Table XXI. Activation Parameters for the Isomerization of *trans*-$RuCl_2(CO)(phosphine)_3$ Complexes

phosphine	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$, cal/(mol K)	$\Delta G_{373}^\ddagger$, kcal/mol	$\Delta V^\ddagger$, mL/mol
Ph_2MeP[a]	28.5 ± 0.5	+14 ± 2	23.8 ± 0.5	+15 ± 2
$PhMe_2P$[b]	31.2 ± 0.5	+15 ± 2	26.1 ± 0.5	+16 ± 2
Me_3P[c]	31.0 ± 0.5	+8 ± 2	28.0 ± 0.5	

[a] In chloroform. [b] In 1,1,2,2-tetrachloroethane. [c] In chlorobenzene.

corresponds to a phosphine concentration of less than 1.5×10^{-5} M.

The relative *rates* of each pathway can now be compared by using this estimate of the free ligand concentration. Multiplying the second-order rate constants k_{-1} and k_2 by the amount of free phosphine allows a direct comparison to the first-order rate constant, k_3. These values are given in Table XX (supplementary material) relative to k_3.

For each complex the indirect pathway of isomerization (k_3) dominates over the direct path (k_2), and the extent of this difference is greater for the Ph_2MeP complex. Presumably the larger size of this ligand acts to hinder its attack on the five-coordinate species, 5C, as it must "squeeze" between the two phosphine ligands in trans positions. Instead, rearrangement occurs to the 5C* species, where the approach of the incoming ligand is much less sterically hindered. For the $PhMe_2P$ complex, the phosphine is smaller and is a better base. The direct attack upon the 5C species is not as unfavorble, although the major path is still that of rearrangement to the 5C* species.

Activation parameters for the isomerization of the *trans*-$RuCl_2(CO)P_3$ complexes without added ligand were obtained either by following the rearrangement by visible spectroscopy or by observing the CO region of the infrared spectrum. For P = Ph_2MeP values of k_{obs} were found from the slope of the first-order plots of ln [trans] vs time. For P = $PhMe_2P$ and Me_3P, k_{obs} was estimated by taking the tangent to the ln [trans] vs time curve at 1 half-life. Values of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ were obtained from Eyring plots and $\Delta V^\ddagger$ from the pressure dependence of k_{obs} (Table XXI). In each case the large positive values of $\Delta S^\ddagger$ and $\Delta V^\ddagger$ suggest that the isomerization proceeds by a dissociative mechanism. The calculated values of $\Delta G^\ddagger$ reflect the increasing difficulty of isomerization as the phosphine becomes smaller and a better ligand.

Conclusions

Both the *trans*-$RuCl_2(CO)P_3$ and *ttt*-$RuCl_2(CO)_2P_2$ complexes isomerize by ligand dissociation according to the same general mechanism. Initial loss of a phosphine ligand trans to CO occurs for the monocarbonyl complexes. The relative rates of this dissociation probably reflect a combination of steric and electronic effects. The larger, less basic ligand (Ph_2MeP) is only weakly bound to the metal and is easily lost. As the phosphine becomes smaller and more basic ($PhMe_2P$, Me_3P), the Ru–P bond becomes stronger and ligand dissociation occurs more slowly.

For the dicarbonyl complexes isomerization is initiated by the loss of a CO ligand trans to CO. Here again, the rate of isomerization decreses with a decrease in the steric bulk of the neighboring phosphine. An increase in the value of $\Delta S^\ddagger$ for the rearrangement as the phosphine becomes larger suggests the importance of steric effects on the rate of complex isomerization. However, electronic effects are also important.

