solvent was removed in vacuo, and the residue was extracted with hexane to give an off-white solid which was recrystallized from the same solvent to give a white solid; mp 280 °C dec. Anal. Calcd for $PtCl_2[P(t\text{-}Bu)_2H]_2$: C, 34.53; H, 6.83; Cl, 12.77; mol wt 558. Found: C, 34.94; H, 6.93; Cl, 11.90; mol wt 556 (benzene) [yield 60%]. ^1H NMR ($CDCl_3$): δ(P–C–C–H) 1.60 [q, ^3J(P–H) + ^5J(P–H) = 14.2 Hz].

Reactions of Tri-*tert*-butylphosphine with Palladium(II) Chloride or Sodium Tetrachloropalladate. (a) $P(t\text{-}Bu)_3$ (3 mmol) was added to DMF (25 mL) containing Na_2PdCl_4 (1 mmol), and the mixture was stirred for 48 h to give a yellowish solution. The solution was filtered, and the solvent was removed in vacuo to give a yellow solid which was washed with cold ethanol (20 mL) and recrystallized from a mixture of benzene and hexane to give a yellow crystalline solid; mp 210 °C dec. Anal. Calcd for $[PdCl\{P(t\text{-}Bu)_2CMe_2CH_2\}]_2$: C, 42.24; H, 7.59; Cl, 10.36; mol wt 685. Found: C, 42.17; H, 7.85; Cl, 9.98; mol wt 694 (benzene) [yield 75%].

(b) A mixture of $P(t\text{-}Bu)_3$ (3 mmol) and $PdCl_2$ or Na_2PdCl_4 (1 mmol) in DMF (25 mL) was heated, with stirring, in an oil bath. As the temperature approached 100 °C, the reddish colour of the solution began to change to green. At 115 °C the solution became dark green when it was cooled to room temperature to give some greenish white solid. More solid was obtained upon concentrating the solution. Filtration and recrystallization of the solid from a mixture of benzene and hexane gave pure *trans*-$PdHCl[P(t\text{-}Bu)_3]_2$ in 90% yield; mp 146 °C. Anal. Calcd for $PdHCl[P(t\text{-}Bu)_3]_2$: C, 52.70; H, 10.06; mol wt 547. Found: C, 52.37, H, 10.19; mol wt 550 (benzene). ^1H NMR (C_6D_6):(δ[P(C–C–H)] 1.5 [t, ^3J(P–H) + ^5J(P–H) = 12.3 Hz]; δ(Pd–H) −18.3 [t, ^2J(P–H) = 12.3 Hz]. $^{31}P\{^1H\}$NMR (C_6D_6): δ 81.7 (s). IR (Nujol mull): ν(Pd–H) 2215, ν(Pd–H) 766, ν(Pd–Cl) 255 cm^{-1}.

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Dehydrogenation of Alcohols and Hydrogenation of Aldehydes Using Homogeneous Ruthenium Catalysts

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A series of ruthenium(II) diphosphine hydrides of the type $RuH_2(CO)(PPh_3)(L\text{–}L)$ (I) where L–L = $Ph_2Ph(CH_2)_nPPh_2$ (n = 1–4), $Ph_2P(CH_2)_2AsPh_2$, and 1,2-$(Ph_2P)_2C_6H_4$ have been prepared and reacted with trifluoroacetic acid ($HOAc_F$) to yield complexes $Ru(OAc_F)_2CO(PPh_3)_m(L\text{–}L)$ where L–L = 1,2-$(PPh_2)_2C_6H_4$ (m = 0, 1), $PPh_2CH_2CH_2AsPh_2$ (m = 1), and $(Ph_2P)_2(CH_2)_n$ (n = 3, 4; m = 0). These complexes have been extensively characterized by ^1H, ^{31}P, and ^{19}F NMR spectroscopy and most of their stereochemistries unambiguously determined. The catalytic activities and lifetimes of these new complexes in alcohol dehydrogenation and ketone hydrogenation were examined and compared to those of of $Ru(OAc_F)_2CO(PPh_3)_2$ (IIa). In contrast to past reports, we find that IIa when used as a dehydrogenation catalyst deactivates due to its tendency to decarbonylate the product aldehydes. Phosphorus-31 NMR analyses reveal that IIa reacts with heptanal to yield $Ru(OAc_F)_2(CO)_2(PPh_3)_2$ (10% conversion in 30 min at 100 °C). While the diphosphine trifluoroacetate complexes are more active than IIa, they also deactivate by decarbonylation of the product aldehyde or ketone. These new diphosphine complexes are also more efficient hydrogenation catalysts than IIa.

Introduction

Dobson and Robinson[1,2] and more recently Rybak and Ziolkowski[3] have described their extensive studies into (trifluoroacetato)ruthenium(II) alcohol dehydrogenation catalysts and their polystyrene supported analogues, respectively. The mechanism originally proposed by Robinson[1] (Scheme I) requires an isomerization whereby the mutually trans phosphine ligands of intermediate **i** must rearrange to a cis configuration (isomer **j**) in order to complete the catalytic cycle. We felt that initially locking the phosphines into a cis configuration by means of a chelating diphosphine (L–L) could affect the rate of the overall reaction if the **i** → **j** rearrangement was involved in the rate-determining step of the overall catalytic sequence. We therefore now wish to report on a series of ruthenium(II) trifluoroacetate diphosphine complexes that we have prepared and compare their catalytic activity to that previously found for $Ru(OAc_F)_2CO(PPh_3)_2$. Products have been characterized by analytical and spectroscopic methods, and where possible, their stereochemistry has been assigned.

Experimental Section

Unless indicated otherwise, all operations were conducted under purified argon or nitrogen, using standard inert atmosphere techniques.[4]

Infrared spectra were determined on a Beckman IR4240 spectrometer. NMR spectra were recorded on a JEOL FX90-Q spectrometer equipped with a broad-band, tunable probe. A Bruker WM250 spectrometer was used to measure 250-MHz ^1H NMR spectra. Phosphorous-31 and ^{19}F chemical shifts were referenced to external 85% H_3PO_4 and internal C_6F_6, respectively. The latter chemical shifts were converted to the δ_{CFCl_3} scale by using the relationship $\delta_{CFCl_3} = -162.28 + \delta_{C_6F_6}$.

(1) Dobson, A.; Robinson, S. D. *Inorg. Chem.* **1977**, *16*, 137.
(2) Robinson, S. D. British Patent 1 530 447, Nov 1, 1978.
(3) Rybak, W. K.; Ziolkowski, J. J. *J. Mol. Catal.* **1981**, *11*, 365.
(4) Shriver, D. F., "The Manipulation of Air-Sensitive Compounds"; McGraw-Hill: New York, 1969.

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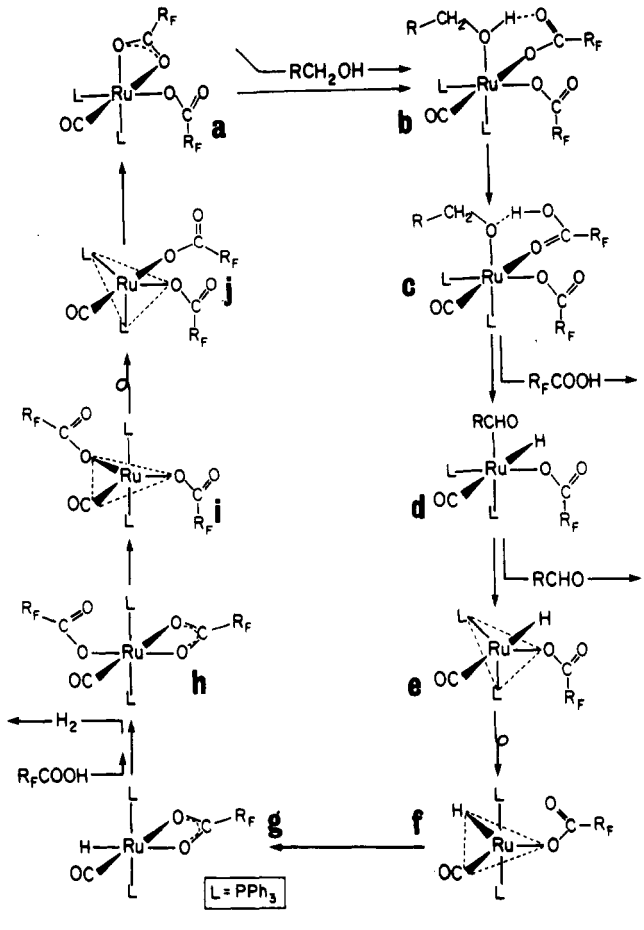
Scheme I



GLC analyses were performed on Hewlett-Packard 5730A gas chromatograph using 30-m SE30 capillary, or 3-m, 10% Carbowax 20M (Chromosorb W) columns. Elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, NY.

