occur because of precipitation of the insoluble polymer $H_2Ge_2O_3 \cdot xH_2O$ after the evolution of 3 mol of hydrogen per germanium atom and the hydrolytic cleavage of the Ge–C bond.

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Registry No. GeH_3CO_2K, 22054-96-2; $H_2Ge_2O_3$, 63937-01-9.

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Nuclear Magnetic Resonance Study of the Hexakis(trimethyl phosphate)gallium(III) and -indium(III) Complexes

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The complexes $\mathrm{Ga(TMPA)_6}^{3+}$ and $\mathrm{In(TMPA)_6}^{3+}$ were studied in deuterated nitromethane by ^1H, ^{31}P, and ^{71}Ga NMR and are compared to $\mathrm{Al(TMPA)_6}^{3+}$. The coupling constants J between the phosphorus and cation nuclei and the quadrupolar relaxation rates T_{1Q}^{-1} of the cation nuclei computed for ^{31}P and ^{71}Ga spectra are $J = 19.9 \pm 0.2$, 33 ± 6, and 48 ± 3 Hz and $T_{1Q}^{-1} = 10$, 280 ± 90, and $850 \pm 150\ \mathrm{s^{-1}}$ at 25 °C for ^{27}Al, ^{71}Ga, and ^{115}In nuclei, respectively. The sequence of T_{1Q}^{-1} values is shown to result from an increasing electric field gradient at the metallic nuclei. This effect is assumed to arise from a progressive release of the steric strain in the first solvation shell. The kinetics of the exchange of free and bound TMPA molecules are investigated. The substitution mechanism is shown to be S_N1 for $\mathrm{Ga(TMPA)_6}^{3+}$ and S_N2 for $\mathrm{In(TMPA)_6}^{3+}$, with the following kinetic parameters: $k(25\ °C) = 5.0\ \mathrm{s^{-1}}$ and $7.2\ \mathrm{M^{-1}\ s^{-1}}$; $\Delta H^{\ddagger} = 21.0$ and 8.5 kcal mol^{-1}; $\Delta S^{\ddagger} = 15.1$ and -26.1 cal K^{-1} mol^{-1}, respectively. This mechanistic change is again assigned to steric reasons.

Introduction

Nuclear magnetic resonance has been widely used to investigate a considerable number of labile solvation complexes of metallic cations. The most direct method uses systems in which the exchange of solvent molecules between the various species is sufficiently slow so that separate resonances are observed for the free and bound solvent.[2] In 1969, we proposed using ^{31}P spectroscopy of organophosphorus ligands, all containing the phosphoryl P=O solvating link.[3] Solvates of aluminum(III),[4] and more recently of beryllium(II),[5] with trialkyl phosphates, phosphonates, and phosphoramides revealed a variety of substitution mechanisms, either dissociative or associative, which were tentatively accounted for by a variable steric strain of the attached ligands. The present paper is devoted to the study of the complexes $[\mathrm{Ga(TMPA)_6}](\mathrm{ClO_4})_3$ (**1**) and $[\mathrm{In(TMPA)_6}](\mathrm{ClO_4})_3$ (**2**), dissolved in nitromethane containing variable amounts of free added trimethyl phosphate (TMPA). Very little is known about ligand exchange rates in complexes of gallium(III) and indium(III). The kinetics of ligand exchange is assumed to be dissociative for the system $\mathrm{Ga(H_2O)_6}^{3+}$ in DMF[7] and Ga(acac)$_3$ in DMF or THF,[8] on the sole basis of larger or smaller values of activation parameters, especially of the positive or negative sign of the activation entropy. Our experiments allow us to measure for both systems the kinetic order with respect to the concentration of the free ligand. Therefore they constitute a firmer basis for comparisons between cations.

