Instead, the entire Mo–O–C–O–Mo ring is enlarged.[15] Populating the π^* orbital has only a small effect on the Mo–Mo bond length.

Acknowledgment. The support of the National Science Foundation is gratefully acknowledged. The authors thank Dr. E. J. Heller for helpful discussions and Prof. W. Trogler for the absorption spectrum.

Registry No. Tetrakis(μ-trifluoroacetato)dimolybdenum(III), 36608-07-8.

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[15] With a localized-bond stretching model, which neglects coupling to other normal modes, these bond lengthenings are roughly estimated to be Mo–O = 0.03 Å and O–C = 0.006 Å.

Articles

Contribution from the Departments of Chemistry, University of Nevada, Reno, Nevada 89557, and University of Hawaii at Manoa, Honolulu, Hawaii 96822, and Equipe CNRS/SNPE, 94320 Thiais, France

Ruthenium(II) Complexes of 1-Substituted 3,4-Dimethylphospholes

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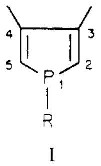
Several ruthenium(II) complexes of 1-substituted 3,4-dimethylphospholes, (RDMP, R = CH_3, n-C_4H_9, t-C_4H_9, C_6H_5, and $C_6H_5CH_2$) have been prepared and characterized by elemental analyses and infrared and ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy. Stable carbonyl complexes of the types *cis*- and *trans*-$Ru(CO)_2(RDMP)_2Cl_2$ and one example of $(RDMP)_3Ru(CO)Cl_2$ (R = C_6H_5) were prepared. In each case, the kinetically formed *trans*-$(RDMP)_2Ru(CO)_2Cl_2$ thermally isomerizes smoothly to the thermodynamically stable *cis*-$(RDMP)_2Ru(CO)_2Cl_2$. These phospholes are shown to be better donors than PPh_3 toward ruthenium(II) as they readily displace PPh_3 from $(PPh_3)_4RuCl_2$ in refluxing hexane to produce *cis*- and *trans*-$(RDMP)_4RuCl_2$ (R = CH_3, n-C_4H_9, C_6H_5, and $C_6H_5CH_2$) in moderate yield. With the sterically more bulky 1-t-C_4H_9DMP, the pentacoordinate $(t\text{-BuDMP})_2(PPh_3)RuCl_2$ is obtained under these same conditions. The kinetically formed *trans*-$(RDMP)_4RuCl_2$ complexes only slowly dissociate in solution and undergo both thermal and photochemical isomerization to the thermodynamically stable *cis*-$(RDMP)_4RuCl_2$ with some attendant decomposition. The pentacoordinate $(t\text{-BuDMP})_2(PPh_3)RuCl_2$ is much more dissociately stable than $(PPh_3)_3RuCl_2$ and displays phosphorus–phosphorus coupling at room temperature whereas, for $(PPh_3)_3RuCl_2$, this coupling is not observable above −90 °C in CH_2Cl_2 solutions. The crystal structure of $(PhDMP)_3Ru(CO)Cl_2$ has been determined by three-dimensional X-ray diffraction techniques. The molecule crystallizes in the triclinic space group $P\bar{1}$ in a unit cell of dimensions a = 13.789 (2) Å, b = 14.752 (3) Å, c = 9.915 (2) Å, α = 98.37 (1)°, β = 111.80 (1)°, γ = 95.08 (1)°, ρ_{calcd} = 1.39 g cm^{-3}, and ρ_{obsd} = 1.40 (5) g cm^{-3} with Z = 2. Refinement converged to R = 0.039 with 4235 independent reflections. Within this molecule, there exist interesting charge-transfer type interactions which seemingly stabilize one particular isomeric configuration. Some of these complexes have been shown to catalyze the hydrogenation of 1-heptene at ambient temperature and pressure at rates comparable to this same catalysis by $(Ph_3P)_3RuCl_2$.

Introduction

In the last decade, considerable interest has been focused on the chemistry of phospholes.[2] Phospholes (I) are structurally similar to the aromatic pyrroles but debate continues as to whether phospholes are aromatic.[2] Evidence supporting some degree of cyclic conjugation in phospholes is based upon[3] complexation experiments and pK_a values, the low rates of quaternization[4] of various phospholes, low phosphorus inversion barriers in phospholes,[5] comparative bond lengths of phospholes and phosphines,[6a] low bond energies of the P=O bond[6b] in some phosphole oxides, and theoretical studies.[7] Overall, these studies indicate that unsubstituted phospholes have limited basicity, are sterically compact, and exhibit variable amounts of delocalization of the phosphorus lone pair. Ring substitution by methyl groups increases the phosphorus donor ability considerably such that stable complexes of the type $(RDMP)_2PdX_2$[8] and $(RDMP)_2PtX_2$[9] are easily formed.



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structure and ring-numbering scheme of 1-R-3,4-dimethylphospholes

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Ruthenium(II) phosphine complexes have been found to be both efficient and selective hydrogenation catalysts[10] with both the catalytic efficiency and the selectivity being greatly dependent upon the nature of the complex. Catalysis by these species is thought to involve phosphine dissociation as a primary step. If these phospholes (RDMP) do indeed provide substitutionally labile complexes, they might be very effective catalysts, *particularly since they are sterically compact.* In addition, it has been found[11] that the complex $RhH(PDBP)_4$ (PDBP = 1-phenyldibenzophosphole) is 7 times more active as a hydrogenation catalyst than the well-known Wilkinson's catalyst $RhCl(PPh_3)_3$, as well as being quite air stable. For these reasons, we have prepared and characterized a series of ruthenium(II) complexes of 1-R-3,4-dimethylphospholes (RDMP), examined their solution behavior, and commenced an investigation of their catalytic activity. For comparison, two complexes of PDBP were also prepared.

Experimental Section

A. Reagents and Physical Measurements. Reagent grade chemicals were used as received or synthesized as described below. All solvents were dried when necessary by standard procedures and stored over Linde 4-Å molecular sieves. Melting points were determined on a Meltemp apparatus and are uncorrected. Elemental analyses were performed by Chemalytics Inc., Tempe, AZ 85282, and Galbraith Laboratories, Inc., Knoxville, TN 37921.

Infrared spectra were recorded on a Perkin-Elmer 599 spectrophotometer as Nujol mulls between CsBr plates.

Electronic spectra were recorded on a Cary 14 spectrophotometer as $CHCl_3$ solutions in 1-cm quartz cells.

The ^{1}H, $^{13}C\{^{1}H\}$, and $^{31}P\{^{1}H\}$ NMR spectra were recorded at 99.54, 25.00, and 40.26 MHz, respectively, on a JEOL FX-100 spectrometer in the FT mode. (The $^{1}H\{^{31}P\}$ NMR spectra were obtained at 100 MHz on a Varian XL-100 spectrometer equipped with a gyrocode frequency synthesizer.) Proton and carbon chemical shifts are downfield relative to internal Me_4Si, while the phosphorus chemical shifts were measured relative to external PPh_3 and corrected to 85% H_3PO_4. A positive sign on the phosphorus chemical shift indicates a downfield position relative to H_3PO_4. Preparation of samples for NMR analyses has been previously described.[12]

Photolyses were carried out in 10-mm Pyrex NMR tubes with use of a hand-held ultraviolet mineral lamp. The progress of the photolyses was monitored by $^{31}P\{^{1}H\}$ NMR spectroscopy.

B. Syntheses. 1. Phospholes. The phospholes, prepared as described previously,[13] are moderately air sensitive and were handled under a nitrogen atmosphere.

2. Bis(phosphole)ruthenium(II) Carbonyl Complexes. The dichlorodicarbonylbis(1-R-3,4-dimethylphosphole)ruthenium complexes were prepared by a slight modification of literature preparations for similar complexes.[14-16] The methods used are exemplified below for the cis and trans complexes of 1-*tert*-butyl-3,4-dimethylphosphole (L) of the type $L_2Ru(CO)_2Cl_2$.

***cis*-Dichlorodicarbonylbis(1-*tert*-butyl-3,4-dimethylphosphole)ruthenium(II).** A solution of 2.24 g (8.55 mmol) of $RuCl_3{\cdot}3H_2O$ in 90 mL of 2-methoxyethanol was refluxed and stirred as carbon monoxide was bubbled through it for 4 h to produce a yellow solution. To that solution was added 2.10 g (12.48 mmol) of 1-*tert*-butyl-3,4-dimethylphosphole, and the solution was refluxed and some solvent was removed with the aid of a Dean–Stark trap until a colorless solid appeared. The solution was cooled, and the off-white solid was removed by filtration, washed with anhydrous diethyl ether, and vacuum-dried, giving a 27% yield of the cis complex; dec pt 252 °C. Anal. Calcd for $C_{22}H_{34}Cl_2RuP_2O_2$: C, 46.83; H, 6.03. Found: C, 46.98; H, 6.15.

***trans*-Dichlorodicarbonylbis(1-*tert*-butyl-3,4-dimethylphosphole)ruthenium(II).** Similarly, a solution containing 1.52 g (5.8 mmol) of $RuCl_3{\cdot}3H_2O$ in 50 mL of absolute ethanol was refluxed and stirred while carbon monoxide was bubbled through it for 5 h. To that *cooled* solution was added 2.00 g (12.0 mmol) of 1-*tert*-butyl-3,4-dimethylphosphole, and the solution was allowed to sit at room temperature until a yellow-orange solid was apparent. The solid was removed by filtration, washed with anhydrous diethyl ether, and vacuum-dried, giving a 50% yield; dec pt 150 °C. Anal. Calcd for $C_{22}H_{34}Cl_2RuP_2O_2$: C, 46.83; H, 6.03. Found: C, 46.59; H, 5.91.