Literature methods were used to prepare $RuH_2(CO)(PPh_3)_3$[5] and $Ru(OAc_F)_2(CO)(PPh_3)_2$.[6] The diphosphines and Arphos were obtained from Strem Chemical, Inc., and used without additional purification. Solvents and alcohols were reagent grade and dried with 3A molecular sieves and deoxygenated with bubbling argon or under vacuum before use. Trifluoroacetic acid was refluxed with the anhydride and fractionally distilled. All other chemicals were used as supplied.

Preparation of $RuH_2(CO)(PPh_3)[1,2\text{-}(Ph_2P)_2C_6H_4]$ (Id). A toluene (25 mL) solution of $RuH_2(CO)(PPh_3)_3$ (Ia, 0.52 g, 0.56 mmol) and 1,2-$(Ph_2P)_2C_6H_4$ (0.25 g, 0.56 mmol) was refluxed for 6 h, yielding a deep brown solution after 1 h. Toluene was stripped under vacuum at room temperature to yield a viscous, brown oil. Methanol (25 mL) was added, and the mixture was stirred for 2 h. The resultant crude powder was filtered off in air and washed with methanol (ca. 75 mL) and hexane (ca. 25 mL). Recrystallization from THF/MeOH by slow concentration under vacuum afforded white crystals of $RuH_2(CO)(PPh_3)[1,2\text{-}(Ph_2P)_2C_6H_4]$ (Id, 0.38 g, 81%): IR (fluorolube mull) 1945 (s, ν(CO)), 1828 (m, ν(RuH)), 1806 (m, ν(RuH)) cm^{-1}. Anal. Calcd for $RuP_3C_{49}H_{41}O$: P, 11.06; C, 70.08; H, 4.92. Found: P, 10.60; C, 70.12; H, 5.10. Complex Id is attacked slowly by air in solution (several hours) and in the solid state (several months).

Analogous $RuH_2(CO)(PPh_3)(L_2)$ complexes were similarly prepared. **$RuH_2(CO)(PPh_3)(Ph_2PCH_2CH_2CH_2PPh_2)$ (If)**: Ia (0.75 g, 0.82 mmol), $Ph_2PCH_2CH_2CH_2PPh_2$ (0.36 g, 0.87 mmol) in 25 mL of PhMe, 1-h reflux, 0.56 g (85%) yield; IR (Nujol mull) 1934 (vs, ν(CO)), 1900 (m, ν(RuH)), 1830 (w, ν(RuH)) cm^{-1}. Anal. Calcd for $RuP_3C_{46}H_{43}O$: Ru, 12.54; P, 11.53. Found: Ru, 12.14; P, 11.31. **$RuH_2(CO)(PPh_3)(Ph_2PCH_2CH_2AsPh_2)$ (Ie)**: Ia (0.50 g, 0.54 mmol), Arphos (0.31 g, 0.70 mmol) in 25 mL of PhMe, 1.5-h reflux, 0.29 g (64%) yield; IR (KBr) 1944 cm^{-1} (vs, ν(CO)). Anal. Calcd for $RuP_2AsC_{45}H_{41}O$: Ru, 12.09; P, 7.41; As, 8.96; C, 64.67; H, 4.94. Found: Ru, 12.28; P, 7.40; As, 9.41; C, 64.82; H, 4.92. **$RuH_2(CO)(PPh_3)(Ph_2PCH_2CH_2PPh_2)$ (Ic)**: Ia (0.52 g, 0.56 mmol), $Ph_2PCH_2CH_2PPh_2$ (0.23 g, 0.58 mmol) in 20 mL of PhMe, 1.5-h reflux, 0.20 g (45%) yield; IR (Nujol mull) 1945 cm^{-1} (s, ν(CO)). Anal. Calcd. for $RuC_{45}H_{41}P_3O$: C, 68.26; H, 5.22. Found: C, 68.70; H, 5.80.

Preparation of $RuH_2(CO)(PPh_3)[Ph_2P(CH_2)_4PPh_2]$ (Ig and Ih). $RuH_2(CO)(PPh_3)_3$ (Ia, 0.510 g, 0.556 mmol) and $Ph_2P(CH_2)_4PPh_2$ (0.287 g, 0.673 mmol) were refluxed for 3 h in toluene (10 mL). When the mixture was cooled to room temperature, petroleum ether (35 mL) was added. White crystals formed within 5 min. After 30 min, the product was filtered off under argon and washed with petroleum ether (60 mL). Recrystallization of the product from boiling toluene (35 mL) afforded 75 mg (16%) of complex Ih. Anal. Calcd for $RuP_3C_{47}H_{45}O$: Ru, 12.33; P, 11.33. Found: Ru, 12.25; P, 11.40. The combined filtrate was allowed to stand for 5 days at ca. −50 °C, yielding ca. 50 mg of off-white crystals. The $^{31}P\{^1H\}$ NMR spectrum of this product indicated that it was a mixture of Ih (24%) and Ig (76%). The filtrate was then concentrated under vacuum to 20 mL. Ethanol (50 mL) was added, and when the mixture was left standing overnight, white crystals of complex Ig were deposited. After the reaction mixture had been allowed to stand for 2 h at −50 °C, complex Ig was filtered off in air and washed with MeOH (50 mL) and petroleum ether (10 mL); yield 0.18 g (39%). Anal. Calcd for $RuP_3C_{47}H_{45}O$: Ru, 12.33; P, 11.33; C, 68.85; H, 5.53. Found: Ru, 12.25; P, 11.45; C, 68.88; H, 5.50.

Preparation of $Ru(OAc_F)_2(CO)(PPh_3)[1,2\text{-}(Ph_2P)_2C_6H_4]$ (IIId). Trifluoroacetic acid (0.31 mL, 4.2 mmol) was added slowly to a benzene (3.5 mL) solution of $RuH_2(CO)(PPh_3)[(Ph_2P)_2C_6H_4]$ (Id). A small amount of gas evolution occurred immediately, and the solution turned yellow within a few seconds. Heptane (20 mL) was added. Slow evaporation in air afforded light yellow crystals of IIId (0.14 g, 52%): IR (CH_2Cl_2) ν(CO) at 1980 (br, s), ν(OCO) at 1720 (w, sh), 1710 (m, sh), 1687 (vs), 1680 (vs), 1642 (w). Anal. Calcd for $RuP_3C_{53}H_{39}F_6O_5$: P, 8.73; C, 59.98; H, 3.70; F, 10.71. Found: P, 8.17; C, 59.85; H, 4.03; F, 11.11.

The analogous complexes $Ru(OAc_F)_2(CO)(PPh_3)_m(L_2)$ (m = 0, II; m = 1, III) were similarly prepared. **$Ru(OAc_F)_2(CO)(PPh_3)(Ph_2PCH_2CH_2AsPh_2)$ (IIIe).** Complex Ie (0.86 mmol) and $HOAc_F$ (1.2 g, 10.7 mmol) were reacted in toluene (10 mL). The large excess of $HOAc_F$ was used in an attempt to isolate only the cis-P_2 isomer of IIIe (see text). After the mixture was left standing for 50 h in air, $^{31}P\{^1H\}$ NMR analysis showed that only 47% of IIIe was in the *cis*-P_2 form. Yield of IIIe·$HOAc_F$: 0.69 g (59%); IR (CH_2Cl_2) 1975 (br, s, ν(CO)), 1780 (m, free $HOAc_F$, ν(CO)), 1682 (vs, ν(OCO)), 1647 (m, ν(OCO)) cm^{-1}. Anal. Calcd for $RuP_2AsC_{51}H_{40}F_9O_7$: Ru, 8.61; P, 5.28; As, 6.38; C, 52.19; H, 3.44; F, 14.57. Found: Ru, 8.52; P, 5.54; As, 5.92; C, 52.33; H, 3.53; F, 15.28. The reaction of Ie (0.178 g, 0.213 mmol) with $HOAc_F$ (0.31 mL, 19 equiv) in benzene (2 mL) afforded 0.14 g (69%) of IIIe consisting of 62% of the cis-P_2 isomer.

$Ru(OAc_F)_2(CO)(Ph_2PCH_2CH_2CH_2PPh_2)$ (IIf): complex If (0.221 g, 0.275 mmol), $HOAc_F$ (0.31 mL, 4.16 mmol) in benzene (3 mL), 0.050 g (24%) yield; IR (CH_2Cl_2) 1974 (s, ν(CO)), 1678 (vs, ν(OCO)), 1650 (m, ν(OCO)) cm^{-1}. Anal. Calcd for $RuP_2F_6C_{32}H_{26}O_5$: P, 8.07; F, 14.85; C, 50.07; H, 3.42. Found: P, 7.77; F, 15.14; C, 49.05; H, 3.64. **$Ru(OAc_F)_2(CO)(Ph_2PCH_2CH_2CH_2CH_2PPh_2)$ (IIg)**: complex Ig (0.060 g, 0.073 mmol), $HOAc_F$ (0.040 mL, 0.54 mmol) in benzene (5 mL), 0.025 g (44%) yield. Anal. Calcd for $RuP_2F_6C_{33}H_{28}O_5$: Ru, 12.93; F, 14.58. Found: Ru, 12.38; F, 14.06. Complexes IIf and IIg tend to form viscous, yellow oils and crystallize only with difficulty from PhH/heptane or CH_2Cl_2/heptane. Usually, large yellow needles of these complexes grow out of the oil which separates on slow solvent evaporation.