Experimental Section

Materials. Trimethyl phosphate was obtained from Aldrich Chemicals and was checked for purity before use. The solvent was 99.3% deuterated nitromethane (C.E.A., France) stored over molecular sieves. Complexes **1** and **2** were prepared in the solid state from the hydrated salts $\mathrm{Ga(ClO_4)_3 \cdot 6H_2O}$ and $\mathrm{In(ClO_4)_3 \cdot 11H_2O}$ (Alfa Inorganics).[9,10] These complexes are extremely hygroscopic and they were prepared in a glove box under purified argon. All of these compounds gave satisfactory elemental analyses. Anal. Calcd for $[\mathrm{Ga(TMPA)_6}](\mathrm{ClO_4})_3$: Ga, 5.77; C, 17.89; H, 4.50; P, 15.38. Found: Ga, 5.89; C, 17.72; H, 4.53; P, 15.20. Calcd for $[\mathrm{In(TMPA)_6}](\mathrm{ClO_4})_3$: In, 9.16; C, 17.23; H, 4.34; P, 14.82. Found: In, 9.38; C, 17.34; H, 4.48; P, 14.74.

NMR Spectroscopy. Proton spectra were taken on a Jeol C60-HL spectrometer operating at 60 MHz with TMS as an internal reference. Phosphorus-31 Fourier transform spectroscopy was performed with a Bruker HX-90 apparatus at 36.43 MHz (128–8192 scans of 4K/8K points over a frequency range of 3–6 kHz). Gallium-71 spectra were obtained from the same spectrometer at 22.63 MHz, using a standard ^{13}C probe and by decreasing the magnetic field from 2.114 to 1.743 T. No field-frequency lock could be used under these conditions. Satisfactory results, however, were obtained by fast accumulation. ^{71}Ga chemical shifts were measured with respect to the resonance of $\mathrm{Ga(H_2O)_6}^{3+}$. This reference was a 0.2 M aqueous solution of $\mathrm{Ga(ClO_4)_3}$ in a 5 mm o.d. tube immersed in a 10 mm o.d. tube filled with the solution being studied.

Line-Shape Measurements. Two types of exchange were examined in this paper: ^1H exchange between two doublets; ^{31}P exchange within a multiplet of ten lines (cf. infra). The corresponding line shapes are computed according to a matrix formulation due to Anderson,[11] Kubo,[12] and Sack.[13] All calculations were performed using the program TRECH[5] on a Texas Instruments 980 A minicomputer equipped with a digital plotter, Hewlett-Packard 7210 A.

Results and Discussion

Structure of the Solvates and Quadrupolar Relaxation Rates. Two ^1H doublets are obtained from 0.1–0.2 M solutions of

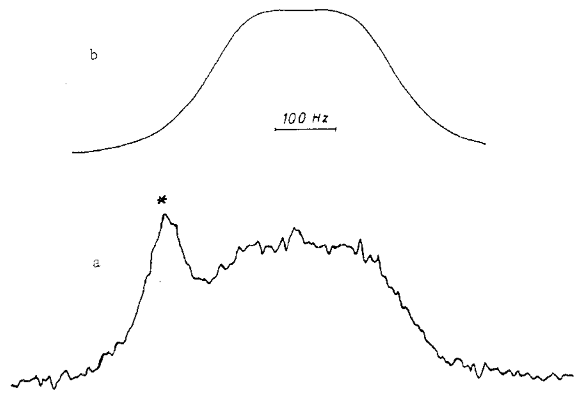

Figure 1. The ^{31}P proton decoupled spectrum of $In(TMPA)_6^{3+}$ in CD_3NO_2 at 25 °C: (a) experimental and (b) calculated curve. An asterisk indicates free TMPA.

