consistent with the fast self-exchange rate for the low-spin Fe(sar)$^{3+/2+}$ system.[16] For [Fe(tacn)$_2$]$^{3+/2+}$ (low spin) bond lengths of 1.99 (Fe^{3+}) and 2.03 Å (Fe^{2+}) have been reported.[24b]

Ni(sar)$^{3+/2+}$. Only two rates of reduction of Ni(sar)$^{3+}$ and one rate of oxidation of Ni(sar)$^{2+}$ could be measured; the reaction between [Ni(tacn)$_2$]$^{3+}$ and Ni(sar)$^{2+}$ is, as for ruthenium, a good approximation to the self-exchange reaction. Structural information is only available for Ni(sar)$^{2+}$ (octahedral, $\langle d \rangle = 2.11$ Å)[22] at present, but for [Ni(tacn)$_2$]$^{3+}$ a tetragonally distorted coordination with $d_{ax} = 2.11$ Å and $d_{eq} = 1.97$ Å has been reported.[25] The value of 1.7×10^3 M^{-1} s^{-1} thus seems to be a reasonable deduction.

Fe(H$_2$O)$_6$$^{3+/2+}$. It was not our intention to assess the electron self-exchange rate constant for this redox couple; in fact in the first refinement the directly measured value of 4 M^{-1} s^{-1} [26] (corrected to $\mu = 0.10$ M, pH 1) was used as a calibrant value but it soon became evident that reactions 17–19 did not fit the consistent picture that emerged from reactions 1–16.[27] We therefore decided to let k_{11}(Fe(H$_2$O)$_6$$^{3+/2+}$) float. Our final value for this "effective" ferric–ferrous electron self-exchange is close to the value ($\sim 10^{-3}$ M^{-1} s^{-1}) that has been derived from a large number of cross-reactions between Fe(H$_2$O)$_6$$^{3+/2+}$ and mostly inert metal complexes.[28] In a recent comparison of the Ru(NH$_3$)$_6$$^{3+/2+}$, Ru(H$_2$O)$_6$$^{3+/2+}$, and Fe(H$_2$O)$_6$$^{3+/2+}$ redox couples using structural and vibrational data,[29] it was noted that the measured Fe(H$_2$O)$_6$$^{3+/2+}$ self-exchange rate was relatively *too fast*. The "effective" self-exchange rate constant deduced here, however, would be very much in keeping with those of the two ruthenium couples. These results and arguments militate against large nonadiabatic effects and in favor of an inner-sphere pathway for the directly measured Fe(H$_2$O)$_6$$^{3+/2+}$ self-exchange reaction.

Conclusions

The analysis of a series of electron-transfer reactions between similar complexes of ruthenium, manganese, iron, and nickel in terms of the Marcus cross-relation have led to estimates of the self-exchange rate constants for the M(sar)$^{3+/2+}$ redox couples (M = Ru, Mn, Fe, Ni) that are satisfactorily interpreted in terms of known structural and kinetic data. No discrepancies were detected that indicated nonadiabatic behavior. Further insight into this problem requires direct measurements of the self-exchange rates themselves and of the temperature dependence of those rates. The classical theories of Marcus and Hush appear to hold very well for the reactions of encapsulated complexes studied so far. It is worth noting also that the largest deviations encountered involve reaction partners of labile metal–aqua systems. Such anomalies have been observed many times and specifically in ref 7, 20, and 28.

Acknowledgment. The authors are grateful to the Microanalytical Service Unit of ANU for analyses.

Registry No. Ru(sar)$^{2+}$, 101482-29-5; Mn(sar)$^{2+}$, 110433-26-6; Ni(sar)$^{2+}$, 110433-27-7; Fe(sar)$^{2+}$, 110433-28-8; (NH$_3$)$_5$Ru(py)$^{3+}$, 33291-25-7; (NH$_3$)$_5$Ru(nic)$^{3+}$, 50762-76-0; (NH$_3$)$_5$Ru(isn)$^{3+}$, 46372-32-1; Ru(tacn)$_2$$^{3+}$, 110433-29-9; Ni(tacn)$_2$$^{3+}$, 86709-81-1; Ru(NH$_3$)$_6$$^{2+}$, 19052-44-9; Co(azacapten)$^{2+}$, 86161-69-5; Fe^{3+}, 20074-52-6.

Supplementary Material Available: A listing of concentrations, first-order rate constants, and experimental conditions for all reactions (Table S) (5 pages). Ordering information is given on any current masthead page.