Alcohol Dehydrogenation. Kinetic runs were monitored either by GLC analyses of aliquots of the reaction mixture or by measuring the rate of hydrogen evolution using a mercury-filled

(5) Ahmad, N.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc., Dalton Trans.* **1972**, 843. Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 45.

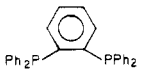
(6) Dobson, A.; Robinson, S. D.; Uttley, M. F. *J. Chem. Soc. Dalton Trans.* **1975**, 370; *Inorg. Synth.* **1977**, *17*, 124.

Table I.[a] ^{1}H NMR Spectra of $RuH_2(CO)(PPh_3)(L\text{-}L)$

compd	L-L	solvent	H_1	H_2	coupling const, Hz
Ic	$PPh_2PCH_2CH_2PPh_2$, dppe	C_6D_6	−7.1	−7.6	NA
Id	1,2-$(Ph_2P)_2C_6H_4$	C_6D_6	−6.62	−6.99	$P\text{-}H_1$ = 20, 26, 78; $P\text{-}H_2$ = 18.5, 25, 25; $H_1\text{-}H_2$ = 4.4
Ie	$Ph_2PCH_2CH_2AsPh_2$, Arphos	PhMe-d_8	−7.55	−8.12	$P\text{-}H_1$ = 21, 27.5; $P\text{-}H_2$ = 19, 23.6; $H_1\text{-}H_2$ = 4.6
If	$Ph_2PCH_2CH_2CH_2PPh_2$, dppp	C_6D_6	−6.98	−6.50	$P\text{-}H_1$ = 20, 26, 72; $P\text{-}H_2$ = 16, 21, 31; H_1H_2 = 5.6
Ig	$Ph_2P(CH_2)_4PPh_2$, dppb	C_6D_6	−7.90	−6.95[b]	NA
Ih	$Ph_2P(CH_2)_4PPh_2$, dppb	C_6D_6	−7.6	−8.0[c]	NA

[a] Chemical shifts in ppm from Me_4Si. Under Ar or N_2 atmosphere. NA = not available. See eq 2 for assignments. [b] Meridional P_3 isomer. [c] Facial P_3 isomer.

Table II. 36.2-MHz $^{31}P\{^1H\}$ NMR Spectra of $RuH_2(CO)(PPh_3)(L\text{-}L)$ Complexes[a]

compd	L-L	solvent	Ph_3P_1	L_2	L_3	J(P-Ru-P), Hz
Ib	$Ph_2PCH_2PPh_2$, dppm[b]	PhMe	(61.76)	−0.21	17.16	J_{13} = 244, J_{12} = 24, J_{23} = 21
Ic	$Ph_2PCH_2CH_2PPh_2$, dppe	THF-d_8	59.66	64.50	79.80	J_{13} = 238, J_{12} = 18, J_{23} = 5
Id		THF-d_8	59.28	65.25	80.28	J_{13} = 238, J_{12} = 19, J_{23} = 8
Ie	$Ph_2PCH_2CH_2AsPh_2$	PhMe-d_8	59.97		81.48	J_{13} = 240
If	$Ph_2P(CH_2)_3PPh_2$, dppp	THF-d_8	58.34	27.64	37.70	J_{13} = 229, J_{12} = 26, J_{23} = 22
Ig	$Ph_2P(CH_2)_4PPh_2$, dppb (*mer* isomer)	C_6D_6	58.46	35.06	52.73	J_{13} = 232, J_{12} = 18, J_{23} = 17
Ih	$Ph_2P(CH_2)_4PPh_2$, dppb (*fac* isomer)	PhMe-d_8	49.85[c]	48.77[c]	36.55[c]	J_{AB} = 17.5, J_{AX} = 5.0, J_{BX} = 7.4
Ia	$(PPh_3)_2$	THF-d_8	56.98	44.54		J_{12} = 18

[a] Chemical shifts in ppm with respect to external 85% H_3PO_4, downfield shifts are positive. See eq 2 for assignments. [b] Complex is $RuH_2(CO)(\eta^2\text{-DPM})(\eta^1\text{-DPM})$ (not isolated); uncoordinated phosphine of η^1-DPM at −4.84 ppm. [c] Assignments not applicable.

gas buret. An efficient, double-jacketed spiral condenser was used to minimize vaporization of $HOAc_F$, particularly when high boiling alcohols were studied.

In a typical kinetic run, monitored by hydrogen evolution, the substrate alcohol (4.50 g) was refluxed for ca. 15 min. A solution of the catalyst (2×10^{-2} mmol) and $HOAc_F$ (10 μL) in 0.50 g of the alcohol was then injected (usually this mixture had to be heated in a stream bath for 2–3 min to disolve the catalyst). The system was allowed to equilibrate for 1–2 min before volume measurements were recorded.

With inactive substrates, particularly low boiling alcohols or primary alcohols, hydrogen evolution was too slow or too limited to yield accurate rate data. Consequently, these reactions were monitored by GLC analyses only.

In our attempts to dehydrogenate methanol to formaldehyde, the reaction mixtures were analyzed by ^{1}H and ^{13}C FT NMR using the JEOL *Double Precision* data processing program to extend the dynamic ranges of the spectra. No HCHO was detected. Only complexes IIa or IIf remained upon evaporation of the methanol under vacuum (i.e., no paraformaldehyde was present).

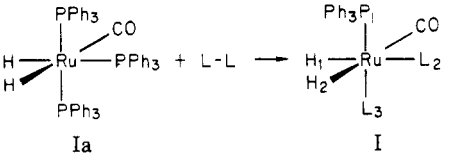
Hydrogenation of Heptanal and Cyclohexanone. Hydrogenations were conducted in a stirring autoclave (Autoclave engineers, Inc.). A typical run is illustrated in the following example: complex IIIe (20.4 mg, 1.74×10^{-2} mmol), cyclohexanone (1.71 g, 17.4 mmol), *n*-decane (0.52 g, internal GLC standard), and toluene (16.48 g, total solvent 17.00 g) were weighed into a glass liner and then charged into the autoclave. The system was purged with nitrogen (two times to 700 psig) and then pressurized with hydrogen to 265 psig. The autoclave was then heated to 87–90 °C for 89 min (system required 10 min to reach reaction temperature). At the end of the reaction, the heater assembly was removed and the autoclave cooled in an ice water bath to ca. 15 °C. The reaction mixture was then removed and analyzed by $^{31}P\{^1H\}$ NMR spectroscopy and GLC on an SE30 capillary column.

Results and Discussion

Synthesis and Characterization of $RuH_2(CO)(PPh_3)(L\text{-}L)$ Complexes. Reaction of $Ru(OAc_F)_2(CO)(PPh_3)_2$ with diphosphines (L–L) produced a mixture of products instead of the desired derivatives $Ru(OAc_F)_2(CO)(L\text{-}L)$. A cleaner reaction is the conversion of the corresponding dihydridoruthenium complexes to the bis(trifluoroacetato) complexes by treatment with excess trifluoroacetic acid ($HOAc_F$).[6,7]

$$RuH_2(CO)(L_n) + 2HOAc_F \rightarrow Ru(OAc_F)_2(CO)(L_n) + H_2 \quad (1)$$

Therefore, a series of $RuH_2(CO)(PPh_3)(L\text{-}L)$ (L–L = diphosphine or $Ph_2PCH_2CH_2AsPh_2$ (Arphos)) complexes were prepared by metathesis of $RuH_2(CO)(PPh_3)_3$, Ia, with L–L.



Ia I (2)

Spectral data for complexes I are summarized in Tables I and II. Except for complexes Ie and Ih, their $^{31}P\{^1H\}$ NMR spectra consisted of three ABX quartets (Figure 1). The ^{1}H NMR spectra of these complexes in the high-field region contained two 16-line multiplets (Figure 2), consistent with coupling of each hydride to four nonequivalent nuclei (i.e., an ABMPX spin system). The large values of $^2J_{PP}$ (ca. 240 Hz) and $^2J_{PH}$ (ca. 75 Hz) are characteristic of two trans phosphines and hydride trans to phosphorus.[8] These data are consistent with a meridional configuration of three phosphine ligands and cis-dihydrides as illustrated in eq 2. ^{31}P peak assignments could be made by knowledge of the Δ_R values expected for these (L–L) diphosphines which would form 4-, 5-, and 6-membered rings. All ^{31}P

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(8) Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231.