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Supplementary Material Available: Tables of kinetic measurements (Table II), crystal and refinement data (Table IIIS), final positional parameters (Tables IVS and VS), bond lengths and angles, and visible absorption maxima (Table XIV), a description of rate measurement techniques, tables of isomerization rates (Tables XV and XVII–XX), figures showing the percent isomer composition during isomerization of *ttt*-$(Ph_2MeP)_2Ru(CO)_2Cl_2$ (Figure 4), the change in the carbonyl region of the IR spectra during isomerization of *ttt*-$(Bzl_3P)_2Ru(CO)_2Cl_2$ (Figure 5) and *trans*-$(Ph_2MeP)_3Ru(CO)Cl_2$ (Figure 9), and the experimental and calculated dependence of k_{obs} on added $PhMe_2P$ (Figure 12), and listings of thermal parameters (17 pages); listings of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

Notes

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Solid-Phase Thermal Isomerization of $(R_3P)_2Ru(CO)_2Cl_2$ and $(R_3P)_3Ru(CO)Cl_2$ Complexes

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and John H. Nelson*

Received September 23, 1987

In the course of the Characterization[1] of a series of $(R_3P)_2Ru(CO)_2Cl_2$ (R_3P = Bzl_3P, Ph_3P, Ph_2MeP, $PhMe_2P$, Me_3P) and $(R_3P)_3Ru(CO)Cl_2$ (R_3P = Ph_2MeP, $PhMe_2P$, Me_3P) complexes, we observed that some of these complexes appeared to undergo geometrical isomerization in the solid state. Solid-state rearrangements are well-known for L_2PtX_2 complexes[2-7] (L = neutral donor ligand, X = halide) and for cobalt(III) and chromium(III) complexes,[8] but there is very little knowledge of such solid-phase reactions of six-coordinate ruthenium(II) complexes. Therefore, an investigation of this series of *trans*-$(R_3P)_3Ru(CO)Cl_2$ and *ttt*-$(R_3P)_2Ru(CO)_2Cl_2$ complexes was undertaken using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). It was of special interest to determine if a relationship exists between the size of the phosphine and the thermal stability of the complex. The rate of geometric isomerization of these complexes in solution increases with an increase in the size of the phosphine.

Experimental Section

The complexes were prepared, characterized, and analyzed as previously described.[1] Differential scanning calorimetry and thermogravimetric analyses were obtained on 2–10-mg samples under flowing nitrogen at a constant heating rate of 20 °C/min with a Perkin-Elmer Model 2000 DSC and TGA instrument coupled with a Model 3500

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Table I. Results of Differential Scanning Calorimetry and Thermal Gravimetric Analysis for *trans*-$(R_3P)_3Ru(CO)Cl_2$ and *ttt*-$(R_3P)_2Ru(CO)_2Cl_2$ Complexes

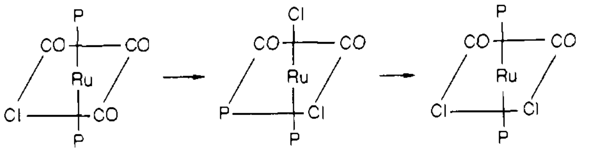
compd. no.	complexes	mass loss at 290 °C, %	mp, °C (isomer)	isomerizn temp, °C	ΔH_f,[a] kcal/mol	ΔH_i,[a] kcal/mol
1	*trans*-$RuCl_2(CO)(Ph_2MeP)_3$	23	238 (cis)	175–220[b]	+6.0 (cis)	−3.6
2	*trans*-$RuCl_2(CO)(PhMe_2P)_3$	4	163 (trans) 176 (cis)	167–181	+8.0[c] (trans)	−4.9
3	*trans*-$RuCl_2(CO)(Me_3P)_3$	12	168 (trans)	169–180	+1.7[c] (trans)	−11.4
4	*ttt*-$RuCl_2(CO)_2(Ph_2MeP)_2$	5	155 (*ttt*) 223 (*cct*)	163–174	+8.5 (*cct*)	−8.8
5	*ttt*-$RuCl_2(CO)_2(PhMe_2P)_2$	5	143 (*ttt*)	157–170	+2.4 (*ttt*)	−1.7
6	*ttt*-$RuCl_2(CO)_2(Me_3P)_2$	52	153 (*ttt*) 198 (*cct*)	163–178	+1.4 (*ttt*)	−3.5
7	*ttt*-$RuCl_2(CO)_2(Bzl_3P)_2$	8	227 (*cct*)	147–165	+14.2 (*cct*)	−8.0
8	*ccc*-$RuCl_2(CO)_2(Ph_2MeP)_2$	8	220 (*cct*)	138–165	+4.1 (*cct*)[d]	−11.5

[a] ΔH is believed accurate to ±1 kcal/mol. [b] 130–155 °C at 10 °C/min scan rate. [c] Value probably too low due to incomplete melting. [d] For pure *cct* isomer, ΔH_f = 13.6 kcal/mol.

computer data station. $RuCl_2(CO)(Ph_2MeP)_3$ was also examined at 10 °C/min with a Perkin-Elmer Model DSC-1B differential scanning calorimeter. DSC calibration was accomplished using indium metal.