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(27) In this fit, k_{11}(M(sar)$^{3+/2+}$) (M = Ru, Mn) values were ~40% lower than in Table II, k_{11}(Fe(sar)$^{3+/2+}$) was unchanged, and k_{11}(Ni(sar)$^{3+/2+}$ shifted to 350 M^{-1} s^{-1}. For reactions 17–19 the discrepancy between k_{exptl} and k_{calcd} was ~1 order of magnitude.

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Syntheses and Phosphorus-31 NMR Studies of Five-Coordinate Platinum(II) Complexes of Tris(2-(diphenylphosphino)ethyl)phosphine and Monodentate Phosphorus Ligands

Peter Brüggeller

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Recently, five-coordinate complexes of Co(I) and Ni(II) containing tripodal tetradentate ligands and neutral P(OR)$_3$ or PR$_3$ ligands in the fifth positions have been prepared.[1,2] All of the complexes possess trigonal-bipyramidal coordination geometries, in which the tripodal ligand occupies one apical and three equatorial positions. The monodentate ligand occupies the second axial position. It has been shown that complexes of Pt(II) of tris(2-(diphenylphosphino)ethyl)phosphine, PP$_3$, have the same stereochemical properties.[3-5] Here the corresponding monophosphito and monophosphino derivatives of the types [Pt(PP$_3$)(P(OR)$_3$)]Cl$_2$ (R = Me = **1a**, R = Et = **1b**) and [Pt(PP$_3$)(PEt$_3$)]Cl$_2$ (**2**) are described, which are the first platinum(II) complexes containing five phosphorus ligands.

Experimental Section

Reagents and Chemicals. Reagent grade chemicals were used as received unless stated otherwise. Tris(2-(diphenylphosphino)ethyl)phosphine (PP$_3$) was purchased from Strem Chemical Co. Trimethyl phosphite was obtained from Fluka; triethyl phosphite and triethylphosphine were obtained from Merck-Schuchardt. Absolute methanol and absolute ethanol were also obtained from Merck-Schuchardt. Other organic solvents were of purum quality and received from Fluka. Et$_2$O was purified by conventional methods. K$_2$PtCl$_4$ was prepared from platinum metal.

Instrumentation. Fourier-mode, broad-band proton-decoupled ^{31}P NMR spectra were obtained by use of a Bruker WP-80 spectrometer. Positive chemical shifts are downfield from 85% H$_3$PO$_4$ used as external standard. Elemental analyses were obtained with a Heraeus EA 425 elemental analyzer.

Synthesis of Platinum(II) Complexes. A Schlenk apparatus and oxygen-free, dry Ar were used in the syntheses of all complexes. Solvents were degassed by several freeze–thaw–pump cycles prior to use.

[PtCl(PP$_3$)]Cl. The complex was prepared according to ref 6, however in a slightly different manner. To K$_2$PtCl$_4$ in water a solution of an equimolar amount of PP$_3$ in CH$_2$Cl$_2$ was added. Then EtOH was added under stirring until a clear orange solution was obtained. The solution was stirred for 12 h and [PtCl(PP$_3$)]Cl was isolated as described.

1a and 1b. [PtCl(PP$_3$)]Cl (0.187 g, 0.200 mmol) was dissolved in absolute MeOH or EtOH (10 mL). The solution was stirred at 273 K and an excess of P(OMe)$_3$ or P(OEt)$_3$ was added dropwise via a syringe, respectively. Immediate decoloring of the solution occurred. The solution was allowed to warm up to room temperature, and Et$_2$O was added until a white solid precipitated. After the mixtures were cooled to 243 K for several hours **1a** and **1b** were collected, washed with Et$_2$O, and dried in vacuo. **1a**: yield 0.091 g (43%); mp = 242–245 °C dec. Anal. Calcd for C$_{45}$H$_{51}$Cl$_2$O$_3$P$_5$Pt: C, 50.95; H, 4.85. Found: C, 50.8; H, 5.0. **1b**: yield 0.143 g (65%); mp = 167–169 °C dec. Anal. Calcd for C$_{48}$H$_{57}$Cl$_2$O$_3$P$_5$Pt: C, 52.3; H, 5.2. Found: C, 52.0; H, 5.4.