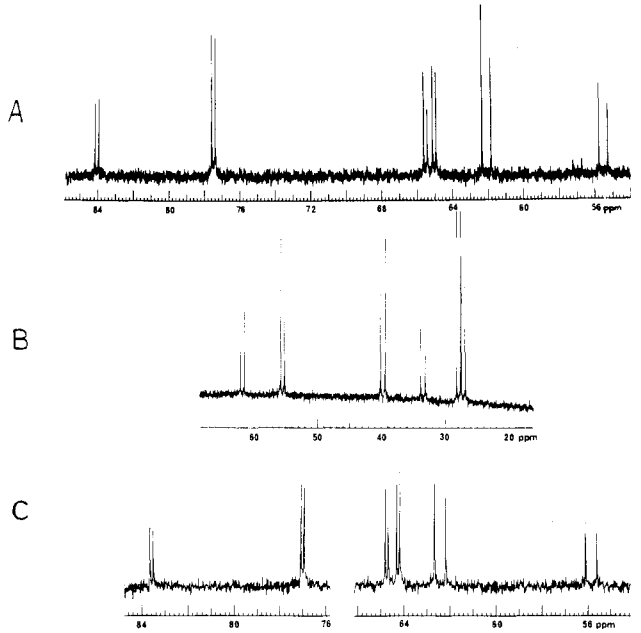


Figure 1. $^{31}P\{^1H\}$ NMR spectra of (A) $RuH_2(CO)(PPh_3)[1,2\text{-}(Ph_2P)_2C_6H_4]$ (Id) in THF-d_8, (B) $RuH_2(CO)(PPh_3)(Ph_2PCH_2CH_2CH_2PPh_2)$ (If) (C) $RuH_2(CO)(PPh_3)(Ph_2PCH_2CH_2PPh_2)$ (Ic) in THF-d_8.

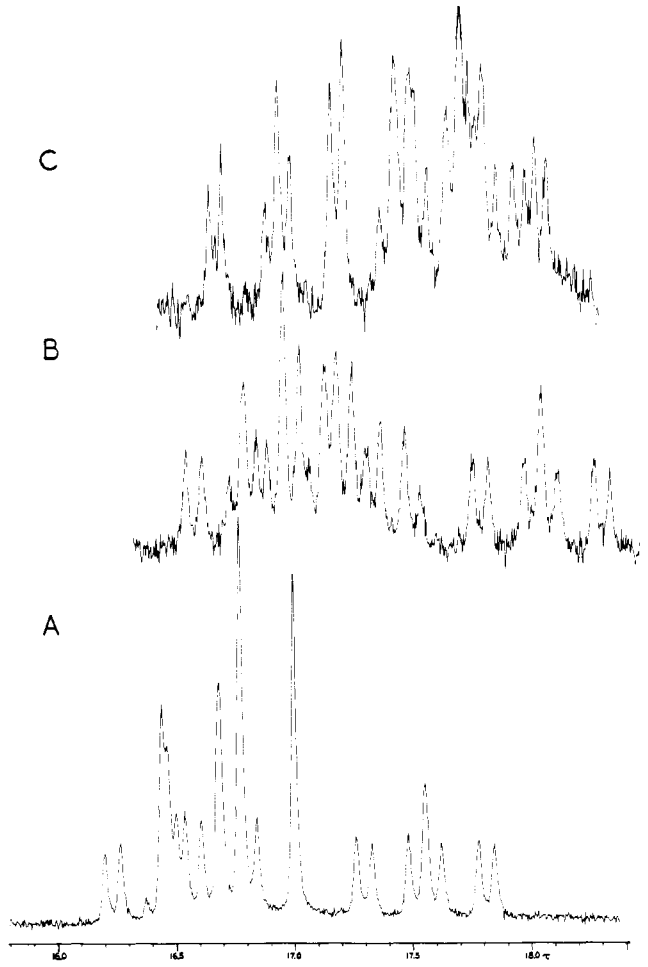


Figure 2. Partial 89.56-MHz ^1H NMR spectrum of (A) $RuH_2(CO)(PPh_3)(Ph_2PCH_2CH_2CH_2PPh_2)$ (If) in toluene-d_8; (B) $RuH_2(CO)(PPh_3)(Ph_2PCH_2CH_2CH_2PPh_2)$ (If) in THF-d_8; (C) $RuH_2(CO)(PPh_3)[1,2\text{-}(Ph_2P)_2C_6H_4]$ (Id) in THF-d_8.

spectra reported here show the expected downfield shift for phosphorus incorporated in 5-membered rings and

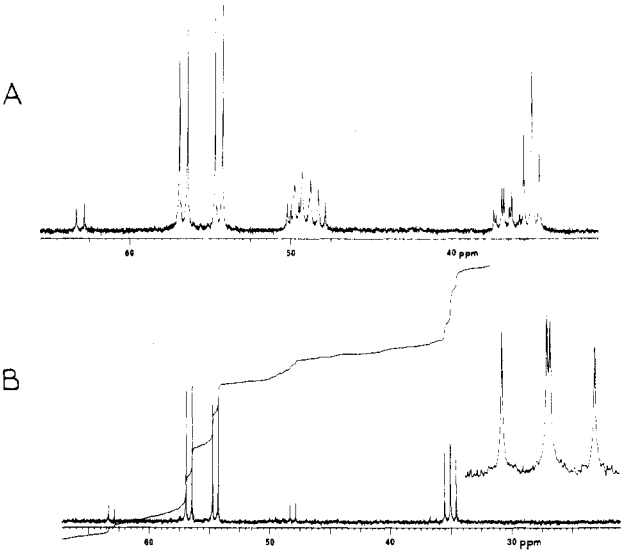


Figure 3. $^{31}P\{^1H\}$ NMR spectra of (A) *mer* and *fac* isomers of $RuH_2(CO)(PPh_3)(Ph_2PCH_2CH_2CH_2CH_2PPh_2)$ in C_6H_6 obtained from $RuH_2(CO)(PPh_3)_3$ and $Ph_2P(CH_2)_4PPh_2$ after 4 h at 130 °C (free PPh_3 resonance at −6.06 ppm is not shown) and (B) mer-$RuH_2(CO)(PPh_3)[Ph_2P(CH_2)_4PPh_2]$ (Ig).

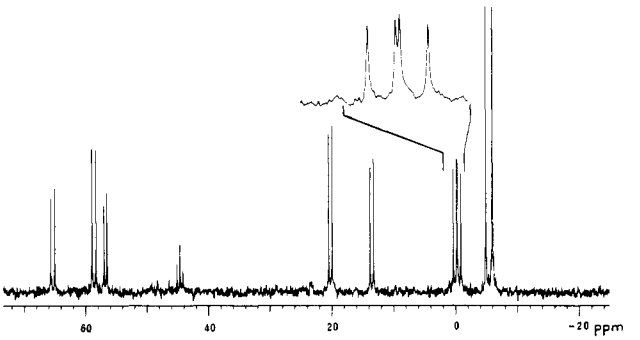


Figure 4. $^{31}P\{^1H\}$ NMR spectrum of toluene solution of $RuH_2(CO)(PPh_3)_3$ (Ia) and $(Ph_2P)_2CH_2$ after 1 h at 120 °C.

upfield shift for phosphorus incorporated in 4-membered rings.[9]

The $^{31}P\{^1H\}$ NMR spectrum of Ie (L–L = $Ph_2PCH_2CH_2AsPh_2$) consisted of an AB quartet with $^2J_{AB}$ = 240 Hz. Its ^1H NMR spectrum in the high-field region showed the presence of two nonequivalent hydride ligands which are cis to each other and to the two phosphines. Consequently, we believe complex Ie has the same geometry as the other tris(phosphine) complexes with the two phosphines trans to each other. No isomer with phosphine trans to arsine was observed.

The reaction of $RuH_2(CO)(PPh_3)_3$ (Ia) with $Ph_2P(CH_2)_4PPh_2$ (dppb) afforded two white crystalline products which were separable by fractional crystallization (Figure 3). The NMR spectra of the major isomer Ig are consistent with the meridional P_3 structure shown in eq 2. The minor, less-soluble isomer is assigned the geometry with a facial arrangement of the three phosphines based on $^{31}P\{^1H\}$ (no large $^2J_{PP}$ values) and ^1H NMR spectra (no large $J_{P\text{-}Ru\text{-}H}$ values).