In a similar manner, the following complexes were prepared.

***cis*-Dichlorodicarbonylbis(1-phenyl-3,4-dimethylphosphole)ruthenium(II).** The yield was 56%. Anal. Calcd for $C_{26}H_{26}Cl_2RuP_2O_2$: C, 51.66; H, 4.30. Found: C, 51.11; H, 4.71. The complex is a colorless solid, mp 208–213 °C.

***trans*-Dichlorodicarbonylbis(1-*n*-butyl-3,4-dimethylphosphole)ruthenium(II)–(ethanol) (1/2).** The yield was 8.7%. Anal. Calcd for $C_{26}H_{46}Cl_2RuP_2O_4$: C, 47.71; H, 7.03. Found: C, 48.15; H, 7.06. The complex is a yellow solid, mp 168–172 °C. IR and NMR spectroscopy confirmed the presence of ethanol.

***cis*-Dichlorodicarbonylbis(1-*n*-butyl-3,4-dimethylphosphole)ruthenium(II).** The yield was 38%. Anal. Calcd for $C_{22}H_{34}Cl_2RuP_2O_2$: C, 46.83; H, 6.03. Found: C, 46.60; H, 5.68. The complex is a colorless solid, mp 119–122 °C.

***trans*-Dichlorodicarbonylbis(1-benzyl-3,4-dimethylphosphole)ruthenium(II).** The yield was 4.2%. Anal. Calcd for $C_{28}H_{30}Cl_2O_2P_2Ru$: C, 53.21; H, 4.75. Found: C, 53.61; H, 4.56. The complex is a yellow solid, mp 143–145 °C.

***trans*-Dichlorodicarbonylbis(1-methyl-3,4-dimethylphosphole)ruthenium(II).** The yield was 51.9%. The complex is a yellow solid, dec pt 112 °C. Spectral data (vide infra) indicate that this material is an impure mixture, and attempts at purification by recrystallization and column chromatography were unsuccessful.

***trans*-Dichlorodicarbonylbis(1-phenyldibenzophosphole)ruthenium(II).** The yield was 52%. Anal. Calcd for $C_{38}H_{26}Cl_2P_2O_2Ru$: C, 60.99; H, 3.47. Found: C, 60.63; H, 3.62. The complex is a yellow solid, dec pt 310–315 °C.

***cis*-Dichlorodicarbonylbis(1-phenyldibenzophosphole)ruthenium(II).** The yield was 29.1%. Anal. Calcd for $C_{38}H_{26}Cl_2P_2O_2Ru$: C, 60.99; H, 3.47. Found: C, 60.80; H, 3.36. The complex is an off-white solid, dec pt 308–310 °C.

Dichlorocarbonyltris(1-phenyl-3,4-dimethylphosphole)ruthenium(II). This complex formed as gold crystals, mp 202–208 °C, as the first product to separate from solution in one preparation of the *trans*-$L_2Ru(CO)_2Cl_2$ complex in 37% yield. Attempts to increase the yield of this complex and to prepare other tris(phosphole) complexes by running reactions with a 3:1 ligand to metal ratio were unsuccessful. In each case an inseparable mixture of products was obtained. Anal. Calcd for $C_{37}H_{39}Cl_2OP_3Ru$: C, 58.14; H, 5.10. Found: C, 57.74; H, 5.11.

3. RuL_nCl_2 Complexes. These complexes were prepared by a simple ligand substitution reaction between the complex $RuCl_2(PPh_3)_4$ and the phosphole ligand.[17,18] The dichlorotetrakis(triphenylphosphine)ruthenium(II) complex was prepared by literature methods.[19] An exemplary substitution reaction is given below.

Dichlorotetrakis(1-phenyl-3,4-dimethylphosphole)ruthenium(II). To a solution of 2.39 g (2.5 mmol) of $RuCl_2(PPh_3)_4$ in 50 mL of degassed hexane was added 1.89 g (10.1 mmol) of 1-phenyl-3,4-dimethylphosphole. The solution was stirred and refluxed under nitrogen for 1.5 h and then cooled. The pink solid (trans isomer) that resulted was separated by filtration, washed with anhydrous diethyl ether, and vacuum-dried for a yield of 74.5%; mp 208–213 °C. Anal. Calcd for $C_{48}H_{42}Cl_2RuP_4$: C, 62.33; H, 5.62. Found: C, 62.39; H, 5.88. After 8 h of reflux, a 98% yield of salmon-colored microcrystals (dec pt 220–222 °C) that is 84.7% cis and 15.3% trans was obtained. Recrystallization from CH_2Cl_2/Et_2O under nitrogen produced yellow crystals of the pure cis isomer (dec pt 225–226 °C).

In a similar manner, the following complexes were prepared.

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Dichlorotetrakis(1-methyl-3,4-dimethylphosphole)ruthenium(II). For the orange trans isomer, the yield was 15.9%. Anal. Calcd for $C_{28}H_{44}Cl_2RuP_4$: C, 49.20; H, 6.51. Found: C, 49.88; H, 6.63. It isomerizes at 160 °C; mp 186–189 °C. For the yellow cis isomer (isolated from the filtrate), the yield was 3.6%; mp 186–189 °C. Anal. Calcd for $C_{28}H_{44}Cl_2RuP_4$: C, 49.20; H, 6.51. Found: C, 49.64; H, 6.44.

Refluxing in hexane for 6 h and isolating as above produces a 24% yield of the cis isomer.

Dichlorotriphenylphosphinebis(1-*tert*-butyl-3,4-dimethylphosphole)ruthenium(II). After 6 h of reflux, the solution was filtered hot and the purple solid was washed with 50 mL of hexane and 50 mL of diethyl ether and vacuum-dried. The yield was 76.5%: purple solid; mp 190–192 °C. Anal. Calcd for $C_{38}H_{41}Cl_2P_3Ru$: C, 59.22; H, 6.36. Found: C, 58.93; H, 6.58.

In a procedure performed as shown above in CH_2Cl_2 solution, a brown solid was precipitated by addition of hexane in 10% yield. This material was shown to be *trans*-L_4RuCl_2 by ^1H and ^{31}P NMR.

Dichlorotetrakis(1-benzyl-3,4-dimethylphosphole)ruthenium(II). For the yellow cis isomer, the yield was 64.3%; mp 170–176 °C. For the orange trans isomer, the yield was 23.5%; dec pt 120–122 °C. The two isomers were made via the same method at different times, with some differences in reaction conditions. The yellow isomer was prepared with slightly less than a stoichiometric amount of ligand and crystallized upon loss of solvent at room temperature. The orange isomer was prepared with slightly more than a stoichiometric amount of ligand and crystallized following refrigeration for several days.

C. Hydrogenation Reactions. Several successful hydrogenation reactions were performed to qualitatively determine the catalytic activity of several of the newly prepared compounds. All reactions were carried out in a like manner, as illustrated by the following example.

Hydrogenation of 1-Heptene. A solution 1.4 M in 1-heptene and 2×10^{-3} M in catalyst (e.g. $RuCl_2(PPh_3)_4$, $RuCl_2(CH_3DMP)_4$, $RuCl_2(t\text{-}BuDMP)_2(PPh_3)$, *cis*-$(Bzl_3P)_2Ru(CO)_2Cl_2$ (Bzl ≡ benzyl)) in benzene/absolute ethanol (1:1) was stirred at ambient temperature and pressure while hydrogen was bubbled through the solution. Small aliquots of the solution were periodically removed for characterization of the species in solution by gas chromatography. Retention times were as follows for a 6 ft × $^1/_4$ in. Carbowax 20 M column in which T_1 = 75 °C and T_2 = 100 °C with a temperature rise rate of 8 °C/min: heptane, 42 s; 1-heptene, 54 s; absolute ethanol, 104 s; benzene, 113 s.

D. X-ray Data Collection. 1. Diffraction. A clear orange 0.14 × 0.20 × 0.26 mm parrallelepiped of $(PhDMP)_3Ru(CO)Cl_2$ was mounted in a fine glass capillary and aligned approximately parallel to the longest dimension. Diffraction intensities were collected at 27–32 °C on a Syntex four-circle computer-controlled diffractometer with graphite-monochromatized Mo Kα radiation (Kα_1, λ = 0.709 30 Å; Kα_2, λ = 0.71309 Å). The cell constants and their standard deviations (see Crystal Data) were determined by a least-squares treatment of the angular coordinates of 15 independent reflections with 2θ values up to 19.2°. Each reflection was scanned at a constant rate of 2.0° min^{-1} by the θ–2θ technique with a scan range ±0.8° (2θ) around the Kα_1–Kα_2 angles. The background to scan time ratio was 1.0.

The intensities of 3 standard reflections, measured every 100 reflections, showed significant anisotropic decreases in intensity (one decreased by 26%, one by 33%, and the third by 3% during the course of data collection). Changes in the centering of the peak profiles of these check reflections were noted also. Consequently, the crystal was recentered three times during data collection and a decay correction based on the mean decrease in the intensities of the check reflections was applied. The cell constants obtained for each centering procedure show small, but concerted, changes (Table I, supplementary material). Similar behavior had been observed earlier for another crystal of this material that had been mounted on the tip of a glass rod. It was thought that the crystal had been improperly mounted, so a second crystal (the one reported here) was mounted in a fine glass capillary. This does not seem to have remedied the problems observed with the first crystal. So it appears that the crystal is in fact changing upon exposure to X-rays.