2. [PtCl(PP$_3$)]Cl (0.187 g, 0.200 mmol) was dissolved in absolute MeOH (10 mL). The solution was stirred at 273 K, and an excess of PEt$_3$ was added dropwise via a syringe. The color of the solution turned slightly yellowish. Et$_2$O was added to the cold solution and a yellowish solid precipitated. **2** was collected, washed with Et$_2$O, and dried under a stream of Ar: yield 0.116 g (55%); mp = 138–141 °C dec. Anal. Calcd for C$_{48}$H$_{57}$Cl$_2$P$_5$Pt: C, 54.65; H, 5.45. Found: C, 54.3; H, 5.4.

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Table I. Phosphorus-31 NMR Data for **1a**, **1b**, and **2**[a]

compd	$\delta(P_1)$	$\delta(P_2)$	$\delta(P_3)$[b]	$^1J(Pt,P_1)$	$^1J(Pt,P_2)$	$^1J(Pt,P_3)$	$^2J(P_1,P_3)$	$^2J(P_2,P_3)$
1a	30.0	132.0	74.7	2425	1618	3459	41	494
1b	26.0	126.4	71.0	2455	1579	3428	42	486
2	25.1	117.4	−14.1	2247	1674	2026	24	274

[a] *J* in Hz. Spectra were run at 300 K; those for **1a** and **2** were measured in absolute MeOH, that for **1b** was run in absolute EtOH, and an internal deuterium lock was used. [b] P_1 is the designation for the PPh_2 groups and P_2 is the *apical* P of PP_3; P_3 is the phosphorus atom of the monodentate ligand.

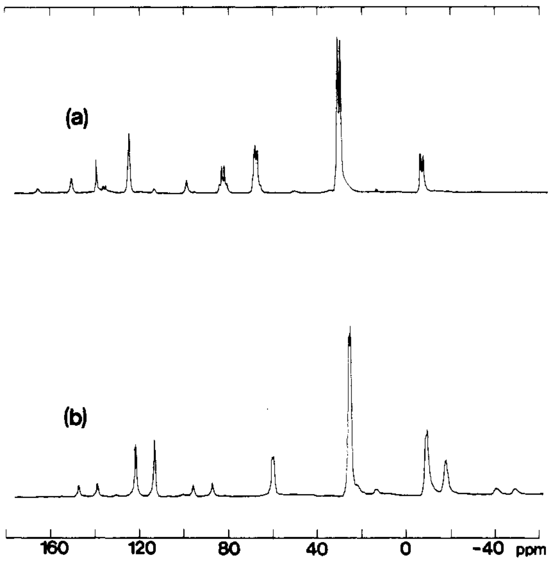

Figure 1. 32.4-MHz $^{31}P\{^1H\}$ NMR spectra of (a) a MeOH solution of **1a** and (b) an EtOH solution of **2** at 300 K.

Results and Discussion

The new complexes were prepared by replacement of the chloride in $[PtCl(PP_3)]^+$ by an appropriate monophosphorus ligand. At 273 K the reaction is fast and completed within a few minutes. However, only monophosphorus ligands with small alkyl groups like methyl or ethyl react that way, whereas ligands with aryl groups like $P(Ph)_3$ or $P(OPh)_3$ do not react even at high temperatures. This is certainly a consequence of the six phenyl groups present in the equatorial positions of PP_3 in trigonal-bipyramidal complexes, which prevent the approach of a sterically hindered fifth ligand.[7] Figure 1 shows the $^{31}P\{^1H\}$ NMR spectra of **1a** and **2**. The spectral pattern of **1a** (Figure 1a) is consistent with an AMX_3 spin system and a trigonal-bipyramidal structure of **1a** in solution. All signals contain the corresponding ^{195}Pt (natural abundance 33.8%) satellites, indicating that five phosphorus ligands are bonded to platinum(II). The resonances of the apical phosphorus of PP_3 and the phosphito ligand, respectively, are second order, where the high-field part of the phosphito resonance is hidden by the low-field satellite of the equatorial PP_3 resonance. The phosphito satellites can be seen at about 136 ppm and at about 15 ppm (only the central two lines of the satellite quartets are well resolved in the drawing, and both corresponding second satellites are hidden by stronger peaks). The ^{31}P NMR spectrum of **1b** is very similar to that of **1a** (see Table I).