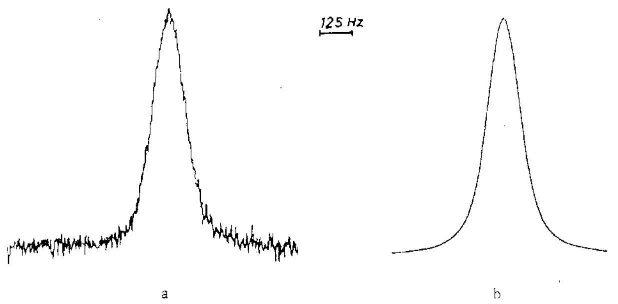

Figure 2. The ^{71}Ga spectrum of $Ga(TMPA)_6^{3+}$ in CD_3NO_2 at 25 °C: (a) experimental and (b) calculated curve.

Table I. Nuclear Properties and Relaxation Rates of ^{27}Al, ^{71}Ga, and ^{115}In (for notations, see the text)

	^{27}Al	^{71}Ga	^{115}In
I	$^5/_2$	$^3/_2$	$^9/_2$
$Q \times 10^{24}$, cm^2 [a]	0.149	0.112	1.16
f_N	7.1×10^{-3}	1.67×10^{-2}	9.97×10^{-2}
R_N	1	2.35	14.04
T_{1Q}^{-1}, s^{-1}	10	280 ± 90	850 ± 150
R_{exptl}	1	28	85

[a] Quoted from "The Handbook of Chemistry and Physics", 55th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1975, p E-69.

complexes **1** or **2** in nitromethane containing a known quantity of added free TMPA. The signals of bound TMPA molecules in both complexes appear at 0.33 ppm downfield from those of the free ligand.

From the ratio of areas of the two doublets, a mean solvation number of 6 ± 0.3 is computed for both solvates, thus suggesting an octahedral arrangement of TMPA ligands around the Ga^{3+} and In^{3+} cations, as in the aluminum complex $Al(TMPA)_6^{3+}$ (**3**). Gallium-71 NMR however does not yield a sharp heptet, as expected from the analogous aluminum-27 NMR spectrum[14] of complex **3**, but a broad singlet. Couplings between ^{71}Ga, or ^{115}In, and ^{31}P nuclei do nevertheless exist, since the ^{31}P lines are reduced to a broad singlet, clearly revealing an unresolved multiplet (Figure 1). Line broadening must be attributed in both cases to quadrupolar relaxation of the metallic nuclei. The broad band of ^{71}Ga (Figure 2) is consequently assumed to result from seven broad overlapping Lorentzian curves, shifted from each other by $^2J_{^{31}P-^{71}Ga}$, of the relative intensities 1, 6, 15, 20, 15, 6, 1, and with a line width of $2\omega = 1/\pi T_{1Q}$ (where T_{1Q} is the quadrupolar relaxation time of ^{71}Ga nuclei). The broad singlet observed by ^{31}P spectroscopy of solvate **2** was assumed to result in a similar manner from the coalescence of ten lines, each one corresponding to one of the ten magnetic states of the ^{115}In nucleus ($I = ^9/_2$) with the same probability. These ten sites are mutually exchanging at a rate $P_{ij}(1/T_{1Q})$, where P_{ij} are matrix elements giving the relative probability of a jump of an ^{115}In between magnetic states i and j, and therefore of a ^{31}P nucleus between the corresponding sites i and j. These probabilities may be computed according to Abragam[15] and used in the form of a 10 × 10 matrix to calculate the shape of the resonance lines. In both cases, the unknown parameters J and $1/T_{1Q}$ were adjusted by trial and error so as to obtain the best fit between experimental and theoretical curves. Results are reported in Table I, together with those previously obtained for the aluminum solvate **3**. The influence of field homogeneity and other than quadrupolar relaxation mechanisms on signal bandwidth is important for T_{1Q}^{-1} values in the case of the ^{27}Al nucleus since the resonance lines are sharp but negligible for the other signals observed which are considerably broader.