Results and Discussion

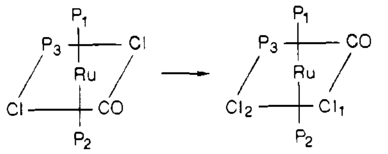
The complexes studied and the results of the thermal analyses are given in Table I. In solution, the *ttt*-$(R_3P)_2Ru(CO)_2Cl_2$ complexes isomerize to the *ccc* isomers, which in turn isomerize to the *cct* isomers as shown in reaction 1. Also, the *trans*-$(R_3P)_3Ru(CO)Cl_2$ complexes isomerize in solution to the cis isomers as shown in reaction 2. These isomerizations are dissociative processes with rates that decrease with increasing phosphine basicity and decreasing phosphine steric bulk.



(1)

ttt, D_{2h} (I) *ccc*, C_1 (III) *cct*, C_{2v} (II)

yellow pale yellow colorless



(2)

trans, C_{2v} *cis*, C_s

yellow colorless to pale yellow

The TGA curves of the title complexes indicate that only *ttt*-$(Me_3P)_2Ru(CO)_2Cl_2$ exhibits a significant mass loss (24%) at temperatures below 260 °C. This mass loss increases to 52% of the original mass and then levels off at 290 °C.

Because there is essentially no mass loss for any of these complexes below 230 °C, any endotherm or exotherm observed by DSC below this temperature is likely to be due to a phase change or isomerization. Whereas melting is an endothermic process, isomerizations such as those in reactions 1 and 2 are expected to be exothermic because the geometric transformation is from a less stable, kinetic isomer to a more stable, thermodynamically preferred product. Visual observations of the changes that occur upon heating these complexes help establish whether isomerization or melting is associated with a particular event on the DSC curve.

Figure 1 shows the DSC curve for complex **1** (Table I), *trans*-$RuCl_2(CO)(Ph_2MeP)_3$. When heated at 20 °C/min, this substance undergoes an exothermic transition, beginning at about 150 °C. At 10 °C/min, the onset of this transition is about 130 °C, making it better separated from other events in the DSC curve. This exotherm is accompanied by a color change from orange to light yellow, the latter color corresponding to that of the cis isomer. No mass loss accompanied the exotherm, and continued heating causes the sample to melt at the melting point of the cis isomer (238 °C) with the same heat of fusion (6.0 kcal/mol) as that determined for the cis isomer. That the exotherm corresponds to the trans-to-cis isomerization of the complex was verified by cooling the sample after completion of the exotherm and obtaining its ^{31}P NMR spectrum in $CDCl_3$. The NMR spectrum indicated complete conversion to the cis isomer.[1]

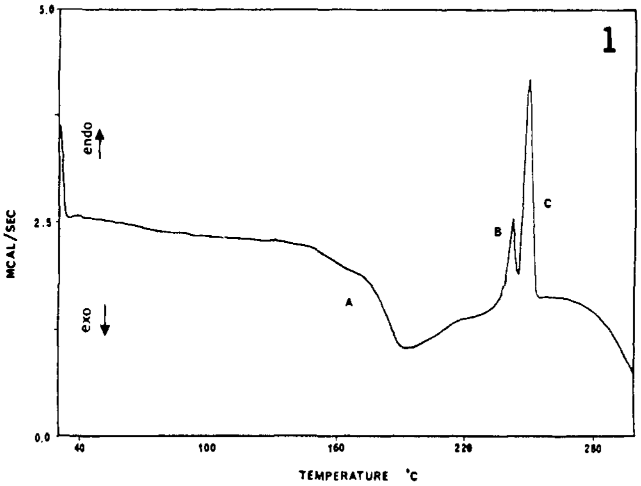


Figure 1. Differential scanning calorimetry curve for *trans*-$RuCl_2(CO)(Ph_2MeP)_3$. The heating rate is 20 °C/min under nitrogen. The number in the upper right corner refers to the compound number given in Table I.