Standard deviations were assigned according to the formula

$$\sigma(I) = [(\mathrm{CT} + B_1 + B_2)\omega^2 + (pI)^2]^{1/2}$$

where CT is the total integrated count, B_1 and B_2 are the background counts, and the intensity is $I = \omega(\mathrm{CT} - B_1 - B_2)$. A value of 0.02 was assigned to the empirical parameter p to account for instrumental inaccuracies. The weights (w) used in the least-squares refinement of the structural parameters were the reciprocal squares of $\sigma(F_o)$. Of the 6491 unique reflections measured (those for which $2\theta < 50°$), 4235 had intensities such that $I > 3\sigma(I)$. All intensities were corrected for Lorentz and polarization effects.[20] The monochromator crystal was assumed to be half-perfect and half-mosaic in character in the polarization correction. An absorption correction[21] (μ = 7.21 cm^{-1}) which approximated the crystal shape by a 6 × 6 × 6 grid was applied; the calculated transmission coefficients ranged from 0.864 and 0.918. The atomic scattering factors for Ru^0, P^0, Cl^0, O^0, C^0, and H (bonded) were used; all but hydrogen were modified to include the real part of the anomalous dispersion correction.[24]

2. Crystal Data: $(Ph\text{-}DMP)_3Ru(CO)Cl_2$, triclinic, $P\bar{1}$, a = 13.789 (2) Å, b = 14.752 (3) Å, c = 9.915 (2) Å, α = 98.37 (1)°, β = 111.80 (1)°, γ = 95.08 (1)°, V = 1830.2 (6) Å^3, mol wt 764.6, ρ_{obsd}(flotation) = 1.40 (5) g cm^{-3}, ρ_{calcd} = 1.39 g cm^3, Z = 2.

3. Structure Determination. The positions of the ruthenium and four of the atoms in its coordination sphere (later identified as C(4), P(6), P(19), and P(32)) were learned from a three-dimensional Patterson function prepared with use of the fast-Fourier algorithm.[25] With the space group $P\bar{1}$ being assumed, the positions of 35 of the 44 non-hydrogen atoms in the structure were located on successive Fourier syntheses. Two cycles of full-matrix least-squares refinement[26] of these 35 atomic positions followed by a difference Fourier function allowed the remaining 9 atoms to be located. In order to reduce the cost of subsequent least-squares refinements, the Ru coordination sphere and the individual phenyl and phosphole rings were refined separately. Two cycles of isotropic (anisotropic for Ru, Cl, and P atoms) refinement followed by two cycles of anisotropic refinement led to the error indices $R_1 = \sum||F_o| - |F_c||/\sum F_o = 0.058$ and $R_2 = [\sum w(F_o - |F_c|)^2/\sum wF_o^2]^{1/2} = 0.062$. The 21 planar hydrogen positions were calculated with the assumption of a C–H distance of 1.00 Å. A difference function showed peaks in the vicinity of each of these calculated positions. Two more cycles of least-squares refinement with the calculated hydrogen positions included in the structure but held fixed in refinement resulted in R_1 = 0.048 and R_2 = 0.054. A subsequent difference function revealed 10 of the 18 methyl hydrogens clearly, and these positions were used to calculate the remaining ones. Several more cycles of least-squares refinements, still one ring or coordination sphere at a time, with hydrogen positions and isotropic thermal parameters (those of the adjacent C atoms were used) held fixed, led to the final error indices R_1 = 0.041 and R_2 = 0.039. The "goodness-of-fit", $[\sum w(F_o - |F_c|)^2/(m - s)]^{1/2}$, is 1.86. The number of observations used in least-squares refinement (4235) is m, and s (397) is the total number of parameters (although only a maximum of 64 were ever refined at one time). The overdetermination ratio (m/s) is 10.7. In the final cycle of refinement, all shifts were less than their corresponding esd's. The largest peak on the final difference function, whose esd was 0.07 e Å^{-3}, was 1.0 e Å^{-3} and was located very near the Ru(II) ion at a chemically implausible position.

Results and Discussion

A. Carbonyl Complexes. When solutions of $RuCl_3{\cdot}3H_2O$ in 2-methoxyethanol or absolute ethanol are refluxed under carbon monoxide and a phosphole is added, complexes of the type $L_2Ru(CO)_2Cl_2$ are formed, which is similar to the behavior of benzylphosphine ligands.[27] Of the five possible

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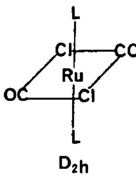
isomers for these complexes (II–VI), isomers II (referred to



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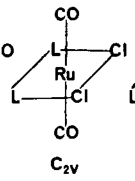

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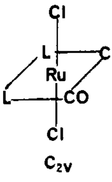
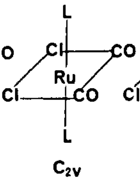
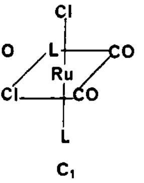


IV



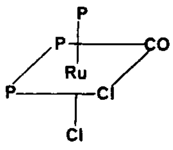
V



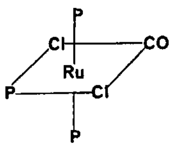
VI

as trans) and V (referred to as cis) were formed predominantly in ethanol and 2-methoxyethanol, respectively. However, the infrared and NMR data for *cis*-(*t*-BuDMP)$_2$Ru(CO)$_2$Cl$_2$ suggest that the isolated solid is a mixture of isomers IV and VI (the all-cis isomer). The yellow to orange trans isomer (II) is the initial kinetic isomer; it is formed at room temperature in ethanol and undergoes thermal isomerization to the thermodyamically stable, colorless cis isomer (V) under reflux in 2-methoxyethanol. With one of the phospholes (PhDMP) the monocarbonyl complex L$_3$Ru(CO)Cl$_2$ formed in reasonable yield from solutions containing only 2 mol of phosphole/mol of ruthenium, suggesting that these phospholes very readily replace carbon monoxide. Attempts at increasing the yield of this complex by running reactions with 3:1 ligand to metal ratios were unsuccessful as in each case an inseparable mixture of products was formed. ^{31}P NMR of the crude reaction mixtures indicated the presence of L$_3$RuCOCl$_2$, L$_2$Ru(CO)$_2$Cl$_2$, and L$_4$RuCl$_2$, further substantiating the ease of replacement of carbon monoxide by phospholes. The isolated complexes were characterized by infrared, ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} spectroscopy, elemental analyses, and in the case of (PhDMP)$_3$RuCOCl$_2$, an X-ray crystal structure.

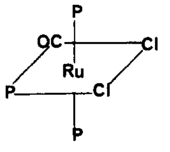
1. Infrared Spectroscopy. The infrared spectral data (Table I) for the dicarbonyl complexes are consistent with what would be expected[28-30] for isomers II and V, except for the colorless (*t*-BuDMP)$_2$Ru(CO)$_2$Cl$_2$. For this complex, the observation of four ν_{CO} and four ν_{RuCl} vibrations suggests that it is a mixture of isomers IV and VI. The monocarbonyl phosphole complex L$_3$Ru(CO)Cl$_2$ exhibits only one ν_{CO} (2000 cm^{-1}) and two ν_{RuCl} bands (325, 375 cm^{-1}). There are three possible isomers for this complex (VII–IX).



VII



VIII



IX

Both ν_{CO} and ν_{RuCl} energies should be affected by the trans influence[31,32] and trans effect (P > CO > Cl)[33] of the other ligands. The high energies of ν_{CO} and ν_{RuCl} led us to suggest that (PhDMP)$_3$RuCOCl$_2$ possesses structure VIII. Structure VII is not consistent with the ^{31}P NMR data (δ 26.7 (d), 20.2 (t); $^2J_{PP}$ = 35.4 Hz). Moreover, X-ray crystallographic data for (PhDMP)$_3$RuCOCl$_2$ confirm structure VIII (vide infra) and Shaw et al.[34] have isolated and supported both structures VIII and IX for (Me$_2$PPh)$_3$RuCOCl$_2$ on the basis of infrared, dipole moment, and ^{1}H NMR data.

Table I. Infrared Spectral Data for L$_2$Ru(CO)$_2$Cl$_2$ [a] (L = Phosphole)

L	isomer	ν_{CO}, cm^{-1}	ν_{RuCl}, cm^{-1}
PhDBP	trans	2000	337
	cis	1980, 2035	290, 337
PhDMP	cis	1990, 2055	285, 312
BzlDMP	trans	2010	327
	cis	2040, 1984	
n-BuDMP	cis	1985, 2043	285, 310
t-BuDMP	trans	1995	330
	cis[b]	1982, 2002, 2020, 2070	335, 320, 290, 272

[a] Nujol mulls on CsBr windows. [b] Sample appears to be an inseparable mixture of cis and all-cis isomers.

Table II. ^{1}H NMR Data for *cis*- and *trans*-(RDMP)$_2$Ru(CO)$_2$Cl$_2$

R	geom	chem shift[a] (line shape,[b] "J"[c]) CH$_3$	ring H	R
Ph	cis	2.12 (s)	6.74 (f, 33.0)	7.4 (m)
Bzl	trans	1.86 (s)	6.5 (f, 32.5)	3.68 (t, 6.1), 7.14 (m)
Bzl	cis	1.78 (s)	6.28 (f, 34)	3.70 (t, 9), 6.9 (m)
n-Bu	cis	2.13 (s)	6.5 (f, 34.7)	3.4 (m), 1.26 (m), 0.83 (t, 11.8)
t-Bu	trans	2.12 (s)	6.7 (f, 31.2)	1.31 (t, 15.1)
t-Bu	cis[d]	2.09 (s)	6.52 (f, 32.6), 6.37 (f, 32.6)	2.09 (s), 1.25 (f, 17.8), 1.17 (f, 17.8)

[a] Chemical shifts are in ppm and relative to Me$_4$Si in CDCl$_3$. [b] Abbreviations: s = singlet, d = doublet, t = triplet, f = filled-in doublet, m = undefined multiplet. [c] "J" = $|^nJ_{PH} + {}^{n+2}J_{PH}|$ (in Hz). [d] Appears to be an inseparable mixture of cis and all-cis isomers.

