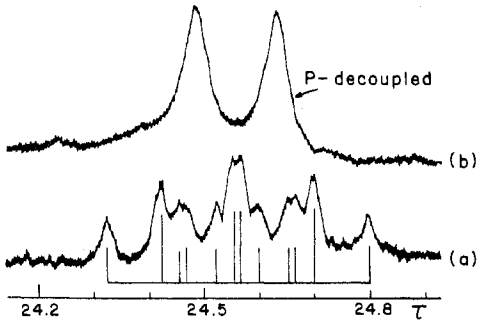


Figure 1. Hydride region of the proton NMR spectrum (100 MHz) of $[RhHCl(ttp)(CH_3CN)]BF_4$ in acetonitrile: curve a is the observed spectrum; curve b corresponds to the same conditions except for phosphorus decoupling at 40.48 MHz.

Table I. Proton NMR Data for the Hydride Complexes $[RhHX(ttp)L]^+$

Complex	τ^a	$^1J_{Rh-H}$, Hz	$^2J_{P_1-H}$, Hz	$^2J_{P_2-H}$, Hz
$[RhHCl(ttp)(MeCN)]BF_4$	24.6	14.7	13.4	9.8
$[RhHCl(ttp)(EtOH)]BF_4$	26.1	15.2	12.7	9.8
$[RhHCl(ttp)(CO)]PF_6$	22.4	15.5	8.9	8.6
$[RhHBr(ttp)(CO)]PF_6$	21.3	15.4	8.5	8.5

[a] Value relative to TMS = 10.00.

Reactions of HBF_4 with RhCl(ttp). If HBF_4·ether is added to a dry benzene solution of RhCl(ttp), the solution turns orange-brown, and an orange-brown solid slowly precipitates. The infrared spectrum of this solid has no obvious Rh–H stretch and if the compound is treated with ethanol, the known compound $[RhHCl(ttp)(EtOH)]BF_4$ is not formed. If, on the other hand, the benzene contains some ethanol (ca. 10%), addition of HBF_4·ether causes only a momentary orange-brown color which then changes to pale yellow. Subsequently, precipitation of the pale yellow solid $[RhHCl(ttp)(EtOH)]BF_4$ occurs. A similar behavior is exhibited if an even weaker coordinating solvent, THF, is used instead of ethanol, forming presumably $[RhHCl(ttp)(THF)]BF_4$.

Results and Discussion

Proton NMR. Resonances in the region τ 20–25 in the proton NMR spectra of the complexes $[RhHX(ttp)(L)]^+$ (where ttp = $PhP(CH_2CH_2CH_2PPh_2)_2$ and L = CH_3CN, CO, C_2H_5OH) appeared as multiplets and were assigned to the H–Rh resonance. First-order coupling of the hydride nucleus with three ^{31}P nuclei and one ^{103}Rh nucleus (all 100% natural abundance with $I = {}^1/_2$) produces a 12-line pattern (i.e., the A portion of an AMQ_2Y spin system). Figure 1 shows the spectrum observed for $[RhHCl(ttp)(CH_3CN)]BF_4$. Similar NMR spectra were observed in the hydride region for both $[RhHCl(ttp)(CO)]PF_6$ and $[RhHBr(ttp)(CO)]PF_6$; both spectra had six distinct peaks, some of which were distorted in shape owing to overlapping peaks. In each case irradiation of the ^{31}P region (40.48 MHz) caused the multiplet pattern to collapse to a doublet, which gave the $^1J_{Rh-H}$ coupling constant directly. The remainder of the multiplet pattern is a doublet of triplets arising from coupling the hydride to the central and terminal phosphorus atoms, respectively, of the ligand $PhP(CH_2CH_2CH_2PPh_2)_2$. The values of coupling constants and chemical shifts for the hydride complexes are shown in Table I.

The 12-line resonance patterns observed for the Rh–CH_3 portion of the proton NMR spectra of $[Rh(CH_3)Cl(ttp)]FSO_3$ and $[Rh(CH_3)Cl(ttp)(L)]FSO_3$ (L = CH_3CN, CO) are all consistent with the A_3 portion of an A_3MQ_2Y system and are all very similar to the Rh–H portions of the spectra of the analogous hydride complexes, although the magnitudes of $^2J_{Rh-H}$ are significantly smaller than the $^1J_{Rh-H}$ values in the hydride complexes. In the case of the five-coordinate complex $[Rh(CH_3)Cl(ttp)]FSO_3$, the Rh–CH_3 resonance is superimposed on the methylene resonances of the ttp ligand at ca. τ 7.4.[13] However, the Rh–CH_3 resonance in each of the six-coordinate complexes that contain either CO or CH_3CN is shifted significantly upfield (to ca. τ 8.75) and is completely separated from the methylene resonances. Presumably, this shift of the Rh–CH_3 resonance is caused primarily by the trans influence of the CO or CH_3CN ligand located trans to the Rh–CH_3 bond in the six-coordinate adducts.[14]

