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Ligand Dissociation in Octahedral Ruthenium(II) Complexes Containing both Unidentate and Bidentate Phosphine Ligands

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The syntheses and molecular structures of the new complexes $RuCl_2(dppm)(PMe_2Ph)_2$, $RuCl_2(dppm)(PMePh_2)_2$, $RuCl_2(dppe)(PMe_2Ph)_2$, and $RuCl_2(dppe)(PMePh_2)_2$ are described (dppm = $Ph_2PCH_2PPh_2$, dppe = $Ph_2PCH_2CH_2PPh_2$). A number of synthetic methods can be used to obtain these complexes including reaction of (a) the chloride-bridged dinuclear complex $[L_3Ru(\mu\text{-}Cl)_3RuL_3]Cl$ with dppm (L = PMe_2Ph) in the absence of solvent, (b) $RuCl_3{\cdot}xH_2O$ with dppm and PMe_2Ph or $PMePh_2$ in methanol, and (c) $RuCl_2(PPh_3)_3$ with dppm and PMe_2Ph or $PMePh_2$ or with dppe and $PMePh_2$ in toluene. By ^{31}P NMR (25 °C), the most favorable geometric orientation appears to be that with the chloride ligands trans to one another. With dppm, this arrangement is quite stable and no evidence of ligand dissociation is observed. However, the complexes containing dppe show a great propensity to dissociate the unidentate phosphine ligands to form chloro-bridged dinuclear complexes.

Introduction

The chemistry of ruthenium phosphine[1] and diphosphine complexes[2] is quite extensive and has been studied in detail by many workers.[3] Complexes containing both unidentate phosphine and bidentate diphosphine ligands, however, have been relatively unexplored. Recent accounts of such complexes of ruthenium[4,5] prompt us now to report the syntheses and molecular structures of several new mixed-phosphine chlororuthenium complexes.

We have found that the mixed complexes $RuCl_2(p\text{-}p)L_2$ (p-p = dppm = bis(diphenylphosphino)methane and dppe = bis(diphenylphosphino)ethane; L = $PMePh_2$, PMe_2Ph) can be obtained by a variety of methods. The ease of synthesis and isolation and the propensity toward isomerization and phosphine dissociation differ considerably for the complexes obtained. In some cases we have used ^{31}P NMR to identify components of mixtures where isolation proved difficult or impractical.

Experimental Section

Syntheses and manipulations of solutions were performed under an atmosphere of prepurified nitrogen with standard Schlenk-line techniques or in a nitrogen filled glovebox. Solvents were of reagent grade and were degassed under vacuum using three freeze-thaw cycles prior to use. Phosphines were obtained from Strem Chemical, Inc. and were used without further purification as was $RuCl_2(PPh_3)_3$. $RuCl_3{\cdot}xH_2O$ (43.34% Ru) was used as obtained from Alfa Products, Inc.—a distributor for Johnson Matthey Chemicals, Ltd. The dinuclear complexes $[L_3Ru(\mu\text{-}Cl)_3RuL_3]Cl$ (I) (L = PMe_2Ph, $PMePh_2$) were synthesized according to literature methods.[6]

$[RuCl_2(PMe_2Ph)_2(dppm)]$ (IIa). Method A. The dinuclear complex $[(Me_2PhP)_3Ru(\mu\text{-}Cl)_3Ru(PMe_2Ph)_3]Cl$ (0.50 g; 0.85 mequiv of Ru) and dppm (0.33 g, 0.86 mmol) were heated together under N_2 in the absence of solvent. The mixture became liquid at ca. 115 °C, and vapors were observed at ca. 170 °C. Heating was continued until the temperature reached 200 °C. The dark red-orange liquid was cooled to room temperature, during which time it partially solidified. This solid was broken up with a spatula and washed with petroleum ether to remove free phosphine. The orange solid was collected by filtration and recrystallized from $CHCl_3/MeOH$ to give 0.42 g (59% yield) of orange crystals (mp 252-3 °C). Anal. Calcd for $C_{41}H_{44}Cl_2P_4Ru$: C, 59.14; H, 5.33. Found: C, 58.82; H, 5.34.