2. ^{1}H NMR Spectroscopy. The geometry of most bis(phosphine) transition-metal complexes can be ascertained via ^{1}H NMR if the phosphine ligands contain α-methyl or α-methylene groups,[35] since these groups exhibit the phenomenon of "virtual coupling". For trans complexes where $^2J_{PP}$ is typically[36] >200 Hz, the α-methyl or α-methylene resonances appear as 1:2:1 triplets, whereas for cis complexes, $^2J_{PP}$ is typically[36] less than 40 Hz and 1:1 doublets are observed for these resonances. For the (RDMP)$_2$Ru(CO)$_2$Cl$_2$ complexes, the ring hydrogen resonances (Table II) all exhibit filled-in doublets for both isomers. Their peak intensities are relatively weak, and the line shapes are not consistent with those of other resonances in the same spectrum. Consequently, they provide little structural information. The complexes *trans*-(PhCH$_2$DMP)$_2$Ru(CO)$_2$Cl$_2$ and *trans*-(*t*-BuDMP)$_2$Ru(CO)$_2$Cl$_2$ were assigned the trans geometry on the basis of the benzyl CH$_2$ and *t*-Bu methyl resonances (both of which were 1:2:1 triplets) and the infrared spectrum, which showed single ν_{CO} and ν_{RuCl} vibrations. The ^{1}H NMR of *cis*-(*t*-BuDMP)$_2$Ru(CO)$_2$Cl$_2$ shows two filled-in doublets for both the ring methylidene and *t*-Bu methyl resonances, suggesting that this complex is a mixture of isomers IV and VI as was also concluded from the infrared spectrum. These results indicate that for all but the most bulky phosphole (*t*-BuDMP) the phospholes are mutually trans in the (RDMP)$_2$Ru(CO)$_2$Cl$_2$ complexes, but the evidence is not conclusive due to the potential ambiguities in structural assignment by ^{1}H NMR for complexes of phospholes.[8,9]

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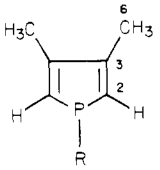
Table III. $^{13}C\{^1H\}$ NMR Data for *cis*- and *trans*-$(RDMP)_2Ru(CO)_2Cl_2$



R	geom	chem shift[a] (line shape,[b] "J"[c]) C$_6$	C$_3$	C$_2$	R
Ph	cis[d]	17.32 (m)	153.2 (t, 11.0)	123.64 (t, 52.5)	128.3 (t, 48.7), 130 (s), 131.9 (t, 1.9)
Bzl	trans[e]	17.30 (t, 12.2)	152.94 (t, 10.0)	124.47 (t, 48.8)	33.48 (t, 19.6), 133.7 (t, 9.0), 129.5 (s), 127.3 (s), 126.5 (s)
n-Bu	cis	17.5 (t, 12.0)	152.59 (t, 9.8)	125.54 (t, 46.4)	25.5 (t, 4.5), 23.9 (t, 13.0), 20.7 (t, 28.0), 13.69 (s)
t-Bu	trans	17.40 (t, 11.0)	151.13 (t, 9.5)	125.64 (t, 42.7)	27.14 (s), 34.02 (t, 23.2)
t-Bu	cis[f]	17.35 (d, 12.2)	153.25 (d, 8.6)	125.35 (d, 17.1)	25.8 (d, 3.7)
			152.90 (d, 9.8)	123.28 (d, 15.9)	27.10 (s), 34.77 (d, 25.6), 35.05 (d, 26.9)

[a] Chemical shifts are in ppm and relative to Me_4Si in $CDCl_3$. [b] Abbreviations: s = singlet, d = doublet, t = triplet, m = undefined multiplet. [c] "J" = $|^nJ_{PC} + {}^{n+2}J_{PC}|$ (in Hz). [d] δ(CO) 217 (t, 6.1). [e] δ(CO) 194.9 (t, 10.0). [f] Mixture of isomers III and V.

3. $^{13}C\{^1H\}$ NMR Spectroscopy. The line shapes in the $^{13}C\{^1H\}$ spectra of bis(phosphine) complexes resemble those in the ^1H NMR spectra in that the ^{13}C line shape is determined by the magnitude of $^2J_{PP}$. The spin system, however, for the ^{13}C nuclei is $A[X]_2$ ($A \equiv {}^{13}C$, $X \equiv {}^{31}P$), rather than the $[A_nX]_2$ of the ^1H spin system, due to the very low natural abundance of ^{13}C.[37] Consequently, it has been shown[38,39] that, for mutually cis phosphorus ligands, the $^{13}C\{^1H\}$ resonances of carbons adjacent to phosphorus may appear as a five-line multiplet, a non-1:2:1 triplet, a doublet of doublets, or a doublet.[40] With mutually trans phosphorus ligands, where $^2J_{PP}$ is large, a 1:2:1 triplet should be observed for these resonances.[37] Well-defined 1:2:1 triplets (Table III) were observed for all the ring carbons of four of the phosphole complexes. The ring methyl carbons also appear as triplets or ill-defined multiplets in all cases except *cis*-$(t\text{-BuDMP})_2Ru(CO)_2Cl_2$. Thus, for these four complexes the phospholes are mutually trans. The $^{13}C\{^1H\}$ NMR spectrum of *cis*-$(t\text{-BuDMP})_2Ru(CO)_2Cl_2$ is complicated and appears to indicate a mixture of two cis isomers (IV and VI) as doublets are observed for all line shapes. It is interesting to note that *cis*-$(t\text{-BuDMP})_2Ru(CO)_2Cl_2$ appears to be photosensitive and changes from colorless to rose on exposure to daylight. Mawby[41] has noted that for $L_2Ru(CO)_2X_2$ (L = phosphorus or arsenic donor; X = Cl, Br, I) UV irradiation causes conversion of the cis isomers to the trans isomers and, furthermore, this rearrangement occurs in some cases via the all-cis isomer.

Several interesting trends in the chemical shifts of the phosphole carbons upon coordination are noted. Upon coordination to ruthenium,[42] the phosphole ring C_3 carbon resonance moves downfield by 4–5 ppm, accompanied by a small increase in the P–C coupling constant. The ring C_2 carbon chemical shift, on the other hand, moves upfield 4–5 ppm and is accompanied by a substantial increase in J_{PC}. These trends could be indicative of 2p–3d π-interaction[40,43] between the ring butadiene moiety and phosphorus with a concomitant increase in the polarization of the C_2–C_3 carbon–carbon double bond upon coordination.[8,9]

The chemical shifts of the carbons in the exocyclic R groups appear to be somewhat less sensitive to coordination to ruthenium. In several cases, singlets were observed for the exocyclic carbon resonances due to fortuitous cancellation of spin–spin coupling.[44]

Table IV. ^{31}P NMR Data for $L_2Ru(CO)_2Cl_2$ (L = Phosphole)

L	isomer	$\delta(^{31}P)_{complex}$[a] (line shape[b])
PhDBP	trans	13.16 (s)
	cis	10.48 (s)
PhDMP	cis	25.25 (s)
BzlDMP	trans	28.94 (s)
	cis	24.42 (s)
n-BuDMP	trans	34.88 (s)
	cis	26.83 (s)
t-BuDMP	trans	51.37 (s)
	cis[c]	74.75, 72.45 (dd, J = 5.0 Hz), 64.1 (s)

[a] Positive chemical shifts are downfield of 85% H_3PO_4 and are in ppm. [b] Abbreviations: s = singlet, dd = doublet of doublets. [c] Appears to be an inseparable mixture of cis (isomer III) and all-cis (isomer V).

4. $^{31}P\{^1H\}$ NMR Spectroscopy. The ^{31}P chemical shift of phospholes is greatly influenced by the electronic nature of the phosphole ring, which in turn is greatly influenced by the substitution pattern of the ring. Quin[45] and Mathey[13] have noted that simple, unsubstituted phospholes show an unusually low-field ^{31}P chemical shift. This deshielding was attributed by Quin[3] to delocatization of the phosphorus lone pair into the ring. However, introduction of ring methyl substituents results in ^{31}P chemical shifts that for 1-R-3,4-dimethylphospholes are very near those of tertiary phosphines. Borleske[46] also noted that the substituent contributions to the ^{31}P chemical shift in phospholes are additive and consequently allow for calculation of ^{31}P chemical shifts for simple phosphole derivatives. MacDougall[40] has listed the observed and calculated ^{31}P chemical shifts for 1-R-3,4-dimethylphospholes using the group contributions of Grim et al.[47a] and taking into account the 3,4-dimethylphospholyl group contribution of Borleske.[46] These data indicate that exocyclic substituents affect the ^{31}P chemical shift of these phospholes in much the same manner as they affect normal phosphines and that the behavior of these 3,4-dimethylphospholes can be expected to be similar to that of normal phosphines.