According to

$$\frac{1}{T_{1Q}} \propto \frac{(2I+3)}{I^2(2I-1)}\left[\frac{e^2Qq}{h}\right]^2 \tau_r \qquad \text{(I)}$$

the large variation of quadrupolar relaxation rates between solvates **1**, **2**, and **3** might be due to the following.[16]

(i) Different Nuclear Constants. The spin number I and the quadrupolar moment Q are combined in a function f_N

$$f_N = \frac{Q^2(2I+3)}{I^2(2I-1)}$$

This factor amounts to 0.0071 for the ^{27}Al nucleus. The relative influence of nuclear parameters is given by the ratio $R_N = f_N/0.0071$, reported in Table I. However the corresponding experimental ratios

$$R_{exptl} = (T_{1Q}^{-1})_M/(T_{1Q}^{-1})_{^{27}Al}$$

where M = ^{71}Ga or ^{115}In, are clearly much larger (Table I), thus showing a predominance of the other factors of eq I.

(ii) Various Rotational Correlation Times τ_r. According to Debye's theory, τ_r is proportional to the cube of the radius a of the complex, i.e., of the sum of the cationic radius (0.51–0.81 Å) and the diameter of one coordinated TMPA molecule (~5 Å). The relative increase of a by about 10% from the aluminum to the indium solvate can account for a 30% increase of the relaxation rate only, well below the experimental ratio R_{exptl}.

(iii) An Increase of the Electric Field Gradient Equation. Since (i) and (ii) constitute only a minor part of the observed increase, (iii) is apparently the predominant factor.

A nearly perfect cubic symmetry accounts for sharp lines of the aluminum(III) complexes, thus requiring that the P=O bond of the ligand should lie on a straight line with the cation Al^{3+}. This is somewhat unexpected since scarce crystallographic data concerning solid adducts such as $VOCl_2$, 2-(O=P(NMe$_2$)$_3$)[17] or $SbCl_5$, O=P(CH$_3$)$_3$[18] show that the angle α V–O–P or Sb–O–P is different from 180° (α = 154 and 145°, respectively). This suggests that the bulky organophosphorus ligands cause an enlargement of the angle α up to about 180° so as to minimize the repulsions between the peripheral methyl groups of the six ligands. This steric hindrance however may decrease as the ionic radius is increased (from Al^{3+} to Ga^{3+} and In^{3+}), therefore accounting for α values progressively smaller than 180°, and consequently for a progressive degradation of the cubic symmetry and an increase of the electric field gradient at the cation nucleus.

Chemical Shifts and Coupling Constants. Some interesting comparisons can be made on the basis of the data reported in Table II.

(a) The proton chemical shifts $\Delta\delta(^1H)$ between bulk and bound solvent molecules are almost independent of the cation.

Table II. ^{1}H and ^{31}P Chemical Shift Differences $\Delta\delta(^1\mathrm{H})$ and $\Delta\delta(^{31}\mathrm{P})$,[a] Chemical Shifts $\Delta\delta(\mathrm{M})$ of the Cation Nucleus M,[b] and Coupling Constants in the Complexes

	$\mathrm{Al(TMPA)_6}^{3+}$	$\mathrm{Ga(TMPA)_6}^{3+}$	$\mathrm{In(TMPA)_6}^{3+}$
$\Delta\delta(^1\mathrm{H})$, ppm	0.325 ± 0.01[c]	0.34 ± 0.01	0.33 ± 0.01
$^3J_{^{31}\mathrm{P-H}}$, Hz	11.2 ± 0.1[d]	11.3 ± 0.1	11.1 ± 0.1
$\Delta\delta(^{31}\mathrm{P})$, ppm	−7.3 ± 0.1[c]	−8.2 ± 0.2	−6.1 ± 0.5
$\Delta\delta(\mathrm{M})$, ppm	−20.5 ± 0.1[e]	−77.5 ± 1	
$^2J_{^{31}\mathrm{P-M}}$, Hz	19.9 ± 0.2[e]	33 ± 6	48 ± 3

[a] ppm, downfield from free TMPA as a reference. [b] ppm, downfield from $\mathrm{M(H_2O)_6}^{3+}$ as a reference. [c] M. R. Khaddar, Thèse de doctorat ès sciences, Nancy, France, 1974. [d] Reference 2d. [e] Reference 4.