X-ray analysis of these complexes[1] indicates that this trans-to-cis isomerization requires only a slight increase in the volume of the unit cell. The unit cell of the cis isomer is only 0.7% larger than that of the trans isomer (3707 vs 3780 Å^3). Furthermore, no fracturing of the crystal was apparent upon heating the trans isomer (presumably because of the small difference in the crystal size of the isomers). These observations suggest that the reorganization energy due to lattice expansion has a negligible effect on the energy change of this process. The heat of isomerization, ΔH_i, obtained from the DSC curve is 3.6 kcal/mol.

Although Figure 1 shows two endotherms (B and C) for the melting of *cis*-$RuCl_2(CO)(Ph_2MeP)_3$ at 20 °C/min, only a single endotherm was obtained at 10 °C/min. The two endotherms observed at the faster scan rate could be due to incomplete isomerization followed by melting of both the cis and trans isomers.

The DSC curve for complex **2** is given in Figure 2. While an endotherm (A) is the first major feature in this case, this does not correspond to the complete melting of the trans isomer. The trans isomer only just begins to melt when isomerization occurs, as shown by the exotherm B. This is followed almost immediately by another endotherm (C) at about 180 °C. This is undoubtedly the melting of the cis isomer, since the cis complex prepared by other methods melts at 177–180 °C.

The DSC curve of complex **3** is similar to that for complex **2**. An initial endotherm indicates that partial melting of the trans complex occurs before isomerization begins. However, in this case no endotherm is present for the melting of the cis complex. This is in spite of the melting of the cis isomer observed visually.

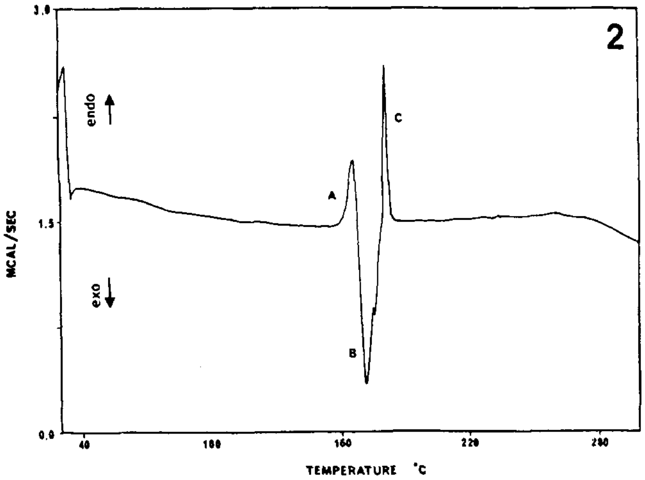


Figure 2. Differential scanning calorimetry curve for *trans*-$RuCl_2(CO)(PhMe_2P)_3$. The heating rate is 20 °C/min under nitrogen. The number in the upper right corner refers to the compound number given in Table I.

Like the trans complexes **2** and **3**, the *ttt* complex **4** undergoes a slight amount of melting before isomerization to the *cct* isomer. The isomerized product melts at 223 °C, about 5 °C lower than that of the pure *cct* isomer (228–230 °C).

The DSC curve for complex **5** shows a much more pronounced endotherm than the previous complexes. Not surprisingly, visual observations show that the *ttt* complex melts entirely before isomerization. No endotherm is seen for the melting of the *cct* isomer, because the *cct* isomer actually melts at a lower temperature than the *ttt* isomer (134–135 vs 143 °C).

For complex **6**, *ttt*-$RuCl_2(CO)_2(Me_3P)_2$, complete melting of the *ttt* isomer occurs before isomerization. However, two exotherms are evident in the DSC curve. The first appears to be the result of the *ttt* to *cct* isomerization in the liquid state. Because the melting point of the *cct* isomer is 196–198 °C, the following exotherm is probably due to the fusion *cct* (liquid) → *cct* (solid). A sharp endotherm observed at 200 °C corresponds to the melting of the *cct* isomer.

The isomerization of complex **7** also occurs in the solid state. An exotherm at 158 °C is well separated from the melting of the *cct* isomer at 228 °C. This correlates well with what was observed for the melting point of the *cct* isomer (227–229 °C).