The $^{31}P\{^1H\}$ NMR data are given in Table IV. Singlets are observed for each complex except *cis*-$(t\text{-BuCMP})_2$Ru-

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Table V. Fractional Atomic Coordinates with Estimated Standard Deviations for $(PhDMP)_3Ru(CO)Cl_2$ [a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Ru(1)	2454.7 (3)	2146.1 (3)	2130.7 (4)	C(23)	4186 (4)	4143 (3)	2073 (5)
Cl(2)	986 (1)	1760 (1)	−230 (1)	C(24)	2829 (6)	5010 (5)	−1417 (8)
Cl(3)	3905 (1)	2613 (1)	4529 (1)	C(25)	4538 (5)	5758 (4)	1670 (8)
C(4)	2996 (4)	1109 (3)	1555 (6)	C(26)	4365 (4)	2408 (3)	638 (7)
O(5)	3279 (4)	465 (3)	1140 (5)	C(27)	4335 (5)	2178 (5)	−762 (7)
P(6)	1644 (1)	1178 (1)	3241 (1)	C(28)	5064 (8)	1663 (7)	−1071 (10)
C(7)	1470 (4)	1645 (3)	4893 (5)	C(29)	5799 (7)	1370 (6)	52 (13)
C(8)	472 (4)	1420 (3)	4742 (5)	C(30)	5869 (6)	1595 (5)	1473 (11)
C(9)	−218 (4)	835 (3)	3286 (6)	C(31)	5149 (5)	2108 (4)	1758 (7)
C(10)	281 (4)	652 (3)	2377 (5)	C(32)	1651 (1)	3462 (1)	2676 (1)
C(11)	17 (5)	1702 (4)	5885 (6)	C(33)	1349 (4)	4259 (3)	1402 (5)
C(12)	−1349 (4)	480 (4)	2927 (6)	C(34)	1805 (4)	5114 (3)	2091 (6)
C(13)	2334 (4)	195 (3)	3689 (6)	C(35)	2463 (4)	5193 (3)	3671 (6)
C(14)	3233 (5)	300 (4)	4929 (9)	C(36)	2433 (4)	4393 (3)	4154 (5)
C(15)	3811 (6)	−422 (5)	5208 (10)	C(37)	1648 (5)	5954 (4)	1362 (7)
C(16)	3474 (6)	−1250 (5)	4232 (12)	C(38)	3103 (4)	6106 (4)	4588 (7)
C(17)	2570 (7)	−1370 (4)	3021 (9)	C(39)	370 (4)	3298 (3)	2854 (6)
C(18)	1987 (5)	−651 (4)	2729 (6)	C(40)	214 (5)	3743 (4)	4066 (7)
P(19)	3414 (1)	3026 (1)	1103 (1)	C(41)	−782 (6)	3665 (4)	4111 (9)
C(20)	2789 (4)	3507 (4)	−530 (5)	C(42)	−1621 (6)	3137 (5)	2949 (10)
C(21)	3179 (5)	4406 (4)	−278 (7)	C(43)	−1469 (5)	2692 (4)	1771 (8)
C(22)	3987 (4)	4768 (3)	1220 (6)	C(44)	470 (5)	2758 (4)	1704 (6)

[a] Positional parameters are given $\times 10^4$. Numbers in parentheses are the estimated standard deviations in the units of the least significant digits given for the corresponding parameters. See Figure 1 for the identities of the atoms.

$(CO)_2Cl_2$, which is an isomeric mixture. For this complex a singlet (IV) and a doublet of doublets (VI) are observed, supporting the arguments based upon the other spectroscopic data that this substance is a mixture of isomers. The integrals of these resonances suggest that the relative proportion of these two species is 2.5:1 for isomer IV:isomer VI.

Where both cis and trans isomers of a complex were isolated, the trans isomer resonates downfield of the cis isomer, as for the analogous benzylphosphine complexes.[27] The chemical shifts for the 1-R-3,4-dimethylphosphole complexes are slightly downfield of those for the benzylphosphines, supporting the suggestion that the phospholes are better σ-donors than the benzylphosphines. Furthermore, the chemical shift difference between the cis and trans isomers of the phosphole complexes is greater than that for the benzylphosphine complexes, indicating that the 3,4-dimethylphospholes are better σ-donors and/or π-acceptors than the benzylphosphines. Neither Shaw[47b] nor we find a correlation between the ^{31}P coordination chemical shift of the complexes and the ^{31}P chemical shift of the free ligands. Such a correlation was observed for both the L_2PdX_2[8] and L_2PtX_2[9] complexes (L = RDMP).

The ^{31}P NMR spectrum of the $L_3RuCOCl_2$ complex displays a 1:1 doublet (δ 26.7) and a 1:2:1 triplet (δ 20.2) in 2:1 relative intensities. In structure VIII, the unique phosphorus (the triplet resonance) is trans to the carbonyl, which effects a greater trans influence than chloride. Since the trans influence decreases[31,32] in the order P > CO > Cl, one would anticipate for structure IX that the triplet would be downfield of the doublet. Hence, the ^{31}P NMR data suggest that $(PhDMP)_3Ru(CO)Cl_2$ possesses structure VII or VIII.

It is interesting to note that $(PhDMP)_3Ru(CO)Cl_2$ crystallized from an ethanol solution containing a 2:1 ligand to metal ratio. The complex *cis*-$(PhDMP)_2Ru(CO)_2Cl_2$ was prepared in refluxing dimethoxyethane under carbon monoxide. These data suggest that phospholes very readily displace carbon monoxide from ruthenium(II) and help to explain why the yields of specific compounds are sometimes low.

5. Structure of $(PhDMP)_3Ru(CO)Cl_2$. The structure of $(PhDMP)_3Ru(CO)Cl_2$ has been confirmed by single-crystal X-ray crystallography. An ORTEP projection of the molecule showing the numbering of the atoms is provided as Figure 1. Stereoview diagrams of the molecule and of the unit cell are provided as parts a and b, respectively, of Figure 2 (supplementary material). Fractional atomic coordinates are given in Table V, and Table VI gives the molecular dimensions. The molecule is an almost perfect, undistorted octahedron. The phosphole, as well as the phenyl rings, is planar and shows no distortion even though the ring methyl carbons are well within van der Waals radii (3.30 Å) of one another (distances: C(11)–C(12), 3.025 Å; C(24)–C(25), 3.056 Å; C(37)–C(38), 3.042 Å). It is even more interesting to note that the ring systems on the two sets of cis-phosphorus nuclei are nearly coplanar and are almost within van der Waals radii. The two phosphole rings P(32) and P(19) have an angle of only 7.3° between them, and the distance between the centers of the two rings is only 3.56 Å, whereas the sum of van der Waals radii for the phosphorus and carbon nuclei is 3.50 Å. There is quite likely an electronic interaction between the π-systems of these rings, and it is suggested that this interaction stabilizes the tris-ligand complex for the PhDMP ligand in this particular geometry.

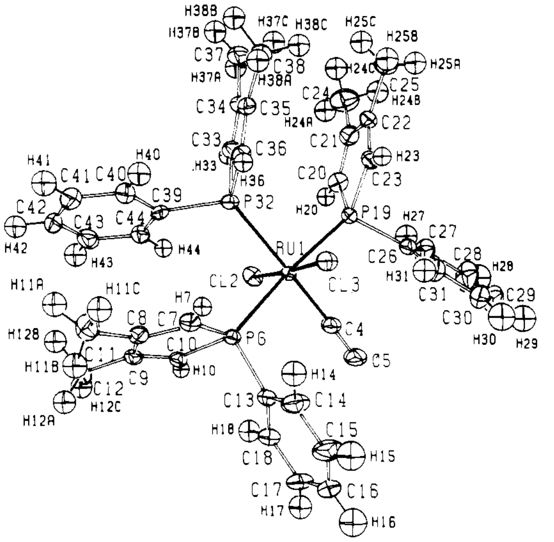


Figure 1. The $(PhDMP)_3Ru(CO)Cl_2$ molecule. Ellipsoids of 50% probability are shown.

The bond lengths for $(PhDMP)_3Ru(CO)Cl_2$ are all as would be expected except the Ru–P bond lengths for the two trans phospholes, which are shorter than would be expected. The Ru–P distances for the phosphole complex are 2.365 and 2.356 Å whereas the Ru–P distance in *trans*-$(Bzl_3P)_2Ru(CO)_2Cl_2$[27]

Table VI. Molecular Dimensions and Esd's[a] for $(PhDMP)_3Ru(CO)Cl_2$

A. Bond Lengths (Å)

Ru(1)-Cl(2)	2.407 (1)	P(19)-C(23)	1.809 (5)
Ru(1)-Cl(3)	2.423 (1)	P(19)-C(26)	1.801 (5)
Ru(1)-C(4)	1.868 (5)	C(20)-C(21)	1.817 (5)
Ru(1)-P(6)	2.365 (1)	C(21)-C(22)	1.337 (8)
Ru(1)-P(19)	2.356 (1)	C(21)-C(24)	1.472 (8)
Ru(1)-P(32)	2.411 (1)	C(22)-C(23)	1.506 (9)
C(4)-O(5)	1.138 (7)	C(22)-C(25)	1.319 (7)
P(6)-C(7)	1.791 (5)	P(32)-C(33)	1.810 (5)
P(6)-C(10)	1.794 (5)	P(32)-C(36)	1.782 (5)
P(6)-C(13)	1.823 (5)	P(32)-C(39)	1.837 (5)
C(7)-C(8)	1.334 (8)	C(33)-C(34)	1.320 (7)
C(8)-C(9)	1.485 (7)	C(34)-C(35)	1.472 (8)
C(8)-C(11)	1.512 (8)	C(34)-C(37)	1.515 (8)
C(9)-C(10)	1.334 (7)	C(35)-C(36)	1.339 (7)
C(9)-C(12)	1.490 (7)	C(35)-C(38)	1.501 (7)
P(19)-C(20)	1.385 (9)		

av Ph C–C bond length 1.374 (10)