Figure 1b shows the first-order ^{31}P spectrum of **2**. It is consistent with an AX_3Y spin system and a trigonal-bipyramidal structure of **2** in solution. As before all signals contain ^{195}Pt satellites indicating that five phosphino ligands are bonded to platinum(II). The monophosphino resonance is partly hidden by the high-field satellite of the equatorial PP_3 resonance and broad arising from an exchange process of bonded and nonbonded monophosphine in solution, which is fast on the NMR time scale at 300 K.

The ^{31}P NMR parameters of **1a**, **1b**, and **2** are summarized in Table I. $^2J(P_1,P_2) + {}^3J(P_1,P_2)$ is zero in all three cases. The ^{31}P signals of P_1, P_2, and P_3 are doublets, doublets, and doublets of quartets, respectively (the P_3 resonance of **2** is split at about 243 K). The ^{31}P resonances of the monophosphorus ligands ($\delta(P_3)$) are shifted towards higher field, when compared with the corresponding values (86.1 ppm for $P(OMe)_3$ and 1.8 ppm for PEt_3) in square-planar complexes of the type $[Pt(ttp)L]X_2$, where ttp is bis(3-(diphenylphosphino)propyl)phenylphosphine, L is the monophosphorus ligand, and X^- is an anion.[8] The same is true for a comparison with the recently published value of $\delta(PEt_3)$ of 6.7 in the square-planar complex $[Pt(triphos)(PEt_3)](BF_4)_2$, where triphos is bis(2-(diphenylphosphino)ethyl)phenylphosphine.[9] The $^1J(^{195}Pt,P_3)$ values of **1a** and **1b** are considerably smaller than the 4189-Hz value found for $[Pt(ttp)(P(OMe)_3)](AsF_6)_2$. $^1J(^{195}Pt,P_3)$ of **2** is also smaller than the values of 2161 Hz for $[Pt(ttp)(PEt_3)]X_2$ and 2317 Hz for $[Pt(triphos)(PEt_3)](BF_4)_2$. The $^2J(P_1,P_3)$ and $^2J(P_2,P_3)$ parameters of **1a**, **1b**, and **2** are very similar to the corresponding values in the cited square-planar complexes, being typically larger for the phosphito complexes since increasing electronegativity of the substituent on phosphorus increases the s character of the phosphorus lone pair.

Table II. Coordination Chemical Shifts and One-Bond Coupling Constants for $[PtL(PP_3)]X$ and $[Pt(PP_3)L]X_2$ Complexes

	coord chem shift[a]		coupling const, Hz	
compd	$\Delta(P_1)$	$\Delta(P_2)$	$^1J(Pt,P_1)$	$^1J(Pt,P_2)$
$[PtCl(PP_3)]Cl$	40.0	138.3	2573	2503
$[Pt(SnCl_3)(PP_3)]BPh_4$	41.1	158.0	2534	1827[b]
$[PtH(PP_3)]Cl$	50.6	155.7	2975	1467[c]
$[Pt(NCS)(PP_3)]BF_4$	44.2	128.2	2521	2534[d]
$[Pt(SCN)(PP_3)]BF_4$	41.2	147.4	2514	2301[d]
1a	44.1	150.9	2425	1618
1b	40.1	145.3	2455	1579
2	39.2	136.3	2247	1674

[a] The coordination chemical shift, Δ, is defined as δ(P(coordinated)) − δ(P(free ligand));[10] $\delta(P_1) = -14.1$ and $\delta(P_2) = -18.9$ for the free ligand PP_3. [b] From ref 4. [c] From ref 5. [d] The complex was prepared by a procedure analogous to that used for the synthesis of $[Ni(NCS)(Ptas)]AsF_6$ in ref 1; a nearly 2:1 S-bonded: N-bonded mixture of the two linkage isomers was obtained.

In Table II the coordination chemical shifts and one-bond coupling constants of PP_3 in a series of new and recently published trigonal-bipyramidal platinum(II) complexes are given. The coordination chemical shift $\Delta(P_1)$ is only slightly influenced by a variation of the ligand L. $\Delta(P_2)$ is in the range 130–160 ppm, which is not as large as the range of $\Delta(P_2)$ values reported for corresponding Co(I) and Ni(II) trigonal-bipyramidal complexes also containing the tetradentate ligand PP_3.[2] The range of $^1J(^{195}Pt,P_1)$ values is similar to that found for the cis coupling constants in the square-planar [PtL(ttp)] X and $[Pt(ttp)L]X_2$ complexes, whereas the trans coupling constants in these complexes reach from about 1500 to 3100 Hz, which is larger than the range of $^1J(^{195}Pt,P_2)$ values in Table II. Both $\Delta(P_2)$ and $^1J(^{195}Pt,P_2)$ parameters have been used to determine the trans influence order of various ligands L in the cited trigonal-bipyramidal and square-planar complexes. A high $\Delta(P_2)$ value corresponds to a high trans influence since the trans influence is determined by the ability of the monodentate ligand L to deshield the apical