Method B. A solution of 0.50 g of $RuCl_3{\cdot}xH_2O$ (2.1 mequiv of Ru) in 20 mL of MeOH was carefully treated with 0.59 g (4.3 mmol) of PMe_2Ph. To this mixture was added 0.82 g (2.1 mmol) of dppm. A considerable amount of precipitate was evident after about 30 min, and the mixture was stirred overnight. The green-brown solid was collected by filtration and dried in vacuo (ca. 1.1 g). Thin-layer chromatography showed that this mixture was largely complex IIa, although small amounts of *trans*-$[RuCl_2(dppm)_2]$ and an unidentified compound were also seen. Repeated recrystallization from $CHCl_3/MeOH$, however, gave only a low yield of IIa (ca 30%).

Method C. A suspension of $RuCl_2(PPh_3)_3$ (1.0 g, 1.0 mmol) in 20 mL of toluene was treated with 0.29 g of PMe_2Ph (2.1 mmol). A green solution resulted. To this was added a solution of 0.40 g of dppm (1.0 mmol) in 10 mL of toluene. This caused the green solution to turn orange. The mixture was filtered to remove a small amount of a green solid and the orange solution was reduced in volume under vacuum. Heptane was added to induce precipitation of an orange powder. Analysis by ^{31}P NMR showed the presence of IIa along with significant amounts of free triphenylphosphine and *trans*-$[RuCl_2(dppm)_2]$.[4] No other resonances were seen, ruling out the presence of other isomers of IIa.

$[RuCl_2(PMe_2Ph)_2(dppe)]$ (IIc). The procedure described above in method C was utilized to synthesize this complex. In this case, the product was isolated by treating the toluene solution with Et_2O and not heptane. After some difficulty, a 50% yield of an orange-yellow precipitate that proved to be spectroscopically pure by ^{31}P NMR was obtained from this solvent system. One molecule of crystallization of Et_2O was seen by proton NMR. Anal. Calcd for $C_{42}H_{46}Cl_2P_4Ru{\cdot}Et_2O$: C, 60.00; H, 6.13. Found: C, 60.94; H, 5.95.

Attempts to recrystallize this compound from $CHCl_3/MeOH/Et_2O$ or toluene/$MeOH/Et_2O$ led to isolation of isomeric mixtures. On occasion, we were able to isolate a spectroscopically pure yellow solid, which we assign to the *cis*-dichloro isomer IVc; however, we were unable to reliably reproduce this synthesis.

$[RuCl_2(PMePh_2)(dppm)]$ (IIb). Method B above was used to obtain this complex in ca. 60% yield. The crude material was recrystallized twice from $CHCl_3/MeOH$; however, ^{31}P NMR still showed some *trans*-$[RuCl_2(dppm)_2]$ as an impurity. Anal. Calcd for $C_{51}H_{48}P_4Cl_2Ru$: C, 64.02; H, 5.07%. Found: C, 63.12; H, 4.99.

$[RuCl_2(PMePh_2)(dppe)]$ (IId). When method C was used to synthesize this complex, a yellow powder, which proved to be a complex mixture, was obtained. The ^{31}P NMR spectrum indicated that the *trans*-chloro isomer (IId) was among the products (see Figure 3).

^{31}P NMR Data Accumulation. All of the ^{31}P NMR experiments were performed by using a superconducting magnet with a field strength of 4.7 T via an IBM SY-200 FTNMR spectrometer equipped with a 10-mm VSP probe (manufactured by Bruker Instruments, Inc.) tuned to 81.015 MHz. All of the samples were analyzed in a 10-mm (o.d.) tube, with deuterated chloroform used as the solvent and as a source for field frequency lock. The chemical shift scale was referenced to phosphoric acid (δ_P = 0.0) contained in a capillary tube in a separate experiment, with resonances downfield of phosphoric acid being positive. Gated broadband (noise modulated) ^1H decoupling was applied in order to avoid NOE effects. A pulse angle of 45° with a relaxation delay of 3 s inserted between each pulse was used.