Reaction of Ia and 1 equiv of $Ph_2PCH_2PPh_2$ (dppm) in refluxing toluene for 1 h afforded a mixture of Ia and Ib. No additional change was apparent when the reaction time was extended to 17 h. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture (Figure 4) contained resonances due to Ia and an ABX pattern assigned to complex Ib. In ad-

(9) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

Table III. NMR Spectra of (Trifluoroacetato)ruthenium Complexes $H_nRu(OAc_F)_{2-n}CO)(PPh_3)_m(L\text{-}L)$[a]

compd	n	m	L–L	solv	$^{31}P\{^1H\}$ NMR			^{19}F NMR, δ_{CFCl_3}		^1H NMR		coupling const, Hz
					Ph_3P_1	P_2	P_3	X_1	X_2	H_1	H_2	
IId	0	0	1,2-$(Ph_2P)_2C_6H_4$ [b]	CH_2Cl_2		69.84		(−75.33,	−75.73)			
IIId	0	1	1,2-$(Ph_2P)C_6H_4$ [b]	CH_2Cl_2	25.0	58.0	52.5	(−73.87,	−75.03)			$P_1P_2 = 23, P_2P_3 = 15, P_1P_3 = 307$
IIIe	0	1	$Ph_2PCH_2CH_2AsPh_2$									
			(a) *trans*-P_2 isomer [b]	PhMe-d_8	26.13		50.12	(−72.49,	−73.81)			$P_1P_3 = 295$
			(b) *cis*-P_2 isomer [b]	PhMe-d_8	25.50	57.40		(−72.64 (d),	−74.14)			$P_1P_2 = 21, P_2$–$^{19}F = 1.2$
IVe	1	1	$Ph_2PCH_2CH_2AsPh_2$	PhMe-d_8	45.16		66.33		−73.61	−5.66		$P_1P_3 = 268, PH_1 = 16.6, 18.1$
IIf	0	0	$Ph_2PCH_2CH_2CH_2PPh_2$ [b,c]	CH_2Cl_2		37.84		(−75.58, br asym s)				
IIIf	0	1	$Ph_2PCH_2CH_2CH_2PPh_2$ [b,c]	C_6H_6	14.0	~21.0	22.0	−73.8	−74.70			$P_1P_3 = 300$
IVf	1	1	$Ph_2PCH_2CH_2CH_2PPh_2$ [b,c]									
			(a) isomer IVf′	C_6D_6	26.0	4.12	42.0			−4.66		$P_2H_1 = 110, PH_1 = 16, 23$
			(b) isomer IVf″	C_6D_6	~27.0	~47.0	~51.0	NA			−2.63	$PH_2 = 15, 21, 24$
IIg	0	0	$Ph_2P(CH_2)_4PPh_2$	C_6D_6		42.78			NA			
IIa	0	2	none [d]	$CDCl_3$	42.75				NA			
IVa	1	3	none [e]	$CDCl_3$	41.0	18.7			NA	−5.6		$PP = 15, P_1H_1 = 24.5, P_2H_1 = 110$

[a] Chemical shifts in δ referenced to (1) ^{31}P NMR (external reference 85% H_3PO_4), (2) ^{19}F NMR (internal reference C_6F_6, converted to $\delta_{CFCl_3} = -162.28 + \delta_{C_6H_6}$); and (3) ^1H NMR ($Me_4Si = 0$). [b] Equilibrium mixture. [c] Prepared in situ, not isolated. [d] Reference 6. [e] Reference 7. X = H or OAc_F

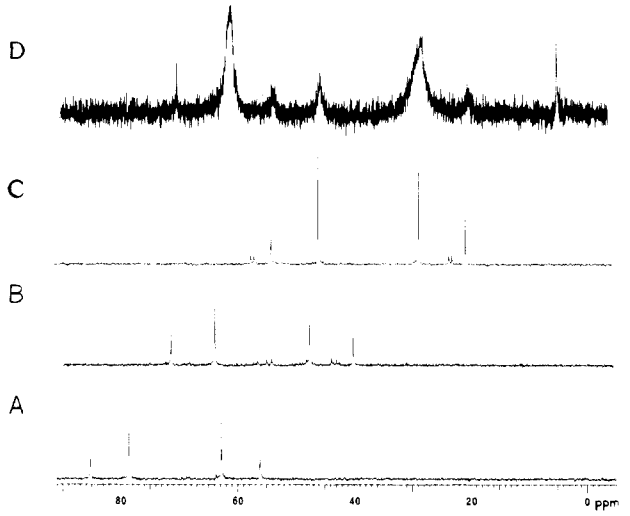
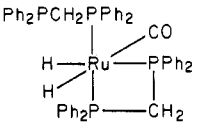


Figure 5. $^{31}P\{^1H\}$ NMR spectra (in C_6H_6): (A) $RuH_2(CO)(PPh_3)(Arphos)$ (Ie); (B) +1.3 equiv of $HOAc_F$; (C) +3.8 equiv of $HOAc_F$; (D) +19.5 equiv of $HOAc_F$. $PHPh_3^+$ observed at 5.13 ppm.

dition, the spectrum contained the expected singlet due to free PPh_3 and a singlet at −4.84 ppm which we tentatively assign to the uncoordinated phosphine of a monodentate $Ph_2PCH_2PPh_2$ ligand. No unreacted $Ph_2PCH_2PPh_2$ was observed (singlet at −27 ppm). These data suggest that Ib has the structure

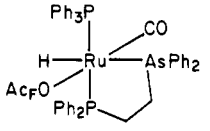


Ib

We had been unable to isolate pure Ib from these reaction mixtures. The introduction of a second equivalent of $Ph_2PCH_2PPh_2$ to the reaction mixture and additional refluxing (1 day) produced a complex mixture. No additional work was attempted with dppm.

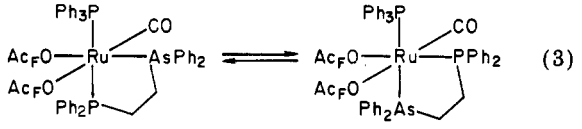
Synthesis of $Ru(OAc_F)_2(CO)(L\text{-}L)(PPh_3)_n$ (n = 0, 1). Robinson et al.[6] prepared $Ru(OAc_F)_2(CO)(PPh_3)_2$, IIa, by reacting complex Ia with $HOAc_F$ (>25× molar excess) in refluxing benzene solution. This procedure with complexes Ic–g yielded intractable yellow oils. To optimize the reaction conditions for these conversions, we monitored these reactions by ^{31}P and ^{19}F NMR spectroscopy. Our results indicate that only 3–10-fold molar excesses of $HOAc_F$ were required and that the reactions occurred smoothly at room temperature (ca. 25 °C). The resultant bis(trifluoroacetato) complexes exhibited three types of behavior in solution.

A. $Ru(OAc_F)_2(CO)(PPh_3)(Ph_2PCH_2CH_2AsPh_2)$, IIIe. upon addition of 1 molar equiv of $HOAc_F$, $RuH_2(CO)(PPh_3)(Arphos)$, Ie, was converted virtually quantitatively to $RuH(OAc_F)(CO)(PPh_3)(Arphos)$, IVe, within 5 min (Figure 5). The ^1H NMR spectrum of this complex contained a quartet at −5.66 ppm (C_6D_6, $^2J_{PH}$ = 16.6 and 18.1 Hz) due to hydride ligand cis to two nonequivalent phosphines. The ν(CO) band of this intermediate at 1936 (s) cm^{-1} suggests that the CO ligand is trans to the monodentate trifluoroacetate ligand instead of the hydride. The complex $RuH(CO)(OAc_F)(PPh_3)_3$ has a similar structure (determined by ^{31}P and ^1H NMR spectroscopy) with the CO trans to OAc_F.[7] The ν(CO) band of this complex is at 1927 cm^{-1}. Accordingly, complex IVe (which was not isolated in this work) is assigned the structure



IVe

Treatment of Ie with an excess (ca. 2×) of $HOAc_F$ afforded the expected bis(trifluoroacetato) complexes as an equilibrium mixture of two isomers with trans (IIIe′) or cis (IIIe″) phosphines. At 25 °C the major isomer is IIIe′ (ca.

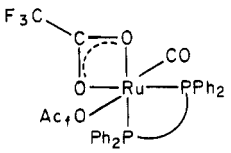


IIIe′ IIIe″ (3)

90%). No dissociation of PPh_3 from these IIIe isomers to yield $Ru(OAc_F)_2(CO)(Arphos)$, IIe, was observed under these conditions. In the presence of ca. 9-fold excess of $HOAc_F$, a small amount of $PHPh_3^+$ (~1%) was observed in the $^{31}P\{^1H\}$ NMR spectrum as well as a singlet at 70.5 ppm which may be due to IIe. However, the major effect of such a large excess of $HOAc_F$ was the conversion of the trans-P_2 isomer (IIIe′) into the thermodynamically less stable isomer IIIe″ (ca. 70%). The broad resonances in the $^{31}P\{^1H\}$ NMR spectrum of these solutions are probably due to rapid exchange of free and coordinated trifluoroacetate. Addition of heptane to the reaction mixture afforded air-stable, light yellow crystals of $Ru(OAc_F)_2(CO)(PPh_3)(Arphos)\cdot HOAc_F$ consisting of 62% of the cis-P_2 isomer IIIe″ (from ^{19}F NMR, Figure 6). Upon dissolution of crystalline IIIe, isomer IIIe″ isomerizes back to the trans-P_2 isomer, IIIe′, with a half-life of approximately 1 day at 25 °C.

In the $^{31}P\{^1H\}$ NMR spectrum of the purified IIIe mixture, the Arphos resonance of the cis-P_2 isomer, IIIe″, appears as a doublet of quartets ($^2J_{PP}$ = 21 Hz, $^5J_{PF}$ = 1.2 Hz). The ^{19}F NMR spectrum of this mixture contain a doublet at −72.7 ppm (δ_{CFCl_3}, toluene-d_8 solution) assigned to a trifluoroacetate ligand of isomer IIIe″. No long-range ^{31}P–^{19}F coupling was observed for the PPh_3 resonance of IIIe″, nor for any of the resonances of the trans-P_2 isomer.