Table II. Proton NMR Data for the Rhodium–Alkyl Complexes

Compd	τ	$^2J_{RhH}$, Hz	$^3J_{HP_1}$, Hz	$^3J_{HP_2}$, Hz
$[Rh(CH_3)Cl(ttp)]FSO_3$	7.40	2.5	3.8	5.5
$[Rh(CH_3)Cl(ttp)(MeCN)]FSO_3$	8.75	2.1	4.4	6.2
$[Rh(CH_3)Cl(ttp)(CO)]FSO_3$	8.71	1.0	6.0	5.8
$[Rh(C_2H_5)Cl(ttp)]PF_6$	6.32 (CH_2)	<3.0	*a*	*a*
	9.50 (CH_3)	1.5	Ca. 0	Ca. 0

[a] Unable to determine.

The proton NMR spectrum of the ethyl group in $[Rh(C_2H_5)Cl(ttp)]PF_6$ appeared as a complex multiplet at τ 6.32 and a triplet of doublets centered at τ 9.50; the two multiplets are assigned to the methylene and methyl protons of the CH_2CH_3 group, respectively. The methyl resonance is split only by the rhodium and the methylene protons of the C_2H_5 group ($^3J_{H-H}$ = 6.4 Hz and $^3J_{Rh-H}$ = 1.5 Hz), since ^{31}P decoupling produced no changes in this portion of the proton spectrum. The methylene portion of the Rh–C_2H_5 resonances is very complicated and it was not analyzed. However, ^{31}P decoupling caused this portion of the proton spectrum to change to a broad quartet. The ^{31}P decoupling confirmed the H–H coupling, but the magnitude of the Rh–H coupling can only be estimated ($^2J_{Rh-H} \approx 3$ Hz) since it was not resolved.

The tendency of $[Rh(H)Cl(ttp)]^+$ and $[Rh(R)Cl(ttp)]^+$ (R = CH_3, C_2H_5) to add small molecules was examined by both infrared and NMR spectroscopy; major differences between the hydride and alkyl cations were observed. For example, neither $[Rh(CH_3)Cl(ttp)]^+$ nor $[Rh(C_2H_5)Cl(ttp)]^+$ forms spectroscopically detectable amounts of the six-coordinate solvate $[Rh(R)Cl(ttp)(C_2H_5OH)]^+$, whereas the solvated hydride cation $[RhHCl(ttp)(C_2H_5OH)]^+$ is crystallized from ethanol solutions. In contrast to the ready formation of $[RhHCl(ttp)(C_2H_5OH)]^+$ in solutions that contain ethanol, addition of HBF_4 or HPF_6 to Rh(ttp)Cl in dry benzene produces a sensitive, uncharacterized solid that does not appear, on the basis of infrared and proton NMR measurements, to contain a Rh–H bond. Also, this solid does not add ethanol to form the cation $[RhHCl(ttp)(C_2H_5OH)]^+$. At 40 °C the Rh–H resonance, as well as the quartet and triplet peaks of C_2H_5OH, is fairly broad. The peaks become much sharper at 10 °C and suggest labile coordination of ethanol at the higher temperatures.

The bright yellow, five-coordinate cation $[Rh(CH_3)Cl(ttp)]^+$ forms a nearly colorless solution in acetonitrile owing to formation of the six-coordinate complex $[Rh(CH_3)Cl(ttp)(CH_3CN)]^+$. The resulting Rh–$CH_3$ proton resonance is shifted 1.35 ppm upfield from the Rh–CH_3 resonance observed for $[Rh(CH_3)Cl(ttp)]FSO_3$ in either nitromethane or dichloromethane (Table II). If small amounts of acetonitrile are added to a solution of $[Rh(CH_3)Cl(ttp)]^+$ in dichloromethane, the Rh–CH_3 resonance is shifted progressively from τ 7.4 toward τ 8.75, the position observed in pure acetonitrile. Also, the CH_3CN resonance remains a sharp peak at 40 °C and is shifted upfield from the free CH_3CN value (see Figure 2 for the case of 1.5 mol of CH_3CN/mol of Rh).