NMR Spectral Simulation. A computer program provided by Bruker Instruments, Inc., known as parameter adjustment in NMR by iteration calculation (PANIC) was used for spectral simulation on an Aspect 2000 computer. PANIC is the microcomputer version of LAOCOON type programs. Initial estimated chemical shifts and coupling constants are

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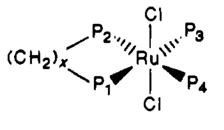
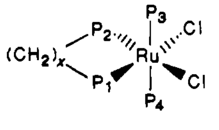
Table I. ^{31}P NMR Data for $RuCl_2(p\text{-}p)L_2$ Complexes



II



IV

			chem. shift, ppm		coupling constants, Hz			
isomer	x	P_3 & P_4	P_1 & P_2	P_3 & P_4	P_1,P_2	P_1,P_3 & P_2,P_4	P_1,P_4 & P_2,P_3	P_3,P_4
IIa	1	$PPhMe_2$	-16.5	2.2	-31.2	-307.0	38.4	-37.4
IIb	1	PPh_2Me	-18.7	4.7	-28.7	-305.1	36.4	-35.8
IIc	2	$PPhMe_2$	36.7	-4.1	-35.1	-297.4	33.2	-17.5
IId	2	PPh_2Me	36.6	-3.4	-33.3	-292.5	32.8	-16.5
IV	2	$PPhMe_2$	51.0	-7.2		30	30	

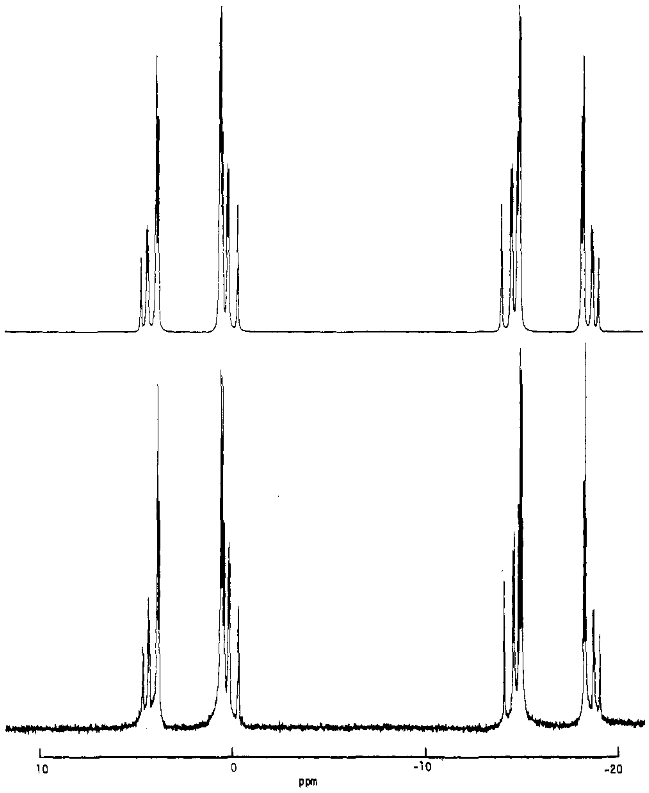
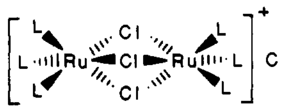


Figure 1. Experimental and calculated (top) ^{31}P spectra of $RuCl_2(dppm)(PMe_2Ph)_2$ (IIa).

incorporated to calculate a spectrum, which is compared to the experimental one. An iteration process is then performed until the differences between the two are minimized.