B. $Ru(OAc_F)_2(CO)(L\text{–}L)$, II. The complexes $Ru(OAc_F)_2(CO)(L_2)$ (IIa, $L_2 = (PPh_3)_2$; IIf, $L_2 = Ph_2P(CH_2)_3PPh_2$; IIg, $L_2 = Ph_2P(CH_2)_4PPh_2$) were formed by addition of ca 10-fold molar excess of $HOAc_F$ to benzene solutions of the corresponding dihydride complexes I. The resultant yellow solutions each contained two sharp singlets in their $^{31}P\{^1H\}$ NMR spectra assignable to free $HPPh_3^+$ and complexes II. Phosphorus-31 NMR spectra of the purified complexes II contain only a single broad resonance ($w_{1/2} \approx 15$ Hz). Infrared and ^{19}F NMR spectra of II show the presence of both mono- and bidentate trifluoroacetate ligands.[7] These data indicate that IIf and IIg has the same



IIf,g

structure as the parent complex IIa. The reaction of $RuH_2(CO)(PPh_3)(Ph_2PCH_2CH_2CH_2PPh_2)$ (If) with only 1 equiv of $HOAc_F$ afforded a complex mixture. At least three sets of ABX multiplets can be identified in the $^{31}P\{^1H\}$ NMR spectrum of this system (Figure 7). Proton NMR spectroscopy in the hydride region indicated that

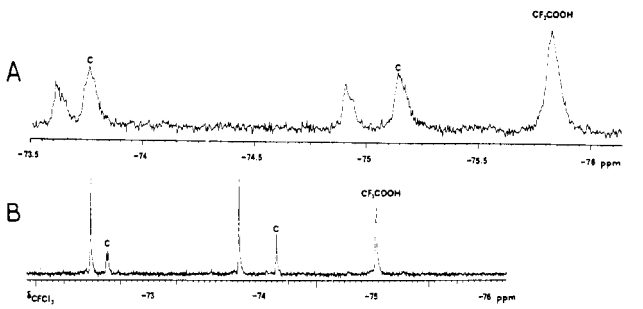


Figure 6. The 84.26-MHz ^{19}F NMR spectrum of $Ru(OAc_F)_2(CO)(PPh_3)(Arphos)\cdot HOAc_F$ (IIIe): (A) freshly prepared CH_2Cl_2 solution; (B) toluene-d_8 solution after 3 h at 100 °C in presence of 3.5 equiv of heptanal (no reaction under these conditions). "C" indicates resonances of the cis-P_2 isomer (IIIe″).

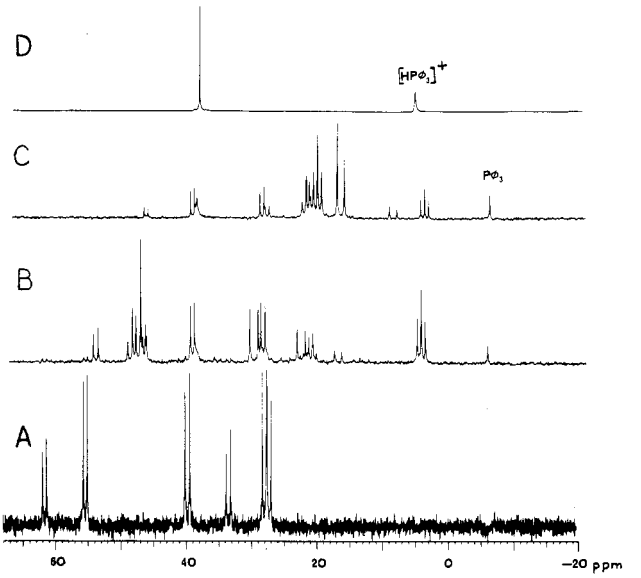
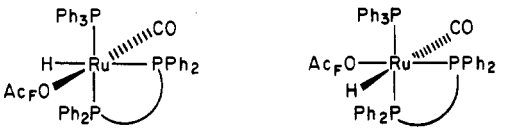


Figure 7. $^{31}P\{^1H\}$ NMR spectra (in C_6H_6): (A) $RuH_2(CO)(PPh_3)(DPPP)$ (If); (B) +1 equiv of $HOAc_F$; (C) +3 equiv of $HOAc_F$; (D) +15 equiv of $HOAc_F$.

two of the intermediates are $RuH(OAc_F)(CO)(PPh_3)(Ph_2PCH_2CH_2CH_2PPh_2)$ (IVf) isomers with the hydride trans to phosphorus (doublet of quartets, $J_{PH_{(trans)}}$ = 110 Hz) or carbonyl (octet, J_{PH} < 25 Hz). The ratio of IVf′ to IVf″ is roughly 1.9 from integration of the hydride



IVf′ IVf″

resonances. The third major complex present is $Ru(OAc_F)_2(CO)(PPh_3)(Ph_2PCH_2CH_2CH_2PPh_2)$ (IIIf, vide infra). The infrared spectrum of this mixture contained a ν(CO) band at 1934 cm^{-1} due to IVf′ and a more intense band at 1977 cm^{-1} assigned to IVf″ and IIIf. Contrast this behavior with that of Ie which formed only one isomer of IVe under the same conditions (vide supra). The infrared spectrum of IVe contained only one strong ν(CO) band at 1936 cm^{-1}.

The introduction of a second equivalent of $HOAc_F$ resulted in the disappearance of resonances due to isomer IVf″ (one set of ABX multiplets in the $^{31}P\{^1H\}$ NMR spectrum and the octet at ca. τ 12.6 in the proton spectrum). A small amount of complex IIf is also present under these conditions (broad singlet at ca. 38 ppm in the ^{31}P NMR spectrum). The strong 1977-cm^{-1} band observed

Table IV. Dehydrogenation of Cyclohexanol Using Ruthenium Catalysts

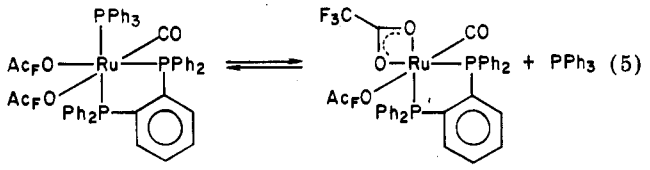
catalyst	substrate	10^5 mol of Ru	initial rate[a]	rel rate	max % reactn
$Ru(OAc_F)_2(CO)(PPh_3)_2$, IIa	cyclohexanol[b]	2.01	1.20	1.00	4.5
		4.54	(8.82)[c]		
$Ru(OAc_F)_2(CO)(PPh_3)[(Ph_2P)_2C_6H_4]$, IIId	cyclohexanol[b]	2.06	1.68	1.40	5.6[d]
$Ru(OAc_F)_2(CO)(PPh_3)(Ph_2PCH_2CH_2AsPh_2)\cdot HOAc_F$, IIIe	cyclohexanol[b]	1.75	2.76 ± 0.08	2.30	22.0
$Ru(OAc_F)_2(CO)(Ph_2PCH_2CH_2PPh_2)$, IIf	cyclohexanol[b]	2.06	4.20	3.50	17.0
IIa	ethanol[c]	4.54	0.45		
	ethanol[e]	2.62	0.074		
IIa	1-propanol[c]	4.54	1.36		
	1-propanol[e]	2.62	0.22		
IIa	2-propanol[c]	4.54	0.20		
	2-propanol[e]	2.62	0.032		
IIa	1-butanol[c]	4.54	4.1		
	1-butanol[e]	2.62	0.67		

[a] Mol of H_2 evolved/mol of Ru/min. [b] Reaction conditions: 175 °C, 5.0×10^{-2} mol of substrate, 1.3×10^{-4} mol of CF_3COOH. [c] References 1 and 2: reflux temperatures, 0.134 mol of substrate, 5.2×10^{-4} mol of CF_3COOH. [d] Kinetic run arbitrarily stopped at this maximum conversion. [e] Reference 3: reflux temperatures, 20 mL of substrate, 3×10^{-4} mol of CCl_3COOH.

previously is replaced by an asymmetric band at ca. 1970 cm^{-1} which is assigned to the ν(CO) modes of complexes IIf and IIIf. The 1934-cm^{-1} band of IV′ is still present but slowly diminishes in intensity. The reactions of complex If with trifluoroacetic acid is summarized in eq 4.

$$\text{If} \rightarrow \text{IIIf} + \text{IVf}' + \text{IVf}'' \rightarrow \text{IIf} + \text{IIIf} + \text{IVf}' \xrightarrow{HOAc_F} \text{IIf} \quad (4)$$

C. $Ru(OAc_F)_2(CO)[1,2\text{-}(Ph_2P)_2C_6H_4](PPh_3)_n$. The $^{31}P\{^1H\}$ NMR spectra of the benzene solution obtained by treating $RuH_2(CO)(PPh_3)[1,2\text{-}(Ph_2P)_2C_6H_4]$ with a ca. 8-fold excess of $HOAc_F$ contained sharp singlets due to $[HPPh_3^+]$, $Ru(OAc_F)_2(CO)[(Ph_2P)_2C_6H_4]$ (IId), and broad resonances assignable to $Ru(OAc_F)_2(CO)(PPh_3)[(Ph_2P)_2C_6H_4]$ (IIId). As in the case of complexes IIe and IIIe, the line-width differences of the resonances of IId and IIId may be caused by different exchange rates between free $HOAc_F$ and coordinated OAc_F^-. Only complex IIId was isolated from these solutions. In solution, purified complex IIId dissociated PPh_3 to yield a mixture of IIId, IId, and PPh_3.