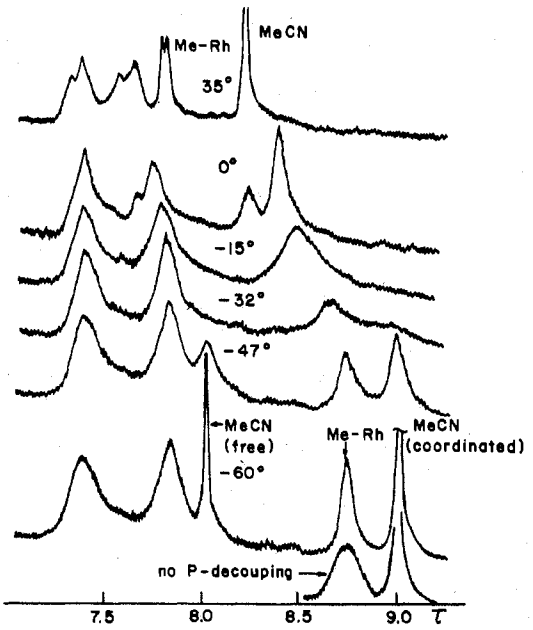


Figure 2. Proton NMR (100 MHz) spectra at different temperatures for $[Rh(CH_3)Cl(ttp)]FSO_3$ plus 1.5 equiv of acetonitrile in dichloromethane.

A limiting spectrum is obtained at −60 °C that has sharp resonances for both coordinated and uncoordinated CH_3CN at τ ca. 9.0 and 8.0, respectively. Thus, the acetonitrile molecule of $[Rh(CH_3)Cl(ttp)(CH_3CN)]^+$ is rapidly exchanging on the NMR time scale at room temperature and down to nearly −60 °C. Under comparable conditions the ethyl derivative $[Rh(C_2H_5)Cl(ttp)]^+$ does not appear to form an acetonitrile adduct. In the corresponding hydride complex, $[Rh(H)Cl(ttp)(CH_3CN)]^+$, acetonitrile is bonded more strongly and exchange is slow even at 40 °C. This was demonstrated by quantitatively displacing the ethanol molecule from $[RhHCl(ttp)(C_2H_5OH)]^+$ with acetonitrile at 40 °C (see Figure 3). Addition of 1 equiv of acetonitrile causes the broad triplet and quartet resonances of the exchanging ethanol molecule to sharpen to the pattern for free ethanol. After addition of more acetonitrile, the spectrum at 40 °C shows coordinated acetonitrile, as well as free ethanol and free acetonitrile. In contrast to the methyl cation, the hydride cation does not exchange CH_3CN on the NMR time scale at 40 °C.

The trend toward adduct formation with acetonitrile is also observed with carbon monoxide. For example, $[Rh(C_2H_5)Cl(ttp)]PF_6$ does not add carbon monoxide at 1 atm CO pressure; however, the corresponding methyl derivative $[Rh(CH_3)Cl(ttp)]^+$ rapidly adds CO to form $[Rh(CH_3)Cl(ttp)(CO)]^+$. The latter complex can be isolated under an atmosphere of CO, but in solution it dissociates carbon monoxide in the absence of a CO atmosphere. The labile nature of the Rh–CO bond also is indicated by the temperature effects on the methyl resonance (P decoupled). The proton NMR spectrum at 35 °C shows a very broad Rh–CH_3 resonance, which sharpens markedly on cooling the solution to −20 °C (see Figure 4). In contrast to the lability of the Rh–CO bond in $[Rh(CH_3)Cl(ttp)(CO)]^+$, the carbonyl hydrides $[RhHX(ttp)(CO)]PF_6$ (X = Cl, Br) show no loss of carbon monoxide in solution. Instead, the carbonyl hydrides dissociate HX slowly if excess HX is not present in solution. The stability of the Rh–CO bond in these carbonyl hydrides facilitates preparation of the six-coordinate complexes by one of three methods: (1) addition of carbon monoxide to $[RhHCl(ttp)(C_2H_5OH)]PF_6$, (2) addition of HX to $[Rh(ttp)(CO)]PF_6$, or (3) addition of HPF_6 to RhX(ttp)(CO).