Results and Discussion

The reactions of complexes of type I with chelating phosphines have been known for quite some time. Chatt and Hayter used



Ia: L = PMe_2Ph
b: L = $PMePh_2$

this method to prepare bis(diphosphine)dichlororuthenium complexes in good yield.[6a] The reactions occur at 150–200 °C in the absence of solvent and with a Ru:chelate ratio of 1:2. We have found for the case of L = PMe_2Ph and diphosphine = dppm, a stable mixed-phosphine complex is obtained when a deficiency of diphosphine is used (Ru:dppm = 1:1). The product shows a complex, non-first-order ^{31}P NMR spectrum, which is consistent with an AA′BB′ spin system (see Figure 1). The NMR data, elemental analysis, and nonconductivity of this complex in nitrobenzene allow the unambiguous assignment as the *trans*-dichloro isomer IIa.

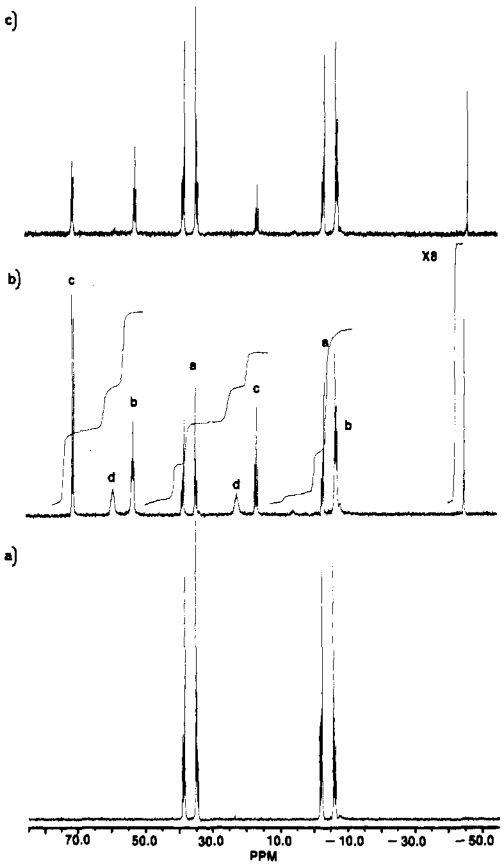
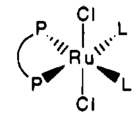


Figure 2. ^{31}P NMR spectra of $RuCl_2(dppe)(PMe_2Ph)_2$ (IIc): (a) spectrum run in $CDCl_3$; (b) spectrum showing the effect of adding MeOH, elapsed time ca. 45 min; ($CDCl_3$:MeOH ~ 1:1). (c) spectrum after adding *t*-BuOMe (see text).



IIa: L = PMe_2Ph; p⌒p = dppm
b: L = $PMePh_2$; p⌒p = dppm
c: L = PMe_2Ph; p⌒p = dppe
d: L = $PMePh_2$; p⌒p = dppe

Curiously, this is the only case where a mixed phosphine complex could be cleanly obtained in this way. Reaction of Ia with dppe (Ru:dppe = 1:1) gave only low yields of *trans*-$RuCl_2(dppe)_2$, as did the $PMePh_2$ analogue Ib. Likewise, reaction of Ib with dppm gave only low yields of *cis*-$RuCl_2(dppm)_2$. (The cis isomer for this complex is known to be the thermodynamically most stable.[7])