B. Bond Angles (deg)

Cl(2)-Ru(1)-C(4)	88.59 (16)	C(20)-P(19)-C(23)	90.2 (2)
Cl(2)-Ru(1)-P(6)	93.53 (4)	P(19)-C(20)-C(21)	110.1 (4)
Cl(2)-Ru(1)-P(19)	89.92 (4)	C(20)-C(21)-C(22)	114.5 (5)
Cl(2)-Ru(1)-P(32)	86.89 (4)	C(20)-C(21)-C(24)	123.5 (6)
Cl(3)-Ru(1)-C(4)	94.32 (17)	C(21)-C(22)-C(23)	113.7 (5)
Cl(3)-Ru(1)-P(6)	87.26 (4)	C(21)-C(22)-C(25)	121.4 (5)
Cl(3)-Ru(1)-P(19)	89.54 (4)	P(19)-C(23)-C(22)	111.6 (4)
Cl(3)-Ru(1)-P(32)	90.20 (4)	P(19)-C(26)-C(27)	124.2 (4)
C(4)-Ru(1)-P(6)	86.76 (17)	P(19)-C(26)-C(31)	18.6 (5)
C(4)-Ru(1)-P(19)	88.45 (17)	Ru(1)-P(32)-C(33)	118.4 (2)
P(6)-Ru(1)-P(32)	94.10 (4)	Ru(1)-P(32)-C(36)	118.9 (2)
P(19)-Ru(1)-P(32)	90.96 (4)	Ru(1)-P(32)-C(39)	120.6 (2)
Ru(1)-C(4)-O(5)	176.5 (5)	C(33)-P(32)-C(36)	90.2 (2)
Ru(1)-P(6)-C(7)	120.2 (2)	P(32)-C(33)-C(34)	110.9 (4)
Ru(1)-P(6)-C(10)	123.0 (2)	C(33)-C(34)-C(35)	113.8 (5)
Ru(1)-P(6)-C(13)	111.6 (2)	C(33)-C(34)-C(37)	124.1 (5)
C(7)-P(6)-C(10)	90.9 (2)	C(10)-P(6)-C(13)	103.1 (2)
P(6)-C(7)-C(8)	110.9 (4)	C(7)-P(6)-C(13)	104.7 (2)
C(7)-C(8)-C(9)	113.8 (4)	C(36)-P(32)-C(39)	104.8 (2)
C(7)-C(8)-C(11)	123.4 (5)	C(33)-P(32)-C(39)	98.2 (2)
C(8)-C(9)-C(10)	113.5 (4)	C(23)-P(19)-C(26)	102.4 (2)
C(8)-C(9)-C(12)	121.8 (4)	C(20)-P(19)-C(26)	102.4
P(6)-C(10)-C(9)	110.9 (3)	C(34)-C(35)-C(36)	113.7 (5)
P(6)-C(13)-C(14)	120.5 (4)	C(34)-C(35)-C(38)	120.5 (4)
P(6)-C(13)-C(18)	120.4 (4)	P(32)-C(36)-C(35)	111.1 (4)
Ru(1)-P(19)-C(20)	123.1 (2)	P(32)-C(39)-C(40)	122.3 (4)
Ru(1)-P(19)-C(23)	122.0 (2)	P(32)-C(39)-C(44)	118.5 (4)
Ru(1)-P(19)-C(26)	112.7 (2)		

av Ph C–C–C angle 119.9 (7)

[a] The esd's are in the units of the least significant figures given for the corresponding parameters.

Table VII. Infrared Spectral Data for $L_{3,4}RuCl_2$[a]

L	isomer	color	ν_{RuCl}, cm^{-1}	other vib, cm^{-1}
$(BzlDMP)_4$	cis	yellow	295, 345	
	trans	orange	340	320
$(PhDMP)_4$	trans	pink	330	275 w, 300, 372
$(CH_3DMP)_4$	cis	yellow	320, 333	
	trans	orange	333	322
(*n*-BuDMP)$_4$	trans	red	345	320
(*t*-BuDMP)$_2$$(PPh_3)$	5-coord	purple	305, 375	
$(PPh_3)_4$	trans	brown	320	280 w

[a] Nujol mulls on CsBr windows.

is 2.398 Å and in *cis*-$(BzlPPh_2)_2Ru(CO)_2Cl_2$[27] is 2.410 Å. These data, in addition to the lower energy ν_{CO} vibrations for the phosphole complexes relative to those for the benzylphosphine complexes, would suggest that the 1-R-3,4-dimethylphospholes are better σ-donors than the benzylphosphine ligands.

B. RuL_nCl_2 Complexes. When a solution containing 1 mol of $(PPh_3)_4RuCl_2$ in hexane was refluxed under nitrogen with 4 or 5 mol of phosphole, a complex of the type L_nRuCl_2 was formed. While the benzylphosphines failed[27] to form this type of complex under these same conditions, the phosphole ligands, perhaps due to both their compact size and their relatively good basicity, readily form them. Complexes were obtained for all of the 1-R-3,4-dimethylphosphole ligands in reasonable yields except for L = CH_3DMP, which was extremely soluble such that the yield was low, and L = *n*-BuDMP, which appeared to form at least two very soluble and inseparable isomers, and only a trace amount was isolated. All of the ligands formed six-coordinated complexes except *t*-BuDMP, which formed a five-coordinate complex under these conditions. There are two isomeric configurations possible for the six-coordinated complexes. Both isomers were isolated for $(BzlDMP)_4RuCl_2$ and $(CH_3DMP)_4RuCl_2$. The trans isomers are orange, and the cis isomers are light yellow. For $(CH_3DMP)_4RuCl_2$, the orange trans isomer was the initial product to precipitate from the hexane solution containing an excess of ligand. Upon recrystallization from CH_2Cl_2/hexane, the trans complex isomerized to the yellow cis isomer. The two $(BzlDMP)_4RuCl_2$ isomers were isolated from different preparations. The yellow cis isomer was prepared with a nearly stoichiometric amount of ligand (ligand to $(PPh_3)_4RuCl_2$ mole ratio 4.8:1) and only isolated after recrystallization of the resulting oil from CH_2Cl_2/hexane. The orange trans isomer, on the other hand, was prepared with an excess of ligand (ligand to $(PPh_3)_4RuCl_2$ mole ratio 5.7:1) and isolated directly from the hexane solution. This suggests that the isomers probably are of similar stabilities and are quite sensitive to the polarity of the solvent as well as free ligand in solution. The free ligand in solution may in fact catalyze cis to trans isomerization and stabilize the trans isomer. The *trans*-$(CH_3DMP)_4RuCl_2$ complex isomerizes in the solid state to the cis isomer at 158 °C but was the only example of these complexes to do so. Three of the RuL_nCl_2 complexes appear to be somewhat light sensitive, with the complexes of L = CH_3DMP and PhDMP turning from orange to yellow and the complex of L = BzlDMP changing from orange to green upon exposure to normal daylight. The *trans*-$(CH_3DMP)_4RuCl_2$ complex was irradiated in $CDCl_3$ solution with ultraviolet light and the process followed by ^{31}P NMR. After approximately 1.3 h of irradiation, two triplets appeared and the chemical shifts confirmed that they were due to the cis isomer. Further irradiation produced more random resonances, indicating decomposition of the sample and/or the solvent.

The complex of L = *t*-BuDMP proved to be very different, structurally, than the other complexes of this series. It is a bright purple five-coordinate complex, and elemental analysis indicates that it has the formula (*t*-BuDMP)$_2$$(PPh_3)RuCl_2$ (confirmed by ^1H and $^{31}P\{^1H\}$ NMR). The complexes were characterized by infrared, ^1H and $^{31}P\{^1H\}$ NMR, and elemental analyses.

1. Infrared Spectroscopy. The ν_{RuCl} frequencies for the RuL_nCl_2 complexes (Table VII) occur in the expected region. Both the cis and the trans isomers were isolated for $(BzlDMP)_4RuCl_2$ and $(CH_3DMP)_4RuCl_2$. The trans isomers should and do exhibit one ν_{RuCl} vibration, and the cis isomers exhibit two RuCl vibrations. ν_{RuCl} for chloride trans to chloride occurs at higher energy than the symmetrical stretch for chloride trans to phosphorus, as would be expected, due to the greater trans influence of phosphorus. The complex (*t*-BuDMP)$_2$$(PPh_3)RuCl_2$ exhibits two ν_{RuCl} vibrations, suggesting mutually cis chlorides.