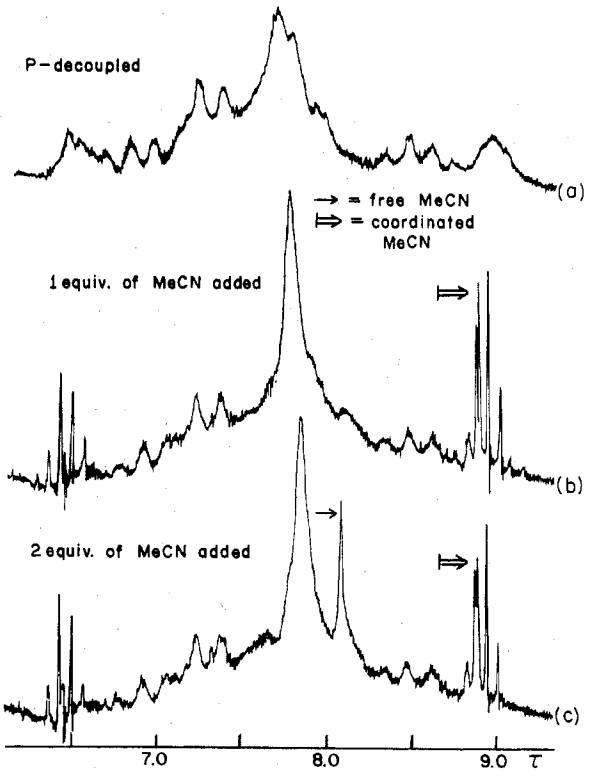


Figure 3. Phosphorus-decoupled proton NMR spectra: (a) $[RhHCl(ttp)(EtOH)]BF_4$ in dichloromethane; (b) as in (a) after addition of 1 equiv of acetonitrile; (c) as in (a) after addition of 2 equiv of acetonitrile.

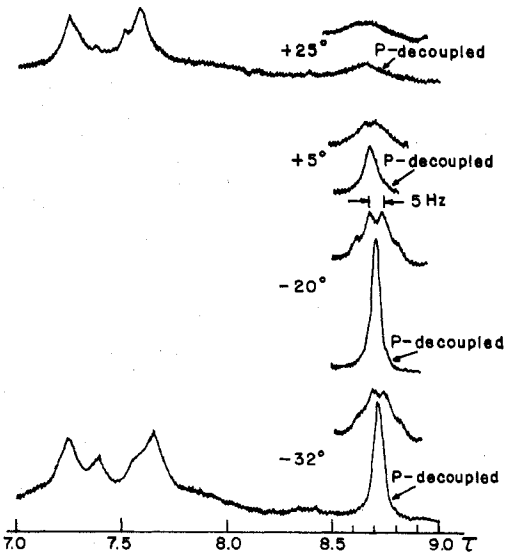


Figure 4. Proton NMR spectra of $[Rh(CH_3)Cl(ttp)(CO)]^+$ in a dichloromethane solution that was saturated with carbon monoxide at atmospheric pressure.

Because the order of addition of the strong ligands H^- and CO in method 1 is different from that in methods 2 and 3, one may expect to obtain different isomers for the resulting $[RhHX(ttp)(CO)]^+$ cation. This point is currently being studied.

Phosphorus-31 NMR. The proton-decoupled ^{31}P NMR spectra of most of these ttp complexes are first order, generally appearing as a doublet of triplets and a doublet of doublets (see Figure 5), as expected for the M_2X portion of an AM_2X spin system. In the case of $[Rh(CH_3)Cl(ttp)]FSO_3$, the chemical shift difference between the two types of phosphorus nuclei is smaller and causes the spectrum to be distorted

Table III. Fourier Transform Phosphorus-31 NMR Data for the Rhodium Complexes of Bis(3-diphenylphosphinopropyl)phenylphosphine

Compd	Solvent	δ_{PPh}[a]	δ_{PPh_2}[a]	$^2J_{P_1-P_2}$, Hz	J_{P_1-Rh}, Hz[b]	J_{P_2-Rh} Hz[c]
$[Rh(ttp)(CO)]PF_6$	CH_3NO_2	6.24	−12.67	52.3	115.2	112.3
$RhCl(ttp)CO$	$CH_2Cl_2 + C_6D_6$	−13.6	9.1	52.2	115.5	114.7
$[Rh(NO)Cl(ttp)]PF_6$	CH_3NO_2	10.81	2.14	30.2	138.9	105.8
$[Rh(CH_3)Cl(ttp)]FSO_3$	CH_3NO_2	11.18	1.15	33.1	114.5	93.4
$[Rh(C_2H_5)Cl(ttp)]PF_6$	CH_3NO_2	11.66	−1.77	34.3	120.0	98.0
$[RhHCl(ttp)(MeCN)]BF_4$	CD_3CN	24.05	10.04	36.8	116.2	89.0
$[RhHCl(ttp)(EtOH)]BF_4$	CH_3NO_2	22.90	9.19	36.7	115.7	89.4
$[RhHCl(ttp)(CO)]PF_6$	CH_3NO_2	1.14	4.90	37.8	89.7	81.3
$[Rh(CH_3)Cl(ttp)(MeCN)]FSO_3$	CD_3CN	11.65	−1.02	32.5	116.2	91.5
$[Rh(CH_3)Cl(ttp)(CO)]FSO_3$	CH_3NO_2	7.04	−4.86	37.9	108.1	83.8

[a] Chemical shifts in ppm relative to external 85% H_3PO_4; positive numbers are downfield from H_3PO_4. [b] P_1 is the central PPh group. [c] P_2 are the terminal PPh_2 groups.