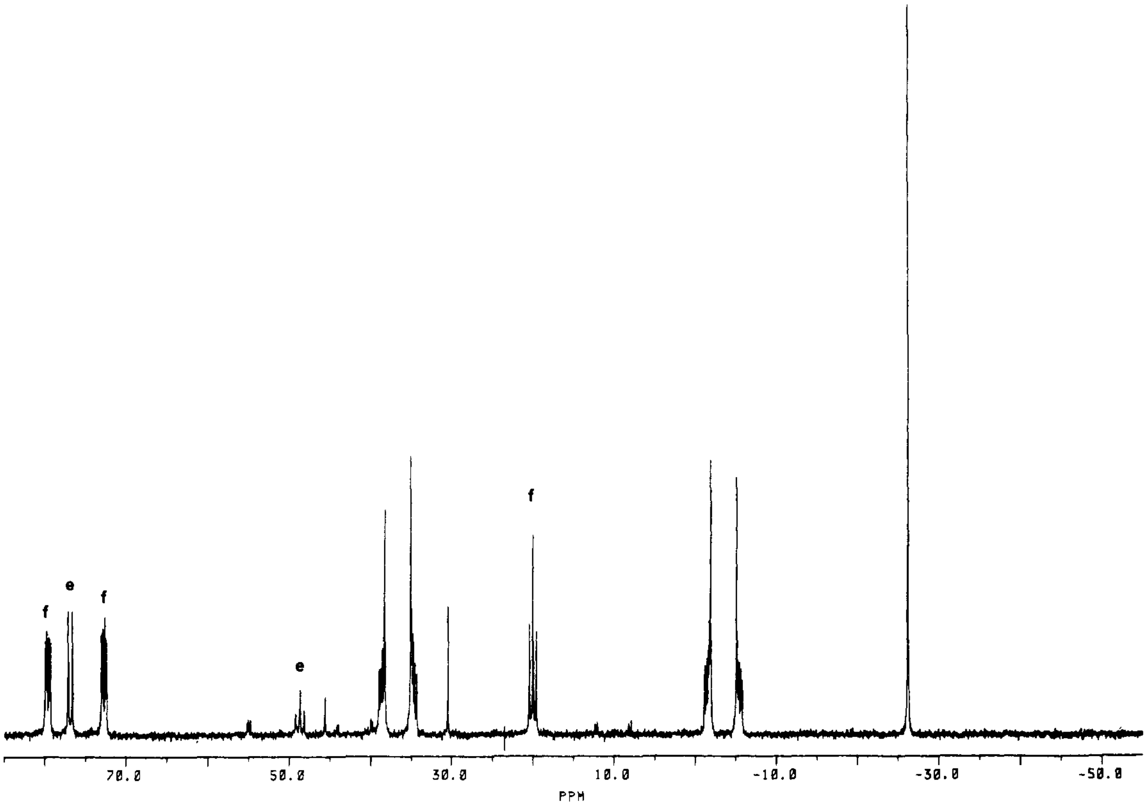
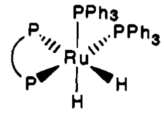


Figure 3. ^{31}P NMR spectrum of product obtained in attempted preparation of $RuCl_2(dppe)(PMePh_2)_2$ (IId). See Experimental Section and text for details.

Fortunately, the analogues of IIa can be readily synthesized by alternate methods. One method involves the simple combination of "$RuCl_3 \cdot xH_2O$", phosphine, and chelate in the proper proportions in methanol at room temperature. Alternatively, $RuCl_2(PPh_3)_3$ may be used as a starting material with toluene as the solvent (see Experimental Section).

The ^{31}P NMR spectral parameters of the new complexes are presented in Table I. Assignments are based on a detailed analysis of IIa. Two-dimensional NMR spectroscopy[8] definitively established that the methylene proton resonance of the dppm ligand at 4.75 ppm is coupled to the ^{31}P resonance centered at ~ -16.5 ppm. Likewise, the PMe_2Ph proton signal at 1.4 ppm is associated with the ^{31}P resonance centered at 2.2 ppm. Assignments for the remaining complexes are based on the application of ring contribution parameters. Thus, upon going from dppm in IIa to dppe in IIc, the chelate ^{31}P resonance shifts approximately 53 ppm downfield. The resonance assignable to PMe_2Ph shifts only about 6 ppm upfield. The large downfield shift is consistent with what one would expect in going from a four-membered ring to a five-membered ring.[9]

In all cases where we were able to isolate a pure and stable product, the complexes showed the ^{31}P spectral pattern indicative of the *trans*-dichloro isomer II. This contrasts with the work of Poilblanc and co-workers who obtained the all-cis isomer of $RuH_2(PPh_3)_2(dppm)$ (III) from $RuH_4(PPh_3)_4$ and dppm in toluene.[5]