2. $^{31}P\{^1H\}$ NMR Spectroscopy. The $^{31}P\{^1H\}$ NMR data are given in Table VIII. The cis complexes show the two triplets expected for the two pairs of chemical-shift-inequivalent phosphorus atoms, and the trans isomers show a singlet. The appearance of a singlet ^{31}P resonance could be due to either

Table VIII. ^{31}P NMR Data for $(RDMP)_nRuCl_2$

R	*n*	isomer geom	$\delta(^{31}P)_{ligand}$	$\delta(^{31}P)_{complex}$[a] (line shape[b])	$-\Delta(^{31}P)_{obsd}$,[c] ppm	$^2J_{PP}$, Hz
Bzl	4	cis	−3.0	48.68 (t)/32.27 (t)	51.68/35.27	30.5
Bzl	4	trans	−3.0	34.45 (s)	37.45	
Ph	4	trans	−2.5	28.52 (s)	31.02	
Ph	4	cis	−2.5	28.93 (t)/43.15 (t)	31.4/45.6	29.3
CH_3	4	cis	−20.2	29.84 (t)/25.49 (t)	60.04/45.69	30.5
CH_3	4	trans	−20.2	25.19 (s)	45.39	
n-Bu	4	trans	−6.5	33.42 (s)	39.92	
t-Bu[d]	2	5-coord	+27.5	68.0 (d)/26.5 (t)	40.5/31.83	31.8
t-Bu	4	trans	+27.5	56.3 (s) ($(PPh_3)_nRuCl_2$)	28.8	
PPh_3[e]	4	trans	−5.33	29.54 (s)	34.87	
PPh_3[e]	3	trans SBP	−5.33	76.29 (t)/24.54 (d)	81.62/29.87	31.7

[a] Positive chemical shifts are downfield of 85% H_3PO_4. [b] Abbreviations: s = singlet, d = doublet, t = triplet. [c] $\Delta(^{31}P)_{obsd} = \delta(^{31}P)_{ligand} - \delta(^{31}P)_{complex}$. [d] Actual formula $(t\text{-BuDMP})_2(PPh_3)RuCl_2$. [e] Spectrum at 183 °C in CH_2Cl_2.

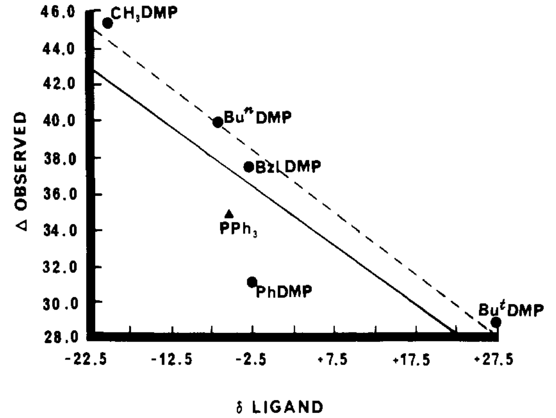
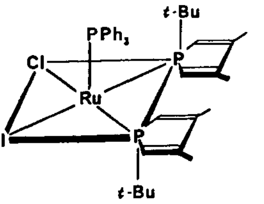


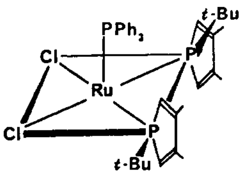
Figure 3. Correlation between $\Delta(^{31}P)_{obsd}$ and $\delta(^{31}P)_{ligand}$ for *trans*-$(RDMP)_4RuCl_2$ complexes. The correlation coefficient $R^2 = 0.98$ excludes $(Ph_3P)_4RuCl_2$ and $(PhDMP)_4RuCl_2$ data and $R^2 = 0.70$ includes these data. See the text for an explanation.

rapid exchange of the phosphole ligand or to equivalency of the four phosphorus nuclei. Proton NMR eliminates rapid exchange since virtual coupling is observed for the ring protons. A correlation between the coordination chemical shift, Δ_{obsd}, and the chemical shift of the free ligand, δ_{ligand}, is observed for the *trans*-L_4RuCl_2 complexes ($R^2 = 0.98$ or 0.70; see Figure 3). The correlation would be much better without the abnormally low Δ_{obsd} for both $(PPh_3)_4RuCl_2$ and $(PhDMP)_4RuCl_2$. The L = PPh_3 complex probably has a low Δ_{obsd} due to the fact that $\delta_{complex}$ is an average of six-coordinate and five-coordinate complexes. This is the only complex of the series in which ligand exchange occurs rapidly at room temperature. The L = PhDMP complex has a low Δ_{obsd} due in small part to the shielding effect of π-back-donation of electron density from the metal to the phosphorus and in large part to the magnetic anisotropy of neighboring phenyl rings.[47c]

The $(PPh_3)_3RuCl_2$ five-coordinate complex shows a singlet at room temperature due to rapid ligand exchange but a doublet and a triplet at −90 °C, where exchange is slow, in agreement with the spectra previously reported by Caulton.[48,49] The crystal structure of $(PPh_3)_3RuCl_2$[50] has confirmed that the molecule is a square-based pyramid with two trans basal phosphines, one apical phosphine, and two trans basal chlorides. The $^{31}P\{^1H\}$ NMR spectrum also shows a doublet and a triplet for the five-coordinate $(t\text{-BuDMP})_2(PPh_3)RuCl_2$ complex, and it was first thought to have a structure very similar to that of the $(PPh_3)_3RuCl_2$ complex. However, although the ^{31}P NMR spectrum indicates that the phosphorus atoms of the two phosphole ligands are equivalent, the proton NMR spectrum indicates that the methyl and ring hydrogens of the two phosphole ligands are inequivalent. Furthermore, the proton NMR spectrum (Figure 4) shows chemical-shift-inequivalent doublets for the *t*-Bu proton resonances, indicating that the two phosphole ligands are cis and not trans and that there are two conformers in solution. This situation could occur for cis phosphole ligands (minor conformer), in which sterically hindered rotation causes the *tert*-butyl substituent of one phosphole to lie below the basal plane of a square pyramid while the *tert*-butyl substituent on the other phosphole is positioned very close to a phenyl ring of the apical triphenylphosphine ligand (X). The interaction of the *tert*-butyl protons with the anisotropic ring current of the phenyl ring would cause a marked shielding of those particular protons,[51] and they occur at high field (δ 0.28, d, *J* = 14 Hz).



X



XI

For the major conformer, the ^1H and $^{13}C\{^1H\}$ NMR data suggest that the phospholes are mutually cis and the planes of their rings are parallel and normal to the basal plane with the *tert*-butyl groups lying in the basal plane (XI). This conclusion is supported by the following observations. The two phosphole phosphorus nuclei are chemical shift equivalent. The ring methyl protons (δ 1.62, d, $^4J_{HH}$ = 2 Hz; δ 1.94, d, $^4J_{HH}$ = 2 Hz) and methylidene protons (δ 5.05, m, δ 6.32, m) are chemical shift inequivalent, and the *tert*-butyl protons (δ 1.00, d, $|^3J_{PH} + {}^5J_{PH}|$ = 14.4 Hz) chemical shift equivalent. These conclusions required the observation of $^1H\{^{31}P\}$ NMR spectra, which are shown in Figure 4. In the $^{13}C\{^1H\}$ spectrum, the phosphole methyl carbons (δ 17.2, 5-line, $|^3J_{PC} + {}^5J_{PC}|$ = 10.7 Hz; δ 17.3, 5-line, $|^3J_{PC} + {}^5J_{PC}|$ = 10.8 Hz) and ring carbons (δ C_3, 147.0, 5-line, $|^2J_{PC} + {}^4J_{PC}|$ = 6.9 Hz; δ 147.4, 5-line, $|^2J_{PC} + {}^4J_{PC}|$ = 7 Hz) are chemical shift inequivalent, while the *tert*-butyl carbons (δ 29.7, s) are chemical shift equivalent. Thus there is hindered rotation about the ruthenium–phosphole bond but not about the phosphole–*tert*-butyl carbon bond.

At first, we attributed the formation of the pentacoordinate complex with the *tert*-butylphosphole to a lower donor ability of this ligand induced by its greater steric bulk. This, however, is not the case as brown trans $(t\text{-BuDMP})_4RuCl_2$ ($\delta(^{31}P$ 56.3) was formed in low yield when the reaction was performed in

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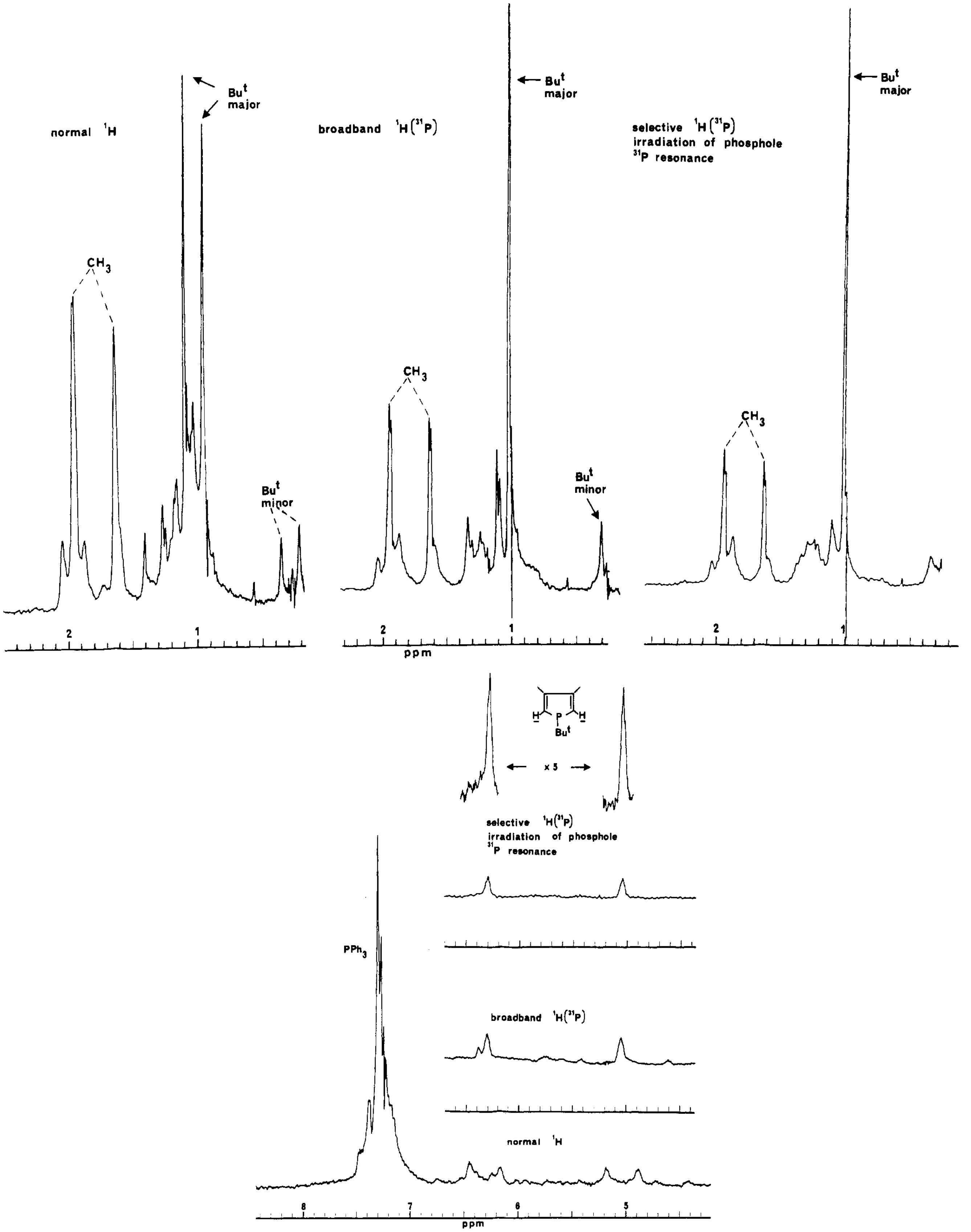