The final complex investigated was *ccc*-$RuCl_2(CO)_2(Ph_2MeP)_2$ (**8**). An exotherm that commences at 138 °C in its DSC curve seems to indicate a solid-state isomerization. When the complex is viewed in a melting point capillary, a color change to dark orange occurred in this temperature region. Considerable compression of the sample occurred, but the sample appeared to remain solid. At 220 °C the orange product melted, which is close to the melting point of the *cct* isomer (228 °C).

The visual observations and DSC results described above seem to indicate that complexes **1**, **4**, **7**, and **8** isomerize in the solid state. For **2** and **3** isomerization commenced in the solid state but melting ensued before isomerization was complete. That the cis (or *cct*) isomer is the product in all cases was verified by ^{31}P NMR spectroscopy.[1] Solid samples of **2–6** and **8** were placed in 10-mm NMR tubes and heated in an oven at 190 °C for 55 min. After the samples were cooled to room temperature, $CDCl_3$ was added to each tube and the NMR spectrum recorded. Each spectrum showed the cis or *cct* isomer to account for greater than 90% of the phosphorus in the sample.

Measurements of the areas under the endotherms and exotherms of the DSC curves allow one to estimate the enthalpy of fusion, ΔH_f, and the enthalpy of isomerization, ΔH_i. The values for the heat of fusion for the trans isomers **2** and **3** are likely to be too low due to the incomplete melting of these complexes. The value for the heat of isomerization for complex **6** may be too high because of the overlapping fusion exotherm.

Certain conclusions can be drawn from the DSC results collected in Table I. First, the temperature at which isomerization occurs is largely independent of the number or identity of the phosphines. All of the complexes appear to isomerize between 140 and 180 °C in the solid state. The enthalpy of isomerization also shows no clear trend based on the phosphine ligand, although for the $(R_3P)_3Ru(CO)Cl_2$ complexes the isomerization enthalpy decreases with increasing steric bulk of the phosphine. Heats of fusion are generally lower for the cis complexes (or *cct* complexes) than for the trans complexes. This is in agreement with what has been found by Kukushkin et al., for a series of platinum complexes[9] of the type *cis*- and *trans*-$PtCl_2(PhNH_2)$(triethyl phosphate).

Although we have made no attempt to investigate the kinetics of these solid-state isomerizations, a qualitative ordering of the relative rates can be obtained by comparing the shapes of the isomerization exotherms for DSC curves obtained at the same heating rate. The rates of isomerization appear to decrease in the order **2** > **4**, **5** > **6** > **3** > **1** > **8**. This ordering is not the same as found for these same complexes in solution.

As an additional consideration, the solid-state isomerizations of these complexes may be useful as a means of preparing the thermodynamically preferred isomers. The ^{31}P NMR data have confirmed that the cis or *cct* isomers are formed in very good yield by this method. In solution thermal isomerization[1] of *ttt*-$(R_3P)_2Ru(CO)_2Cl_2$ may lead to mixtures of *ccc*-$(R_3P)_2Ru(CO)_2Cl_2$, *cct*-$(R_3P)_2Ru(CO)_2Cl_2$, $[(R_3P)_2Ru(CO)Cl_2]_2$, and *trans*-$(R_3P)_3Ru(CO)Cl_2$.

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Supplementary Material Available: Differential scanning calorimetry curves for compounds **3–8** (6 pages). Ordering information is given on any current masthead page.

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Synthesis and Structure of a Heterometallic Cluster with a Novel Layered Structure: $[W(CO)_5SnClFe(CO)_4]_2[Na_2((C_2H_5)_2O)_4(C_4H_8O_2)]$

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Recently, considerable attention has been focused on transition-metal complexes with "naked" main-group ligands.[1,2] Continuing our own work on main group–transition metal interactions[3,4] which has added examples of one- and two-coordinate thallium[5,6] to these, we attempted to create an example of a substituent-free complex derived from Sn(II). Thus, we examined the reaction between $(OC)_5WSnCl_2$(tetrahydrofuran)[4] and $Fe(CO)_4^{-2}$ expecting to form the hypothetical "$(OC)_5WSn{=}Fe$-

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