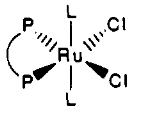


III

P⌒P = dppm

In our work, the isolation of only the *trans*-dichloro isomer of $RuCl_2(dppm)(PMePh)_2$ by three significantly different modes of preparation is noteworthy. The fact that this isomer is formed in high- and low-temperature reactions suggests that this isomer is both the kinetic and thermodynamic isomer. As noted previously, for $RuCl_2(dppm)_2$, the trans isomer is known to thermally isomerize to the cis isomer at ca. 80 °C in dichloroethane.[7] With $RuCl_2(dppe)_2$, only the trans isomer is known and this was ascribed to the steric strain imposed by the phenyl rings.[6a] Thus, systems involving six-coordinate ruthenium are quite sensitive to steric size, and the prediction of geometry on the basis of steric factors is difficult.

While the dppm derivatives appear to give stable products, the dppe derivatives show more interesting behavior. For example, upon attempting to recrystallize the *trans*-dichloro isomer IIc from methanol/chloroform/ether solution, we obtained a new complex, which gave a simple A_2X_2 pattern in the ^{31}P spectrum. We assign this isomer to the *cis*-dichloro complex IVc.



IVc

L = PMe_2Ph

P⌒P = dppe

We were intrigued by this transformation, particularly since the dppm analogues seem to show such a strong preference for the *trans*-dichloro orientation II. We were also perplexed by our inability to reliably reproduce the isomerization to make pure IVc. Mixtures were often, but not always, obtained. It appears that the solvent system is of critical importance. Figure 2 shows by ^{31}P NMR the transformation taking place as a $CDCl_3$ solution of IIc is treated successively with methanol and *tert*-butyl methyl ether. Upon addition of methanol, the yellow-orange solution darkens considerably within ca. 45 min.

The spectrum of the dark red-orange solution is shown in Figure 2b and is quite different from the starting spectrum. The complex

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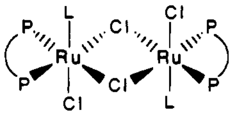
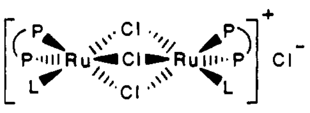
AA′BB′ pattern due to the starting material (signified as a in the figure) has decreased in intensity. Free PMe_2Ph is evident at −46 ppm. The *cis*-dichloro isomer IVc is present as two triplets (b), one underneath part of the AA′BB′ spectrum at ca. −8 ppm. A component is also present that exhibits an A_2X splitting pattern (c). Finally, two broad multiplets (1:1) are seen at 59 and 22 ppm (d). Upon addition of *tert*-butyl methyl ether, the color immediately fades to yellow and the spectrum shown in Figure 2c results. The relative intensities of resonances due to components a–c have changed while component d has completely disappeared. Upon standing and cooling, the solution deposited a yellow solid, which proved to be a mixture of IIc and IVc.

The behavior of this system is peculiar. It seems clear that the more polar $CDCl_3/CH_3OH$ solvent system favors phosphine dissociation. The A_2X pattern of component c is similar to those obtained by Caulton and Garrou while spectroscopically monitoring the reaction of $RuCl_2(PPh_3)_3$ with bis(diphenylphosphino)propane.[4] They suggested V and VI as possible structures for these species. Both of these could serve as intermediates for the II–IV transformation.



V



VI

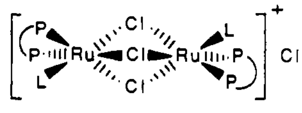
The additional component (d) in our spectra seems to be associated with the dark red-orange color observed upon adding methanol to the $CDCl_3$ solution. The large number of six-coordinate Ru(II) phosphine complexes has allowed the generalization to be made that such complexes are either colorless, yellow, or light orange.[10] However, five-coordinate Ru(II) complexes such as $RuCl_2(PPh_3)_3$ are intensely colored. It is likely then, that d is a five-coordinate species, whose spectrum is broadened by fluxionality or ligand exchange. Any number of isomers can be drawn for such a complex,[2b] but it is clear that it would be of the type $[RuCl(P\text{-}P)L_2]Cl$ and that it would necessarily be nonrigid at 25 °C in order for the two phosphorus resonances to be present in a 1:1 ratio.