As electrostatic interactions are supposed to be predominant according to Buckingham,[19] this result would again suggest a decrease of the angle α from the aluminum to the indium complex and an approach of the methoxy group toward the cation keeping the proton–cation distance nearly constant, in spite of an increasing ionic radius.

(b) The coupling constant $^3J_{^{31}\mathrm{P-H}}$ is larger for the bound than for the free ($J = 10.9 \pm 0.1$ Hz) ligand molecules.

(c) The coupling constant $^2J_{^{31}\mathrm{P-M}^{3+}}$ is largely increasing in the series: $\mathrm{M^{3+} = Al^{3+}, Ga^{3+}, In^{3+}}$. As the coupling constants are proportional to the nuclear magnetogyric ratios, a better comparison involves the so-called reduced coupling constants $K = 2\pi J/h\gamma_\mathrm{P}\gamma_\mathrm{M}$. Their relative values with respect to $K(^{27}\mathrm{Al})$ are 1, 1.42, and 2.87, respectively. This steady increase along a column of the periodic table could be a general trend, suggested by other scattered data from literature, for example: $^1J_{^{13}\mathrm{C-X}} = 35.7$,[20] −52,[21,22] and +250[23] Hz when X = ^{13}C, ^{29}Si, and ^{207}Pb in compounds of the kind $\mathrm{(CH_3)_4X}$, allowing the computation of relative K values of 1, 1.84, and 8.42. The change in this property of homologues could reflect, according to current theories of coupling constants, an increasing s character of the bond between the cation and the ligand and a decreasing average excitation energy of the complex.[24]

(d) The ^{31}P line of the TMPA molecules is shifted downfield in the complex. However, the chemical shift differences $\Delta\delta(^{31}\mathrm{P})$ show no simple law of variation. These results show an electron release from the phosphoryl bond to the cation, and, presumably, a back-donation from the oxygen doublets of the methoxy substituents to the phosphoryl bond, resulting in a variable electronic density at the phosphorus atom.

(e) The gallium-71 line in $\mathrm{Ga(TMPA)_6}^{3+}$ is 77.5 ppm upfield from the signal of $\mathrm{Ga(H_2O)_6}^{3+}$, confirming the much better electron donor properties of TMPA compared with $\mathrm{H_2O}$, in agreement with Gutmann's donor number scale[25] (DN = 23 and 18, respectively).

Kinetic Measurements. The coalescence of NMR spectra on increasing the temperature yields the rate constant k_t for the exchange of one ligand molecule A between the free ($\mathrm{A_f}$) and bound ($\mathrm{A_b}$) solvent sites:

$$\mathrm{A_b} \xrightarrow{k_\mathrm{t}} \mathrm{A_f}$$

Measurements are carried out by ^{1}H NMR in anhydrous nitromethane with variable concentrations of salt C_s and of free added ligand C_f at various temperatures (Tables III and IV). *The NMR site exchange around the gallium(III) cation is found to be independent of* C_f and is accordingly equal to the chemical rate constant k_e for a dissociative $\mathrm{S_N1}$ mechanism with a pentacoordinated intermediate:

$$\mathrm{Ga(TMPA)_6}^{3+} \xrightarrow{k_\mathrm{e}} \mathrm{Ga(TMPA)_5}^{3+} + \mathrm{TMPA}$$

$$\mathrm{Ga(TMPA)_5}^{3+} + \mathrm{TMPA^*(free)} \xrightarrow{\text{fast}} \mathrm{Ga(TMPA)_5(TMPA^*)}^{3+}$$

The values of the activation parameters obtained for the three sets of concentrations C_s, C_f agree quite satisfactorily. Their mean values are given in Table V.