IIId IId + PPh_3 (5)

Catalytic Activity. Alcohol Dehydrogenation. From the different solution behavior noted above, the relative activities of these complexes in catalyzing alcohol dehydrogenation can be predicted. Both complexes II and III are coordinatively saturated and cannot accommodate an additional ligand. For a vacant coordination site to be created for the activation of an alcohol molecule, the chelate trifluoroacetate ligand in complexes II must become monodentate. This bidentate–monodentate isomerization is much more facile than the required PPh_3 dissociation from complexes III.[10] Since the degree of PPh_3 dissociation is much larger with IIId, than with IIIe (at least at 25 °C), the activity order should be IIf > IIId > IIIe > IIa. Because of the unexpected, premature catalyst deactivation processes found in this study (vide infra), only a few representative bis(trifluoroacetato) complexes were screened for comparative catalytic activity.

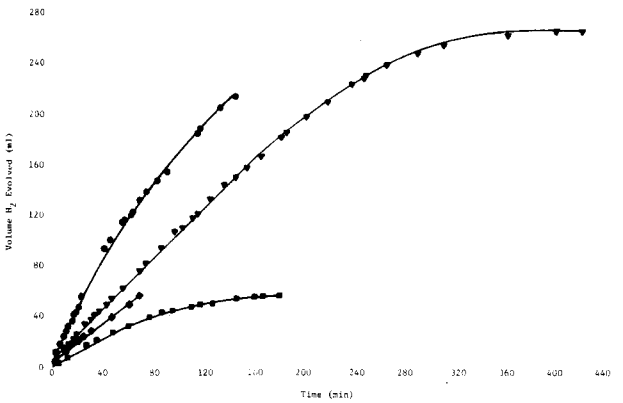


Figure 8. Dehydrogenation of cyclohexanol using catalyst: ■, $Ru(OAc_F)_2(CO)(PPh_3)_2$, ♦, $Ru(OAc_F)_2(CO)(PPh_3)[(PPh_2)_2C_6H_4]$, ▼, $Ru(OAc_F)_2(CO)(PPh_3)(Ph_2PCH_2CH_2AsPh_2)\cdot HOAc_F$, ●, $Ru(OAc_F)_2(CO)(Ph_2PCH_2CH_2CH_2PPh_2)$. Reaction conditions were 175 °C, 2.0×10^{-2} mmol of catalyst, 5.00 g of substrate, and 10.0 μL of CF_3COOH.

The rates of conversion of cyclohexanol to cyclohexanone at 175 °C using these catalysts are summarized in Table IV along with comparative data for other alcohols.[1-3] As expected, the chelate-modified catalysts are more active than $Ru(OAc_F)_2(CO)(PPh_3)_2$, IIa. The fact that IIIe is more active than IIId may indicate that the difference in the degree of PPh_3 dissociation between these two complexes at 25 °C is unimportant at higher temperatures. This point was not investigated further. The main unexpected result was that catalyst IIa deactivated rapidly, generally after roughly 100 turnovers (or ca 4% conversion). In contrast, the modified catalysts were still active to greater than 20% conversion (500 turnovers; Figure 8). The deactivation of the latter catalysts, we believe, is due in part to loss of $HOAc_F$ (bp 72 °C) at the 175 °C reaction temperature.

All of these ruthenium complexes seem to be specific for secondary alcohols. Little or no conversion of primary alcohols to aldehydes was observed. In attempts to dehydrogenate ethanol, 2-propanol, and 1-butanol at their reflux temperatures with these catalysts, very little hydrogen evolution was measured within 5 h. After the mixtures were refluxed for up to 20 h, some acetone and butanal were detected by GLC analyses, but the conversions amounted to less than two turnovers. With 1-heptanol, complexes IIa and IIe did form larger quantities of

(10) Hoffman, P. R.; Caulton, K. G. *J. Am. Chem. Soc.* **1975**, *97*, 4221.

Table V. Hydrogenation of Heptanal or Cyclohexanone with Ruthenium Catalysts[a]

catalyst	substrate	% conv	% select
$Ru(OAc_F)_2(CO)(PPh_3)_2$, IIa	heptanal	36	50
$Ru(OAc_F)_2(CO)(Ph_2PCH_2CH_2CH_2PPh_2)$, IIf	heptanal	80	68
$Ru(OAc_F)_2(CO)(PPh_3)$(Arphos)·$HOAc_F$, IIIe	heptanal	84	62
$Ru(OAc_F)_2(CO)(PPh_3)_2$, IIa	cyclohexanone	3	99
$Ru(OAc_F)_2(CO)(Ph_2PCH_2CH_2CH_2PPh_2)$, IIf	cyclohexanone	99	99
$RuH_2(CO)(Ph_3)(Ph_2PCH_2CH_2CH_2PPh_2)$, If	cyclohexanone	59	99
$Ru(OAc_F)_2(CO)(PPh_3)$(Arphos)·$HOAc_F$, IIIe	cyclohexanone	9	99

[a] Reaction conditions: 1.0 mmolal catalyst, 1.0 molal substrate in 4% *n*-decane/toluene (w/w); 84–89 °C; 20 atm of H_2; 90 min.

heptanal, with IIe approximately twice as efficient as IIa, but the reactions stopped after less than 12 catalytic cycles. No conversion of methanol to formaldehyde was observed at 150 °C with IIa or IIf in ca. 9 h (under 1400 psig argon). Because of these low catalytic activities, we felt that more detailed kinetic studies of the dehydrogenation of primary alcohols were unwarranted.

Dobson and Robinson[1] and, more recently, Rybak and Ziolkowski[3] reported that $Ru(OAc_F)_2(CO)(PPh_3)_2$, IIa, did dehydrogenate primary alcohols to aldehydes, but they disagreed on the specific activities (initial rates only) of IIa in catalyzing the conversions of ethanol, 1-propanol, and 1-butanol (Table IV). Under comparable reaction conditions, the former workers reported activities that were 6 times higher than those determined by the latter group and ca. 7 times higher than those obtained here. Both groups were vague in describing the stability of catalyst IIa. In any event, the activities of complexes II toward primary alcohols in our hands are too low to be of any practical value.

Catalyst Deactivation. The low activities and short catalyst lifetimes may in part be attributed to the loss of CF_3COOH required to regenerate complexes II from intermediates $RuH(OAc_F)(CO)L_n$ (n = 2, 3), but deactivation or decomposition of the catalyst is also a major factor.

After our unsuccessful attempt to convert cyclopentylmethanol to cyclopentylcarboxaldehyde using IIe, we analyzed the reaction mixture by $^{31}P\{^1H\}$ NMR spectroscopy. The spectrum indicated that IIe had partially decomposed to a mixture of (phosphine)ruthenium complexes during the course of the reaction (170 °C, 18.5 h, ca. 6 equiv excess $HOAc_F$). The major species present was the intermediate $RuH(OAc_F)(CO)(PPh_3)$(Arphos), IVe, indicating that the bis(trifluoroacetato) complex was not being regenerated, probably due to physical loss of $HOAc_F$ from the solution. Under these conditions, we believe most of the trifluoroacetic acid will be in vapor phase rather than in solution. The actual acid concentration in solution would be difficult to control as it depends on such variables as condenser efficiency and amount of dead space in the reactor. This problem can be resolved by continual addition of excess $HOAc_F$. The use of more than ca. 12 equiv of $HOAc_F$[1] or use of higher boiling carboxylic acids such as CCl_3COOH[1,3] results in even lower activities. However, the large differences in catalyst lifetimes between IIa and the modified chelate complexes IId–f cannot be attributed entirely to the loss of regenerating carboxylic acid.

The deactivation of catalysts II can be due to thermal decomposition or side reactions, yielding inactive products. In general, metal complexes with chelating phosphines are more thermally stable than the analogous complexes with monodentate phosphine.[11] The enhanced catalyst lifetimes of complexes IIf and IIId,e can be due in part to this chelate effect, especially at the higher temperatures required to obtain reasonable reaction rates.