The complex behavior of $RuCl_2(dppe)(PMe_2Ph)_2$ serves to demonstrate the subtle factors that determine the most stable configuration in these complexes. Of the possible six-coordinate isomers, the all-cis isomer (III) is clearly the most sterically hindered. We were not able to isolate or even spectroscopically observe this configuration; however, Poilblanc's work shows that this isomer is attainable with sterically nondemanding ligands (i.e. hydrides).[5] The remaining two configurations (II and IV) are sterically similar, with isomer IV being slightly more crowded because both chelate phosphorus atoms are cis to three other phosphorus atoms.

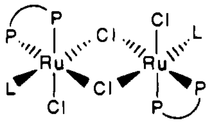
On the other hand, because of electronic considerations, strong trans directors prefer not to be trans to one another.[11] Thus, in $RuCl_2(dppm)_2$, the kinetically favored and less sterically hindered trans complex isomerizes on heating to the thermodynamically more stable and electronically more favorable cis isomer. Similarly, to minimize trans phosphine interactions, isomer IV is electronically more favorable than isomer II. Apparently, for the particular case of $RuCl_2(dppe)(PMe_2Ph)_2$, the opposing influences are so closely balanced that the interconversion between the two isomers can be effected simply by changing the polarity of the solvent mixture.

If the steric crowding is increased further, as in $RuCl_2(dppe)(PMePh_2)_2$, dissociation is expected to be even more facile. This was evidenced by our inability to obtain a pure sample of IId. Figure 3 shows the ^{31}P NMR spectrum obtained in $CDCl_3$ from an attempted preparation of IId. The *trans*-dichloro complex is indeed present as seen by the presence of the expected AA′BB′ pattern at 37 and −3 ppm. In addition, a great deal of free $PMePh_2$ is present at −27 ppm (this, despite the fact that the NMR sample was prepared from a free-flowing solid). A doublet at 77 ppm and a triplet at 49 ppm (relative intensity 2:1, $J = 42.5$ Hz) represented by component e in Figure 3 can again be assigned to structure V or VI. Finally, a component f is present that exhibits an ABX splitting pattern. The two close doublets of doublets at 80 and 73 ppm ($J_{AB} = 13$ Hz, $J_{AX} = 35$ Hz) are associated with the collapsed triplet at 20 ppm (relative intensities 1:1:1).

Component f requires a configuration with all the phosphines on each Ru inequivalent, such as VII or VIII. Five-coordinate species are also possible,[2b,12] although in this case, we did not observe the dark, intense colors usually associated with such complexes. The important point is that phosphine dissociation is facile with the dppe complexes and is consistent with the greater steric demands of this ligand. While $RuCl_2(dppe)(PMe_2Ph)_2$ requires the introduction of a polar donor solvent to effect dissociation, $RuCl_2(dppe)(PMePh_2)_2$ appears to dissociate phosphine in chloroform alone. Similar evidence for steric crowding in Ru(II) six-coordinate phosphine complexes was seen by Stephenson.[13] In contrast, the dppm derivatives IIa and IIb are completely stable and never showed any signs of phosphine dissociation.



VII



VIII

Obviously, the effect of phosphine dissociation is very important in considering the catalytic properties of these complexes. One might expect that the proper combination of uni- and bidentate phosphines would give unique properties in sterically sensitive catalytic reactions.

Acknowledgment. We thank Dr. Robert E. Stevens and Daniel V. Laciak for helpful discussions. We are also grateful to Paul M. Michalko and A. Diane Gauthier for collection of NMR data. Finally, we thank Air Products and Chemicals for permission to publish this work.

Registry No. I (L = PMe_2Ph), 58452-13-4; IIa, 104421-72-9; IIb, 104421-73-0; IIc, 104421-74-1; IId, 104421-75-2; IVc, 104486-14-8; $RuCl_2(PPh_3)_3$, 15529-49-4.

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