Figure 4. ^1H, $^1H\{^{31}P\}$ broad-band, and $^1H\{^{31}P\}$ selective NMR spectra of (t-BuDMP)$_2$(PPh$_3$)RuCl$_2$ in CDCl$_3$ at 303 K. See text for an explanation of the interpretation of these spectra.

dichloromethane rather than hexane. Hence, it is simply the low solubility of (t-BuDMP)$_2$(PPh$_3$)RuCl$_2$ in hexane that gives rise to its formation.

All these complexes slowly decompose (hours to days) in solution by phosphole dissociation (to produce dimers?). To gain more information regarding dissociation in solution, electronic spectral data (Table IX) as a function of concentration were obtained for two complexes. The data for (t-BuDMP)$_2$(PPh$_3$)RuCl$_2$ compares well with that given by James[52] for (PPh$_3$)$_3$RuCl$_2$, a known five-coordinate complex

Table IX. Electronic Spectroscopy Data for Selected Complexes

complex	concn, M[a]	peak position, nm	extinction coeff
(*t*-BuDMP)$_2$(PPh$_3$)RuCl$_2$[b]	1.0×10^{-3}	517, 714	770, 360
(PPh$_3$)$_3$RuCl$_2$[c]	1×10^{-3}	480, 750	1350, 515
trans-(BzlDMP)$_4$RuCl$_2$	1×10^{-3}	508	250
	1×10^{-4}	488	750

[a] All solvents were CH_2Cl_2 except for (PPh$_3$)$_3$RuCl$_2$, in which benzene was the solvent. [b] Obeys the Beer-Lambert law only for freshly prepared solutions. [c] Agrees with the data in ref 52.

which rapidly dissociates in solution. The complex *trans*-(BzlDMP)$_4$RuCl$_2$ does not obey the Beer-Lambert law, suggesting that at low concentration it also dissociates.

The unusual behavior of the ruthenium phosphole complexes could indicate great potential for catalysis. It has been shown, qualitatively, that these complexes are in fact hydrogenation catalysts. Four complexes were qualitatively tested for catalytic activity as described in the Experimental Section (viz. (PPh$_3$)$_3$RuCl$_2$, (CH$_3$DMP)$_4$RuCl$_2$, (*t*-BuDMP)$_2$(PPh$_3$)RuCl$_2$, and *cis*-(Bzl$_3$P)$_2$Ru(CO)$_2$Cl$_2$) and all exhibited the ability to catalyze the hydrogenation of 1-heptene to heptane at roughly comparable rates. It remains to be seen just how effective or selective these complexes will be as catalysts, and further study is in progress.

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Registry No. *trans*-(PhDBP)$_2$Ru(CO)$_2$Cl$_2$, 86495-08-1; *cis*-(PhDBP)$_2$Ru(CO)$_2$Cl$_2$, 86421-44-5; *cis*-(PhDMP)$_2$Ru(CO)$_2$Cl$_2$, 86495-69-4; *trans*-(BzlDMP)$_2$Ru(CO)$_2$Cl$_2$, 86421-45-6; *cis*-(BzlDMP)$_2$Ru(CO)$_2$Cl$_2$, 86470-38-4; *cis*-(*n*-BuDMP)$_2$Ru(CO)$_2$Cl$_2$, 86421-46-7; *trans*-(*t*-BuDMP)$_2$Ru(CO)$_2$Cl$_2$, 86421-47-8; *cis*-(*t*-BuDMP)$_2$Ru(CO)$_2$Cl$_2$, 86470-39-5; *cis*-(BzlDMP)$_4$RuCl$_2$, 86421-48-9; *trans*-(BzlDMP)$_4$RuCl$_2$, 86470-40-8; *trans*-(PhDMP)$_4$RuCl$_2$, 86421-49-0; *cis*-(PhDMP)$_4$RuCl$_2$, 86470-41-9; *cis*-(CH$_3$DMP)$_4$RuCl$_2$, 86421-50-3; *trans*-(CH$_3$DMP)$_4$RuCl$_2$, 86470-42-0; *trans*-(*n*-BuDMP)$_4$RuCl$_2$, 86436-03-5; (*t*-BuDMP)$_2$(PPh$_3$)RuCl$_2$, 86421-51-4; *trans*-(*t*-BuDMP)$_4$RuCl$_2$, 86421-52-5; *trans*-(PPh$_3$)$_4$RuCl$_2$, 86470-43-1; *trans*-(PPh$_3$)$_3$RuCl$_2$, 41756-81-4; *trans*-(*n*-BuDMP)$_2$Ru(CO)$_2$Cl$_2$, 86495-09-2; *trans*-(CH$_3$DMP)$_2$Ru(CO)$_2$Cl$_2$, 86421-53-6; *trans*-(PhDMP)$_2$Ru(CO)$_2$Cl$_2$, 86421-54-7; (PhDMP)$_3$Ru(CO)Cl$_2$, 86436-04-6; 1-heptene, 592-76-7.

Supplementary Material Available: Stereoviews of the (PhDMP)$_3$Ru(CO)Cl$_2$ molecule and the unit cell and listings of the changes in cell constants, thermal parameters, coefficients of least-squares planes, and observed and calculated structure factors (27 pages). Ordering information is given on any current masthead page.

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Synthesis and Spectroscopic Characterization of Trihydrido Mixed-Metal Tetranuclear Clusters $(\mu\text{-}H)_3M_3Ni(\eta^5\text{-}C_5H_5)(CO)_9$ (M = Ru, Os). Low-Temperature X-ray Diffraction Study of the Osmium Derivative

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Simple synthetic reactions to produce hydrido mixed-metal clusters through a hydrogen-assisted condensation of triruthenium or triosmium carbonyl clusters with a cyclopentadienyl nickel dimer $[(\eta^5\text{-}C_5H_5)Ni(CO)]_2$ are reported. The resulting tetranuclear cluster complexes $(\mu\text{-}H)_3M_3Ni(\eta^5\text{-}C_5H_5)(CO)_9$ (M = Ru, Os) have been obtained in ca. 70% yield (based on $M_3(CO)_{12}$) and characterized by microanalysis, mass spectrometry (including a detailed analysis of the parent ion multiplet), and IR and ^{1}H NMR spectra. The osmium derivative has been characterized by a low-temperature X-ray diffraction experiment. X-ray data (−165 °C): orthorhombic, space group *Ccmm*, $a = 10.274$ (2) Å, $b = 14.735$ (8) Å, $c = 35.488$ (5) Å, $V = 5372$ Å^3; $R(F) = 0.046$, $R_w(F) = 0.041$ for 1316 reflections with $F_o^2 > 3\sigma(F_o)^2$. The tetranuclear mixed-metal cluster crystallizes with $^1/_2$ mol of $(\mu\text{-}H)_2Os_3(CO)_{10}$. It possesses a tetrahedral closo arrangement for the Os_3Ni core (crystallographic symmetry C_s). Bond distances of interest are Os–Os = 2.869 (2) and 2.866 (2) Å and Os–Ni = 2.564 (5) and 2.563 (5) Å. The three hydride ligands are expected to bridge osmium–osmium vectors. Variable-temperature ^{1}H NMR experiments for both ruthenium and osmium derivatives show an invariant hydride signal within the range +20 to −90 °C.

Introduction

We are evaluating the scope of a simple synthetic approach of new mixed-metal clusters through a hydrogen-assisted condensation of pure polynuclear carbonyl complexes of the second- and third-row transition metals with first-row transition-metal complexes.

At moderate temperature, condensations induced by molecular hydrogen at atmospheric pressure have been observed, leading to some remarkable syntheses of homonuclear hydrido transition-metal cluster complexes in high yield and purity.[1,2] More recently, direct conversion of a metallo-ligated cluster to a closed polyhedron was obtained in the presence of molecular hydrogen, yielding the pentahydrido mixed-metal derivative $(\mu\text{-}H)_5Os_3Re(CO)_{12}$.[3] In keeping with this, we attempted the synthesis of hydrido mixed-metal Ru–Ni and Os–Ni cluster complexes, which are rare in comparison with other series.[4]

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