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phosphorus atom.[1] A high $^1J(^{195}Pt,P_2)$ value corresponds to a small trans influence, which is represented in that case by the platinum 6s character of the Pt–L bond increasing at the expense of the trans Pt–P bond that is in competition for the same s ± d hybrid orbital.[8] The two trans influence orders obtained from the $\Delta(P_2)$ and $^1J(^{195}Pt,P_2)$ parameters, respectively, are $SnCl_3^- \sim H^- > P(OMe)_3 \sim SCN^- \sim P(OEt)_3 > Cl^- \sim PEt_3 > NCS^-$ and $H^- > P(OEt)_3 \sim P(OMe)_3 \sim PEt_3 > SnCl_3^- > SCN^- > Cl^- \sim NCS^-$.

At first glance the two series look different. However, both series have common trends that are in agreement with previously published trans influence series.[1,2,8] The position of the hydride in front of the two series is characteristic for the strong Pt–H interaction found in platinum(II) hydrides.[8] Typically phosphites exert a stronger trans influence than phosphines do.[1,8] The same is true for S-bonded versus N-bonded thiocyanate, and the position of chloride and N-bonded species at the end of the series is characteristic, too.

Acknowledgment. This work was supported by the Land Vorarlberg, Austria.

Registry No. **1a**, 110795-97-6; **1b**, 110795-98-7; **2**, 110795-99-8; $[PtCl(PP_3)]Cl$, 104845-13-8; $[Pt(NCS)(PP_3)]BF_4$, 110796-01-5; $[Pt(SCN)(PP_3)]BF_4$, 110796-03-7; K_2PtCl_4, 10025-99-7.

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Reactions of $Rh_2(O_2CCH_3)_2(C_6H_4PPh_2)_2 \cdot 2CH_3COOH$ with Chlorotrimethylsilane in the Presence of Monodentate Phosphines To Give $[Rh_2Cl_2(C_6H_4PPh_2)_2(PPh_3)_2]$ and $[Rh_2Cl_2(C_6H_4PPh_2)_2(PMe_3)_2]$

F. Albert Cotton,* Kim R. Dunbar, and Cassandra T. Eagle

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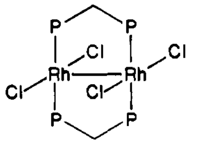
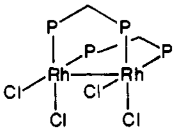
One of our recent interests in this laboratory has been to extend the chemistry of the Rh_2^{4+} unit in new directions.[1] We have found that a powerful method for doing this is to employ Me_3SiCl as a reagent for replacing $MeCO_2^-$ ligands by Cl^- ligands, while simultaneously providing phosphine ligands to complete the coordination sphere. When $Rh_2(O_2CMe)_4$ was reacted with 2 equiv of Me_3SiCl and dppm ($Ph_2PCH_2PPh_2$) or $Rh_2(O_2CMe)_2(C_6H_4PPh_2)_2$ with 2 Me_3SiCl and dmpm ($Me_2PCH_2PMe_2$), products with four bridging ligands and two axial Cl ligands, viz., $Rh_2(O_2CMe)_2(dppm)_2Cl_2$[1b] and $Rh_2(C_6H_4PPh_2)_2(dmpm)_2Cl_2$,[1] were isolated and characterized. These results are chemically and structurally quite reasonable and were not considered surprising.

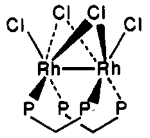
After the preparation of $Rh_2(O_2CMe)_2(dppm)_2Cl_2$ had been accomplished by using 2 equiv of Me_3SiCl to replace two $MeCO_2^-$ ligands from $Rh_2(O_2CMe)_4$, a similar reaction employing 4 equiv was carried out with the goal of obtaining a product of type I, or possibly II. A product of this stoichiometry was in fact obtained, but its structure was different from either of those anticipated, namely of type III.[1b] The explanation presented for this is that a structure of type III permits all of the metal–ligand bonds present in I or II to be retained, including the Rh–Rh single bond, while also allowing the formation of two more Rh–Cl bonds when two Cl atoms become bridging instead of terminal.