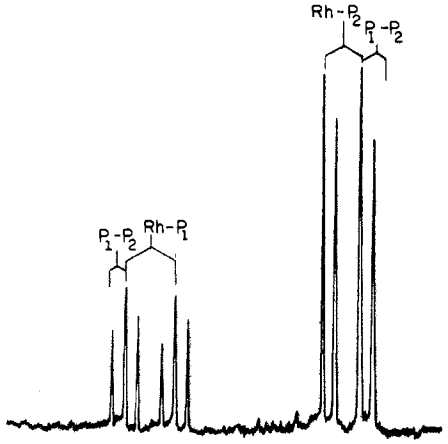
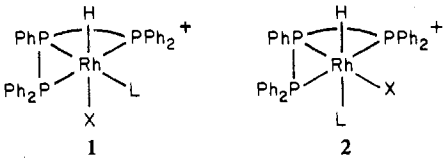


Figure 5. Proton-noise-decoupled, Fourier-transform ^{31}P NMR spectrum of $[Rh(CH_3)Cl(ttp)(CH_3CN)]FSO_3$ in CD_3CN.

somewhat from first order, while the spectrum of $[RhHCl(ttp)(CO)]PF_6$ was significantly second order. In all cases the two rhodium–phosphorus and the phosphorus–phosphorus coupling constants were obtained directly from the spectra; the data are given in Table III. For the metal hydride complexes, phosphorus–hydride coupling was observed, but the P–H coupling constants were obtained more accurately from the ^1H spectra of the hydride resonance region (see Table I).

Stereochemistry of the Complexes. All of the cationic hydrides reported herein {e.g., $[RhHCl(ttp)(L)]^+$ (L = CO, CH_3CN, C_2H_5OH) and $[RhHBr(ttp)(CO)]^+$} are six-coordinate. The ^{31}P NMR spectra of the complexes show that both terminal phosphorus atoms (P_2) are equivalent. Thus, the structures of the complexes must contain the three phosphorus nuclei of the ttp ligand in a meridional arrangement as shown in **1** and **2**.

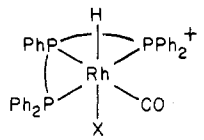


1 **2**

X = Cl, Br
L = CO, CH_3CN, C_2H_5OH

Additional stereochemical information may be obtained from the magnitudes of the P–H coupling constants of these hydride complexes. In metal hydride complexes of phosphines, generally the phosphorus–hydride coupling constants are much larger for a trans P–M–H arrangement than for a cis P–M–H arrangement, i.e., $^2J_{P-H(trans)} >> {}^2J_{P-H(cis)}$.[15-17] The different ranges of J are particularly diagonostic for the second and third transition series. These ttp, six-coordinate, rhodium–hydride complexes all have small and approximately equal $^2J_{P-H}$ values, which is consistent with either structure **1** or **2**, where the hydride is located cis to all three phosphorus atoms.

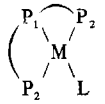
Although a distinction between structures **1** and **2** for the hydride complexes (L = CH_3CN, C_2H_5OH) cannot be made from the available infrared and NMR data, the structure of the carbonyl hydrides is more definite. Vaska[18] reported that the Fermi interaction in complexes having CO trans to a hydride ligand leads to a significant shift in ν_{CO} when the corresponding deuterium complex is examined. In such compounds an anomalous ratio of ν_{MH}/ν_{MD} is obtained also. For example, the ν_{CO} for $OsH_2(CO)(PPh_3)_3$ is shifted by 32 cm^{-1} on deuteration, and the ν_{MH}/ν_{MD} ratio for the hydride trans to CO is 1.372, whereas the ratio for the hydride cis to CO has a more normal value of 1.397. Our complex $[RhClH(ttp)(CO)]^+$ showed essentially no shift in ν_{CO} on deuteration, and the ν_{RhH}/ν_{RhD} ratio was 1.398. Similar results were found for the bromide complex. Thus, the carbonyl complexes can be assigned structure **3**. Structure



3
X = Cl, Br

3 is expected from the synthesis route since the polar aqueous solutions of HX would favor a two-step reaction sequence involving addition of a proton to the nucleophilic rhodium atom in $[Rh(ttp)CO]^+$ and then association of the chloride ion trans to the H–Rh bond because of the strong trans influence of the hydride ligand.