Quite different results are obtained with $\mathrm{In(TMPA)_6}^{3+}$ for which the NMR transfer rate k_t is proportional to the concentration of free TMPA:

$$k_\mathrm{t} = k_\mathrm{e}[\mathrm{TMPA}]$$

This rate law suggests a bimolecular substitution reaction which is first order with respect to the complex as well as to the free ligand, thus corresponding to an $\mathrm{S_N2}$ mechanism in the terminology of Hughes–Ingold.[26] It means that the reaction passes via a heptacoordinated transition state. On the other hand, in the interpretation of Langford and Gray,[27] the reaction mechanism would be either associative (A) or an interchange mechanism (I).

Reaction mechanisms of this kind where a molecule previously being free (TMPA in our case) is fixed in the transition state are supposed to be accompanied, in the absence of specific ligand–solvent interactions, by an important decrease of entropy, i.e., $\Delta S^\ddagger < 0$.

Table III. Kinetic Parameters for Ligand Exchange of $\mathrm{Ga(TMPA)_6}^{3+}$ in $\mathrm{CD_3NO_2}$ by ^{1}H NMR

	k_e, s^{-1}, for T =					
Concn C_s and C_f (M)	291.7 K	297.2 K	302.2 K	308.2 K	312.7 K	319.2 K
0.0915 and 0.593		4.5 ± 0.2	8.0 ± 0.4	16 ± 1	28 ± 2	54 ± 3
0.209 and 0.609	2.2 ± 0.2	4.1 ± 0.2	8.2 ± 0.4	16 ± 1	29 ± 2	57 ± 5
0.198 and 1.153		4.4 ± 0.2	8.6 ± 0.4	16.5 ± 1	28 ± 2	52 ± 3

Table IV. Kinetic Parameters for Ligand Exchange of $\mathrm{In(TMPA)_6}^{3+}$ in $\mathrm{CD_3NO_2}$ by ^{1}H NMR

Concn	k_e, M^{-1} s^{-1}, for T =					
C_s and C_f (M)	283.7 K	288.2 K	297.7 K	309.2 K	318.2 K	330.2 K
0.102 and 0.609	3.0 ± 0.2		6.7 ± 0.3	10.2 ± 0.5	21.4 ± 1.0	
0.184 and 1.196	3.5 ± 0.2	4.6 ± 0.2		12.1 ± 0.5	20.1 ± 1.0	29.3 ± 1.0
0.198 and 0.709	3.4 ± 0.2	4.2 ± 0.2	7.1 ± 0.3	12.4 ± 0.5	20.4 ± 1.0	29.6 ± 1.0

Table V. Kinetic Parameters for Trimethyl Phosphate Exchange on Various Cations.

Cation	Coord no.	Ionic radius, Å	Substn mechanism	k_e(25 °C), s^{-1} or M^{-1} s^{-1}	$\Delta H^\ddagger$(25 °C), kcal mol^{-1}	$\Delta S^\ddagger$(25 °C), eu
$\mathrm{Be^{2+}}$[a]	4	0.35	$\mathrm{S_N2}$	1.5 ± 0.2	13.4 ± 0.4	−12.9 ± 1.3
$\mathrm{Al^{3+}}$[b]	6	0.51	$\mathrm{S_N1}$	0.38 ± 0.02	23.5 ± 1.5	18.2 ± 5
$\mathrm{Ga^{3+}}$[c]	6	0.62	$\mathrm{S_N1}$	5.0 ± 0.2	21.0 ± 0.8	15.1 ± 1.2
$\mathrm{In^{3+}}$[c]	6	0.81	$\mathrm{S_N2}$	7.2 ± 0.3	8.5 ± 0.5	−26.1 ± 1.4

[a] Reference 5. [b] Reference 4. [c] This work.