I



II



III

To pursue this type of chemistry further, we have now examined some similar reactions, but with the use of monophosphines rather than the potentially bridging diphosphinomethanes. The results of these studies are reported here.

Experimental Section

The starting materials, $Rh_2(O_2CCH_3)_4$[2] and $Rh_2(O_2CCH_3)_2C_6H_4PPh_2 \cdot 2CH_3COOH$,[3] were prepared according to published procedures. Chlorotrimethylsilane (Me_3SiCl) was obtained from Aldrich Chemical Co. and used without further purification. Triphenylphosphine (PPh_3) and trimethylphosphine (PMe_3) were purchased from Strem Chemicals. PPh_3 was recrystallized from ethanol; PMe_3 was used as received. All solvents were dried and freshly distilled under dinitrogen prior to use.

Complexes **1** and **2** were prepared under an argon atmosphere by the same general route. $Rh_2(O_2CCH_3)_2(C_6H_4PPh_2)_2 \cdot 2CH_3COOH$ (0.150 g, 0.155 mmol) was dissolved in 15 mL of THF. The solution was warmed to 60 °C and Me_3SiCl (80 μL, 4 equiv) was injected into the reaction vessel. The reaction mixture was then treated with 2.1 equiv of the appropriate phosphine. The solutions were refluxed for 30 min, cooled to room temperature, and then concentrated under vacuum to ca. 5 mL. The precipitated products were washed with three 5-mL portions of Et_2O and dried under vacuum. Complex **1** was recrystallized from $CHCl_3$ solution by introducing an upper layer of Et_2O. A higher yield of crystalline material was formed when a trace quantity of PPh_3 was added to the $CHCl_3$ solution (yield 0.168 g, 82%). IR (Nujol mull, CsI): 1585 (w), 1575 (w), 1560 (m), 1540 (w), 1483 (s), 1435 (s), 1415 (m), 1320 (w), 1240 (m), 1190 (w), 1160 (w), 1120 (w), 1090 (s), 1075 (w), 1030 (w), 1005 (w), 750 (s), 730 (s), 720 (w), 700 (s), 625 (w), 550 (s), 500 (m), 490 (m), 465 (m), 420 (w) cm^{-1}. Complex **2** was recrystallized from a mixture of THF and toluene that was carefully layered with a mixture of Et_2O and hexane. In contrast to the case for **1**, **2** crystallized more readily in the absence of excess monodentate ligand (yield 0.112 g, 76%). IR (Nujol mull, CsI): 1582 (w), 1565 (m), 1542 (m), 1435 (m), 1410 (m), 1300 (m), 1285 (m), 1235 (w), 1185 (w), 1170 (w), 1115 (w), 1095 (m), 1090 (m), 1075 (w), 1030 (w), 1015 (m), 1005 (w), 900 (s), 845 (m), 745 (s), 735 (s), 715 (s), 675 (w), 650 (w), 545 (s), 530 (w), 505 (s), 485 (m), 445 (w), 430 (w) cm^{-1}.

X-ray Crystallography. The structures of **1** and **2** were determined by general procedures that have been fully described elsewhere.[4] Data reductions were carried out by standard methods using well-established computational procedures.[5] The crystal parameters and basic information pertaining to data collection and structure refinement are summarized in Table I. Tables II and III list the positional parameters for structures **1** and **2**, respectively. Selected bond distances and angles of **1** and **2** are found in Tables IV and V, respectively. Complete tables of bond distances and angles as well as anisotropic thermal parameters and structure factors are available as supplementary material.

$Rh_2Cl_2(C_6H_4PPh_2)_2(PPh_3)_2$ (1). A bright red prism of **1** was mounted on a glass fiber. A rotation photograph indicated that the crystal diffracted well. An automatic search routine was used to locate 25 high-angle reflections. The reduced cell dimensions indicated that the crystal belonged to the monoclinic crystal system, which was verified by axial photography. Systematic absences led to the choice of two possible space groups, *C*2/*c* and *Cc*. The former was found to be correct on the basis of successful refinement. The ω–2θ scan motion was used to gather 5582 possible data points in the range $4 < 2\theta < 50°$. Three standard reflections measured following every 150 scans did not significantly change in intensity over the 22 h of beam exposure, and no decay correction was applied. Azimuthal scans of six reflections with Eulerian angle χ near

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