Additional support for structure **3** is obtained from the J_{Rh-P} and J_{Rh-H} values, since direct metal–ligand coupling constants are useful stereochemical probes that are sensitive to the trans influence of other ligands.[15-17] Thus, the $^1J_{M-P}$ values are significantly larger when the phosphorus atom is trans to a ligand that is a low trans-influencing ligand (e.g., halides) than when it is trans to a higher trans-influencing ligand (e.g., PR_3, H, or CO). Thus, the arrangement

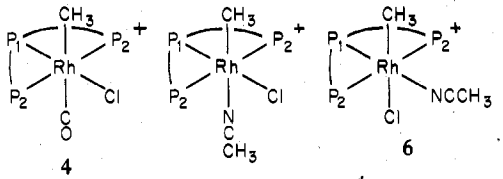


provides an ideal case for evaluating the trans influence of L. For the four-coordinate, planar complex $[Rh(ttp)(CO)]^+$, the values of $^1J_{Rh-P_2}$ (P trans to P) and $^1J_{Rh-P_1}$ (P_1 trans to CO) are nearly equal, 112 and 115 Hz, respectively. However, in the known square-pyramidal cation $[RhCl(ttp)(NO)]^+$ $^1J_{Rh-P_2}$ is 106 Hz (P trans to P) and $^1J_{Rh-P_1}$ is 139 Hz (P trans to Cl), a difference of 33 Hz (Table III). In the six-coordinate solvates $[RhHCl(ttp)(L)]^+$ (L = CH_3CN, C_2H_5OH), $^1J_{Rh-P_1}$ (where P_1 must be trans to a weak solvent ligand or to Cl)

is 26–27 Hz larger than $^1J_{Rh-P_2}$ (P trans to P), whereas $^1J_{Rh-P_1}$ for $[RhHCl(ttp)(CO)]^+$ is only 8 Hz larger than $^1J_{Rh-P_2}$. The coupling constants are consistent with assignment of structure **3**, which has the good π-acceptor ligand, CO, trans to P_1. The magnitudes of $^1J_{Rh-H}$, $^2J_{P_1-H}$, and $^2J_{P_2-H}$ also suggest structure **3** for the carbonyl hydrides $[RhHX(ttp)(CO)]^+$ and are consistent with either structure **1** or **2** for the solvated hydride cations $[RhHX(ttp)(L)]^+$.

Five-coordinate Rh(III) complexes are unusual; however, for the alkyl cations $[Rh(R)Cl(ttp)]^+$ one can exclude the possibility of a six-coordinate, dimeric cation on the basis of infrared spectroscopy, conductance data, and molecular weight data. The slope of the linear plot of equivalent conductance against the square root of concentration over the concentration range $(7.5–3.8) \times 10^{-4}$ M in nitromethane clearly indicates a uni-univalent electrolyte. Also, the experimental molecular weight of $[Rh(CH_3)Cl(ttp)]FSO_3$ in chloroform is 815, which is exactly the value for the monomeric ion pair. The infrared spectra of the solids $[Rh(R)Cl(ttp)]FSO_3$ show no splitting of bands appropriate for a coordinated FSO_3^- ion. In addition, the ^{31}P NMR data are consistent with a five-coordinate square-pyramidal structure for the alkyl cations $[RhCl(R)(ttp)]^+$, analogous to the known structures of $[RhCl(NO)(ttp)]^+$ [12] and $[RhCl(N_2Ph)(ttp)]^+$.[19] Thus, the total data indicate that the triphosphine ligand and chloride occupy the square-pyramidal base and the alkyl group is located at the apex.

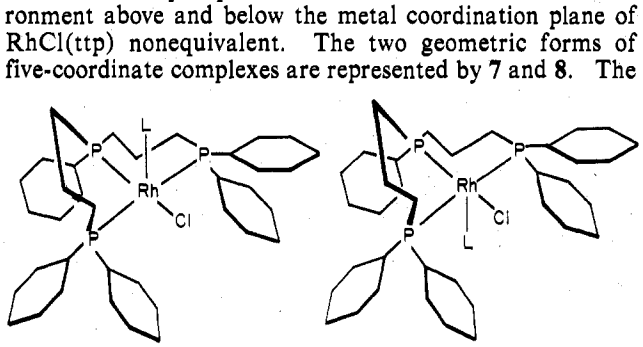
For the six-coordinate rhodium–methyl cations $[RhCl(CH_3)(ttp)L]^+$ (L = CH_3CN, CO) the ^{31}P spectra require chemically equivalent P_2 phosphorus atoms. In both complexes $^1J_{Rh-P_1}$ is larger than $^1J_{Rh-P_2}$ by ~25 Hz, which suggests that a ligand of low trans influence is trans to P_1. Thus, the carbonyl adduct $[RhClMe(CO)(ttp)]^+$ must have structure **4**, in which CO is cis to P_1 and trans to CH_3. This structure



4 5 6

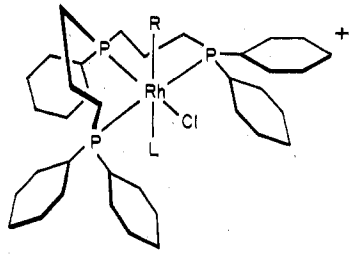
differs from that of the analogous hydride case, $[RhHCl(ttp)(CO)]^+$, which has CO trans to P_1 and cis to H. Since both acetonitrile and chloride are weak ligands, the NMR data do not distinguish unambiguously between the isomers **5** and **6**. However, structure **5** is favored on the basis of the preparative method and the structures of several related complexes.