Phosphorus-31 NMR analysis of a solution obtained by refluxing a mixture of IIa (0.107 mmol), $HOAc_F$ (0.72 mmol), 1-heptanol (1.00 g), and *n*-decane (10.0 g) for 4 h showed that no IIa was left at the end of the reaction. This spectrum consisted of a singlet at 28.0 ppm which we assign to $Ru(OAc_F)_2(CO)_2(PPh_3)_2$, V (lit. value:[6] 30.3 ppm in $CDCl_3$). Complex V is inert in catalyzing this conversion and could have been formed by stoichiometric decarbonylation[12] of the heptanal produced in this reaction (yield of heptanal was 4%).

$$CH_3(CH_2)_5CHO + Ru(OAc_F)_2(CO)(PPh_3)_2 \rightarrow n\text{-}C_6H_{14} + Ru(OAc_F)_2(CO)_2(PPh_3)_2 \quad (6)$$

This decarbonylation reaction was confirmed in a separate experiment in which complex IIa (0.082 mmol) was reacted with a 4.5-fold molar excess of heptanal in toluene-d_8 (2.8 mL) at 100 °C. Phosphorus-31 NMR analysis showed that ca. 10% of complex IIa had been converted to V (singlet at 29.4 ppm) within 30 min. Additional heating (2.5 h) afforded a complex mixture suggesting that other decomposition reactions had occurred. The conversion of complex IIa to V may be cleaner by using a larger excess of heptanal. A small amount of hexane was found by GLC analysis of the reaction mixture. Under the same conditions, $Ru(OAc_F)_2(CO)(PPh_3)$(Arphos), IIIe, did not react with heptanal over 3.5 h. After 13 h at 175 °C in 10% heptanol/decane, complex IIIe had decomposed mainly to $Ru(OAc_F)_2(CO)_2$(Arphos) (broad singlet at 28.2 ppm, $w_{1/2}$ = 14.5 Hz).

Prior workers[1] claimed that complex IIa was not carbonylated by alcohols, aldehydes, or ketones under conditions of dehydrogenation catalysis but did not specify which substrates, products, or reaction conditions were employed in reaching this conclusion. We have found that the formation of complex V did not occur with low boiling alcohols (e.g., methanol, ethanol, 2-propanol). However, the ruthenium catalysts studied here were ineffective in converting these alcohols to carbonyl products which poison the catalysts. This catalyst poisoning could be minimized by continuous removal of the aldehyde by fractional distillation. However, this process would also eliminate the carboxylic acid needed to regenerate the catalyst. The volatile trifluoroacetic acid could be replaced with polymer-bound carboxylic acids, but the activities of these catalysts would be greatly reduced.[3]

Hydrogenation of Ketones and Aldehydes. Since similar Ru(II) complexes have been shown to be active for the hydrogenation of aldehydes and ketones to alcohols,[13–15] we set out to also study our diphosphine com-

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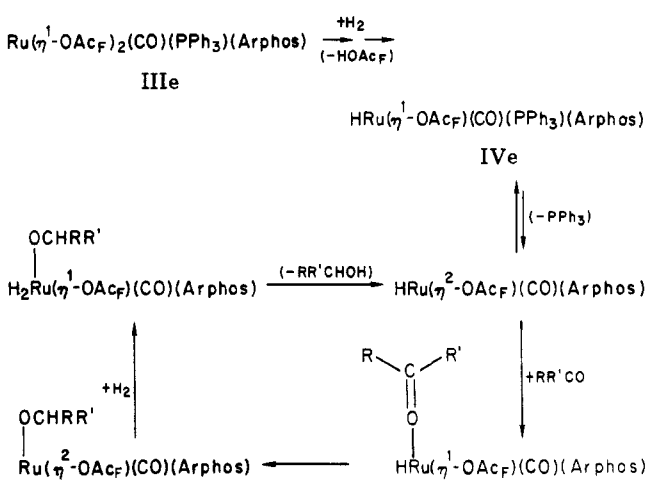
Scheme II



plexes as hydrogenation catalysts, compare their activities to IIa, and compare the conditions necessary for hydrogenation vs. dehydrogenation. The reaction sequence shown in Scheme I can be reversed to envision the reduction of carbonyl compounds to alcohols. Strohmier and Weigelt[14] reported that $RuH_2(CO)(PPh_3)_3$ (Ia) and $Ru(OAc_F)_2(CO)(PPh_3)_2$ (IIa) catalyze ketone hydrogenation. We have found that the modified complexes If, IIf, and IIIe are much more efficient hydrogenation catalysts than IIa (Table V). Complex Ia was not screened in this work, but Strohmeier and Weigelt[14] reported that IIa is much more efficient than Ia in catalyzing cyclohexanone hydrogenation.

After GLC analyses, the reaction mixtures were analyzed by $^{31}P\{^1H\}$ NMR spectroscopy. In the hydrogenation of heptanal, catalysts IIa, IIIe, and IIf were not present at the end of the reaction. The first catalyst was almost entirely converted to $Ru(OAc_F)_2(CO)_2(PPh_3)_2$, V, by decarbonylation of heptanal. The lower heptanal conversion with this catalyst may be due to this premature catalyst poisoning. Complex IIf appears to have similarly reacted to form the analogous complex $Ru(OAc_F)_2(CO)_2(Ph_2PCH_2CH_2CH_2PPh_2)$ ($^{31}P\{^1H\}$ NMR: broad singlet at 32.90 ppm, $w_{1/2}\sim 7$ Hz). The ^{31}P NMR spectrum of a reaction mixture with catalyst IIIe contained a large, broad singlet at 28 ppm which is attributable to $Ru(OAc_F)_2(CO)_2$(Arphos) and numerous resonances in the 55–to 75-ppm region. Apparently, complex IIIe decomposed under these reaction conditions to yield a mixture of catalytically active, (phosphine)ruthenium complexes (no free PPh_3 or $Ph_2PCH_2CH_2AsPh_2$ was observed).

In cyclohexanone hydrogenation, the catalysts can be divided into two categories. Phosphorus-31 NMR analyses indicated that the less active catalysts IIa and IIIe did not decompose during the reaction. Approximately 35% of IIa decarbonylated cyclohexanone to yield $Ru(OAc_F)_2(CO)_2(PPh_3)_2$, V. This deactivation process was not as extensive as that found in IIa-catalyzed heptanal hydrogenations. Transition-metal complexes stoichiometrically decarbonylate aldehydes more readily than ketones.[12]

Only $RuH(OAc_F)(CO)(PPh_3)$(Arphos), IVe, was detected in solution when IIIe was used. Complex IVe is probably the actual catalyst precursor in this reaction (Scheme II). The catalytic cycle shown in Scheme II is essentially the reverse of that shown in Scheme I.

The fact that complex IIIe is roughly 3 times as active as IIa in cyclohexanone hydrogenation suggests that the isomer of intermediate $HRu(\eta^2\text{-}OAc_F)(CO)(PPh_3)_2$ with trans-PPh_3 ligands (*g* in Scheme I) which inhibits the IIa-catalyzed dehydrogenation of alcohols[1] also inhibits the reverse reaction (ketone hydrogenation). The Arphos analogue, $HRu(\eta^2\text{-}OAc_F)(CO)(Ph_2PCH_2CH_2AsPh_2)$, cannot form an analogous inactive intermediate due to the steric constraints imposed by the chelate ligand.

The most active cyclohexanone hydrogenation catalyst $Ru(OAc_F)_2(CO)(Ph_2PCH_2CH_2CH_2PPh_2)$, IIf, was converted to a mixture of ruthenium complexes with broad resonances in the 37–43-ppm region of the $^{31}P\{^1H\}$ NMR spectrum (the phosphorus NMR spectrum of complex IIf consists of a broad singlet ($w_{1/2}$ = 14 Hz) at 37.8 ppm in CH_2Cl_2 solution). Sanchez-Delgado and co-workers[13,15] studied the kinetics of aldehyde and ketone hydrogenation using a variety of (phosphine)ruthenium catalysts and found that the most efficient catalyst tested, $RuHCl(CO)(PPh_3)_3$, decomposed during the reaction to an intractable mixture of ruthenium species which actually catalyzed the reaction. Our most active chelate-modified catalysts appear to similarly decompose to yield mixtures with activities comparable to those generated by the decomposition of $RuHCl(CO)(PPh_3)_3$.

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Note Added in Proof. S. D. Robinson[16] has suggested that the discrepancy in the catalytic activities of complex IIa may be due to differences in the configuration of our reactor systems. The larger dead space, or less efficient condensor used in the work described in ref 1 and 2, may have resulted in lower concentrations of aldehyde or ketone in solution, thus retarding the rate of catalyst deactivation. However, this phenomenon would also decrease the catalytic activity due to decreased concentration of trifluoroacetic acid. Since we both agree that there is no hydrogen evolution from reaction of methanol, it is clear that there was no constant source of error leading them to systematic over estimation of their rates of gas evolution.

Registry No. Ia, 22337-78-6; Ib, 80515-23-7; Ic, 80515-24-8; Id, 80515-35-1; Ie, 80515-25-9; If, 80515-26-0; Ig, 80515-27-1; Ih, 80581-15-3; IIa, 80558-89-0; IId, 80515-28-2; IIf, 80515-29-3; IIg, 80515-30-6; IIId, 80515-31-7; IIIe′, 80515-32-8; IIIe″, 80558-90-3; IIIf, 80515-33-9; IVa, 61966-66-3; IVe, 80532-10-1; IVf′, 80515-34-0; IVf″, 80558-91-4.

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