In our experiments we determined the order of the reaction as well as the activation parameters. The results confirm this hypothesis.

The conclusion agrees well with our previous observations[5] concerning a series of solvates of Be^{2+}, including the complex $Be(TMPA)_4^{2+}$.

In this series an increase of steric hindrance leads to a change of the reaction mechanism from S_N2 to S_N1, accompanied by an increase of the activation parameters.

Steric hindrance, i.e., repulsions between coordinated molecules of TMPA, might be one reason for the variety of mechanisms found for the trivalent non-transition-metal cations Al^{3+}, Ga^{3+}, and In^{3+}. The arrangement of six TMPA molecules around the comparatively small cations Al^{3+}, Ga^{3+} is so compact that a heptacoordinated transition state is impossible, thus promoting an S_N1 type substitution mechanism. It should be noticed that the exchange rate is faster with Ga^{3+} than with Al^{3+}, as can be expected from the increased ionic radius.[28] On the contrary, the relief of the steric strain around the much bigger In^{3+} cation permits a heptacoordinated transition state and therefore an S_N2 mechanism.

In conclusion, this mechanistic interpretation agrees with the previous one explaining the increased quadrupolar relaxation rate on passing from Al^{3+} to In^{3+} solvates. Their mutual agreement favors decisively the assumption of the steric strain of the ligands to be the major structural factor in these complexes.

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Registry No. 1, 63625-66-1; **2**, 63641-43-0; ^{27}Al, 7429-90-5; ^{71}Ga, 14391-03-8; ^{115}In, 14191-71-0; Ga^{3+}, 22537-33-3; In^{3+}, 22537-49-1.

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Interactions between Rhodium(I) Centers in Dimeric Complexes

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The electronic spectra of solutions of the dimeric complexes $[Rh(CO)Cl\{Ph_2P(CH_2)_nPPh_2\}]_2$, n = 1, 3, and 4, $Rh_2(CO)_4(O_2CCH_3)_2$, and $Rh_2(CO)_4Cl_2$ are compared with the spectra of $Rh(CO)Cl(PPh_3)_2$, $Rh(CO)_2(O_2C_5H_7)$, and $Rh(CO)_2Cl_2^-$. In dimeric complexes in which the planar Rh(I) units are held in close, face to face proximity there is a pronounced shift of the metal-to-ligand charge-transfer absorption to low energies. The products obtained from reaction of $[Rh(CO)Cl\{Ph_2P(CH_2)_nPPh_2\}]_2$, n = 1, 3, or 4, with iodine, tetracyanoethylene (TCNE), and sulfur dioxide are compared with the products obtained from $Rh(CO)Cl(PPh_3)_2$. When the two Rh centers are held closely together Rh(II) products with direct Rh–Rh bonds can form; $[Rh(CO)ClI\{Ph_2PCH_2PPh_2\}]_2$ is an example. In some reactions the Rh–P bonds break and re-form to create higher polymeric products; $[Rh(CO)_2ClI_2\{Ph_2P(CH_2)_nPPh_2\}]_x$, n = 3 or 4, and $[Rh(CO)Cl(TCNE)\{Ph_2P(CH_2)_4PPh_4\}]_x$ are examples. In other reactions a substrate attacks only one Rh center while the other Rh center remains four-coordinate; examples of such products are $(TCNE)Rh(CO)Cl\{Ph_2P(CH_2)_3PPh_2\}_2Rh(CO)Cl$ and $O_2SRh(CO)Cl\{Ph_2P(CH_2)_nPPh_2\}_2Rh(CO)Cl$ (n = 3 or 4).

Introduction

Previous studies from this laboratory have been concerned with the interaction between several metal centers in a single molecule.[1,2] In the present study examples of complexes containing two planar Rh(I) centers which are linked by a variety of bridging ligands are considered. By altering these bridging groups both the distance between the rhodium centers and the relative orientation of the two coordination planes can