Diastereomers. Another aspect of the stereochemistry of these complexes is concerned with the existence of "top–bottom" diastereomers. The orientation of the phenyl group on the central phosphorus atom makes the chemical environment above and below the metal coordination plane of RhCl(ttp) nonequivalent. The two geometric forms of five-coordinate complexes are represented by **7** and **8**. The



7 8

three x-ray crystal structure analyses on ttp complexes[12,19] show only one of the two possible diastereomers, i.e., structure **7**. In addition to the downward projection of the phenyl group on the central phosphorus atom, the x-ray results show that two phenyl groups on the terminal phosphorus atoms are projected below the $RhClP_3$ plane and make the region below the plane very crowded. Thus, the most probable metal site for addition of a bulky ligand would be the "top" side of RhCl(ttp). The structures of both $[Rh(NO)(Cl)(ttp)]^+$ and $[RhCl(N_2Ph)(ttp)]^+$ show only diastereomer **7** and most probably the alkyl cations $[RhCl(R)(ttp)]^+$ (R = CH_3, C_2H_5) have the same type of structure. In the six-coordinate adducts the sixth ligand presumably must fit into the crowded "bottom" site as illustrated by **9**.

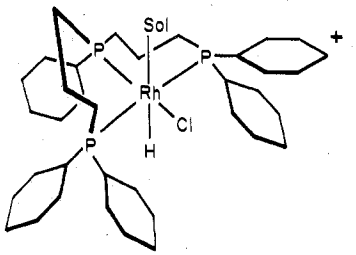


9
R = CH_3, C_2H_5
L = C_2H_5OH, CH_3CN, CO

Adducts of the C_2H_5–Rh complex are less stable than those of CH_3–Rh. This is consistent with steric interactions from the larger C_2H_5 group causing the phenyl groups on the terminal phosphorus atoms to protrude more into the hole trans to L in structure **7**.

It is significant that the rhodium–ethyl complex is thermally stable and does not readily undergo β elimination of ethylene, as do many other ethyl derivatives of transition metals. This stability may be promoted by the steric and structural requirements of the ligand, which do not allow low-energy rearrangements in these Rh(III) complexes to a structure with a coordination vacancy cis to the alkyl group. (That is, no structural transformation can occur that would permit the ethyl group to rearrange to a Rh–H linkage with elimination of ethylene.)

In contrast to the lability of the carbon monoxide and acetonitrile adducts of the alkyl–rhodium cations, the hydride adducts of CO and CH_3CN are very stable. This stability may result from the fact that the small hydride ligand can fit into the cavity, thus allowing rhodium to adopt the other diastereomer. This would give structure **10** in which larger ligands



10
Sol = C_2H_5OH, CH_3CN

(e.g., C_2H_5OH) can occupy the open "top" site in the complex.

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Registry No. RhCl(ttp), 34964-03-9; RhCl(ttp)CO, 50898-48-1; $[Rh(ttp)CO]PF_6$, 36480-96-3; $[Rh(ttp)(CH_3CN)]BF_4$, 58463-85-7; $[RhHCl(ttp)(C_2H_5OH)]BF_4$, 50589-19-0; $[RhCl(CH_3)(ttp)]FSO_3$, 50831-19-1; $[RhCl(C_2H_5)ttp]PF_6$, 58463-87-9; $[RhHCl(ttp)(CH_3CN)]BF_4$, 58463-89-1; $[RhHCl(ttp)(CO)]PF_6$, 58463-91-5;

$[RhDCl(ttp)(CO)]PF_6$, 58463-93-7; $[RhHBr(ttp)(CO)]PF_6$, 58485-80-6; $[RhDBr(ttp)(CO)]PF_6$, 58463-95-9; $[Rh(CH_3)Cl(ttp)(CO)]FSO_3$, 58463-97-1; $[Rh(CH_3)Cl(ttp)(MeCN)]FSO_3$, 58463-99-3; $[Rh(NO)Cl(ttp)]PF_6$, 50981-73-2.

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Synthesis of Macrocyclic Tetramines by Metal Ion Assisted Cyclization Reactions

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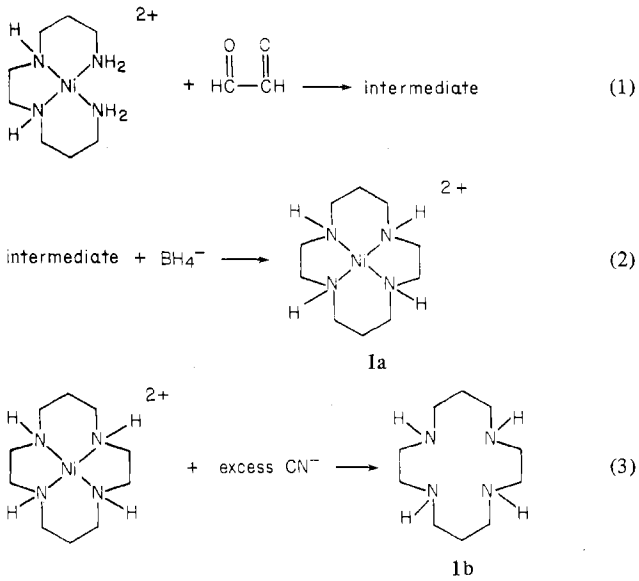
Eleven substituted 1,4,8,11-tetraazacyclotetradecanenickel(II) complexes were prepared by the nickel ion assisted cyclization of 1,5,8,12-tetraazadodecanes with glyoxal and reduction of the unsaturated complex obtained in the cyclization reaction. Sodium borohydride or hydrogen and Raney nickel catalyst were used for the reduction. With two exceptions, yields of the saturated complexes were in the range 50–75%. Macrocyclic tetramines were obtained by decomposition of the nickel complexes with cyanide ion. 1,5,9,15-Tetraazacyclopentadecane was prepared in 45% yield from 1,5,9,13-tetraazatridecane by this method.

Introduction

In earlier reports[1,2] we described the preparation of complex **1a** and the free base **1b** through the reactions described in Scheme I. Yields of **1a** and **1b** in excess of 65% are routine by this route and the entire reaction sequence can be conducted in an open beaker. This synthesis of **1b** is far superior to the earliest versions[3] and provides a more convenient route than the general cyclization procedure recently developed by Atkins and Richman.[4] With respect to metal-assisted cyclization reactions, in general, this example is one of the highest yielding presently known, and it is better than a similar reaction with 2,3-butanedione (biacetyl).[5]

Some of our more recent work on N-alkylation reactions of **1a** resulted in a need for authentic samples of certain partially methylated and benzylated forms of this complex.[6] Because of this we have explored the utility of reactions 1 and 2 as means of synthesizing substituted 14-membered macrocyclic ligand complexes. As this paper reports, this scheme is very useful for the synthesis of such complexes, as well as the free amines, since any substituted ligand can be removed from the metal through a reaction corresponding to (3). As a part of our efforts to define the general utility of cyclization reactions of tetradentate ligands with glyoxal we have also attempted to use tetramines that would produce 15- and 13-membered rings and to use metal ions other than nickel as the template for the reaction. A moderate-yield synthesis for a saturated 15-membered system is reported; however, we were unsuccessful in preparing 13-membered rings.

Scheme I



Experimental Section

Ligands. A complete listing of ligands used in this study and references to syntheses of those prepared previously is given in Chart I. Unless otherwise stated, other tetradentate ligands were prepared by cyanoethylation of the appropriate difunctional precursor followed by catalytic reduction of the crude dinitrile. Procedures used were similar to those of Israel et al.[7] and Dehayes and Busch[8] (50 psi of H_2 and Grace Chemical Grade 28 Raney nickel were used in all hydrogenations). The identity of each ligand was established by its NMR spectrum (chloroform solution). Unless otherwise indicated spectra were obtained at 100 MHz.

6,6-Dimethyl-1,5,8,12-tetraazadodecane, 3, was prepared from 20 g (0.23 mol) of 1,2-diamino-2-methylpropane (Aldrich) and 25 g (0.45 mol) of acrylonitrile; bp 105 °C (0.05 mm); yield 15 g, 28%. (This preparation was complicated by formation of other products.) NMR: τ 9.0 (s) 6 H; 8.7 (s) 6 H; 8.46 (m) 4 H; 7.2–7.6 (m) 10 H.

4,9-Dimethyl-1,5,8,12-tetraazadodecane, 4, was prepared from 15 g (0.25 mol) of ethylenediamine and 35 g (0.5 mol) of crotonitrile. The dinitrile was formed by heating for 2 days at 70–80 °C; bp 95 °C (0.05 mm); yield 17 g, 35%. NMR: τ 8.97 (d, J = 6 Hz) 6 H; 8.86 (s) 6 H; 8.52 (quartet of doublets) 4 H; 7.32 (m) 10 H.