Formation of Ruthenium Thiolates via Complexes of Molecular Hydrogen

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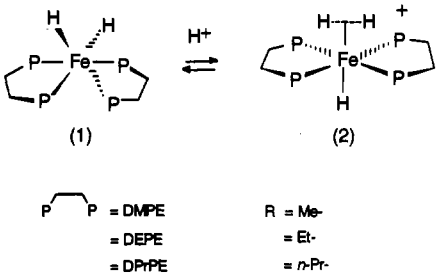
$RuH_2(DMPE)_2$ [DMPE = 1,2-bis(dimethylphosphino)ethane] was synthesized by reduction of *trans*-$RuCl_2(DMPE)_2$ with sodium/2-propanol. Protonation of $RuH_2(DMPE)_2$ with weak organic acids such as methanol, ethanol, and thiols affords the molecular hydrogen complex *trans*-$[RuH(\eta^2\text{-}H_2)(DMPE)_2]^+$, which has an η^2-bound H_2 ligand and a σ-bound hydride ligand. T_1 measurements and the observation of a large $^1J_{HD}$ coupling in the η^2-HD isotopomer ligand support the "nonclassical" structure. In the ^1H NMR spectrum of the *trans*-$[RuH(\eta^2\text{-}HD)(DMPE)_2]^+$ isotopomer, the proton–proton coupling (across the metal center) between σ-H and ^1H in the η^2-HD was measured at 4.5 Hz. Between 220 and 300 K, the molecular hydrogen complex undergoes *intermolecular* exchange with the protonating reagent and all the ruthenium-bound hydrogens in the molecular hydrogen complex undergo *intramolecular* exchange. The weakly bound η^2-H_2 ligand is readily displaced by alkane- and arenethiols to give *trans*-monothiolate hydrides. With thiophenol, a second substitution occurs to give a dithiolate complex. Crystals of *trans*-$Ru(SPh)_2(DMPE)_2$ are monoclinic, space group $P2_1/a$, with $a = 15.035(3)$ Å, $b = 9.881(3)$ Å, $c = 19.604(4)$ Å, $\beta = 97.51(2)°$, $Z = 4$, and $R = 0.029$ [3348 reflections used with $I > 2.5\sigma(I)$]. The structural analysis shows that Ru is coordinated by two bidentate phosphine and two monodentate benzenethiolate ligands in a *trans* arrangement.

Introduction

A variety of metal hydrides are now known where protonation by acids affords complexes containing molecular hydrogen coordinated in an η^2-fashion.[1,2] We have previously demonstrated[3] that the dihydrides of iron bis(dialkylphosphino)ethanes, *cis*-$FeH_2(PP)_2$ (**1**) [PP = $R_2PCH_2CH_2PR_2$, where R = Me (PP = DMPE), Et (PP = DEPE), and *n*-Pr (PP = DPrPE)], can be reversibly protonated by simple alcohols like ethanol and propanol to give the corresponding molecular hydrogen complexes *trans*-$[FeH(\eta^2\text{-}H_2)(PP)_2]^+$ (**2**) (Scheme 1). In solution, the η^2-coordinated H_2 ligands in these complexes can easily be substituted by better ligands such as X^-,[3] RS^-,[4] and $RC{\equiv}C^-$[5] (X = halide; R = alkyl, aryl) under mild conditions.

The ruthenium dihydride $RuH_2(DMPE)_2$ (**3**) has been synthesized previously,[6,7a] and Morris *et al.*[2a] have isolated $[MH(\eta^2\text{-}H_2)(DPPE)_2]^+$ [M = Fe, Ru; DPPE = 1,2-bis(diphenylphosphino)ethane] by protonation of the corresponding dihydrides with strong acid. X-ray crystallography has confirmed the "nonclassical" η^2-mode of coordination of H_2 to the metal, and a number of other molecular hydrogen complexes of ruthenium (containing η^2-H_2, σ-H) have now been reported and characterized.[8]

Scheme 1



We report here an alternative synthesis of $RuH_2(DMPE)_2$ (**3**) as well as the formation and characterization of the corresponding molecular hydrogen complex $[RuH(\eta^2\text{-}H_2)(DMPE)_2]^+$ (**4**) and reactions of **4** with alkane- and arenethiols.

Results and Discussion

Preparation of $RuH_2(DMPE)_2$ (3). $RuH_2(DMPE)_2$ (**3**) was first synthesized from *trans*-hydridobromo-bis{1,2-bis(dimethylphosphino)ethane}ruthenium(II) by Chatt and Davidson.[7a] The preparation of dihydride **3** from *trans*-$RuCl_2(DMPE)_2$ (**5**) and *cis*-$RuBr_2(DMPE)_2$ by reduction with molten potassium and lithium aluminum hydride, respectively, has also been reported.[7] Dihydride **3** has also been synthesized by reaction of *cis*-$RuHNp(DMPE)_2$ (**5**) (Np = 2-naphthyl) with hydrogen (1 atm) in toluene at 65 °C.[6]

Reduction of dichloride **5** with common reducing agents such as sodium borohydride, zinc borohydride, or potassium hydride fails to give dihydride **3**. Although lithium aluminum hydride reduction of **5** for 20 h affords the desired dihydride, the yield (<20%) is low, mainly due to difficulty in separating the lithium and aluminum byproducts from the product dihydride.

In this work, $RuH_2(DMPE)_2$ (**3**) was prepared by treatment of *trans*-$RuCl_2(DMPE)_2$ with sodium metal and 2-propanol (4

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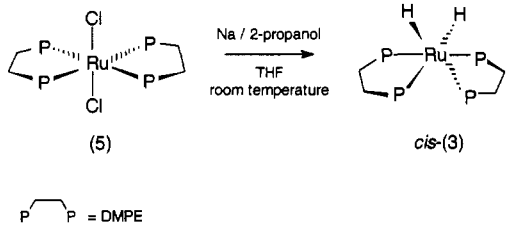
Scheme 2



equiv) in THF at room temperature (Scheme 2). On addition of the reducing agent, the characteristic yellow color of the reaction mixture fades to colorless over a period of about 1 h. The desired dihydride was obtained as a white solid in 53% yield and >99% purity (by microanalysis) after sublimation. Using the same method, $RuH_2(DEPE)_2$ was also obtained from *cis*-$RuCl_2(DEPE)_2$ as a white crystalline solid in *ca.* 60% yield.

This approach to the synthesis of metal hydrides (reduction of metal halides to metal hydrides) with alcohol/base was first reported by Chatt, Duncanson, and Shaw,[7b] and the reaction mechanism has subsequently been investigated in detail.[9] A number of transition metal hydrides have now been prepared using this method.[10]

Properties of $RuH_2(DMPE)_2$ (3). $RuH_2(DMPE)_2$ is a white solid which is readily soluble in most organic solvents (THF, benzene, toluene, pentane, cyclopentene, hexane, *etc.*). The complex is extremely air-sensitive, and the color changes to blue-black within minutes on exposure to air. $RuH_2(DMPE)_2$ has a single ultraviolet absorption maximum at 209 nm with an extinction coefficient of *ca.* 4600 M^{-1} cm^{-1}. In solution, $RuH_2(DMPE)_2$ exists as an equilibrium mixture of *cis* and *trans* isomers, with the *cis* isomer predominating. The ratio of *cis*- and *trans*-dihydrides is solvent-dependent; at 240 K, the ratio of *cis*:*trans* is about 25:1 in THF solution, whereas in toluene at the same temperature this ratio is about 12:1.

The $^{31}P\{^1H\}$ NMR spectrum of *cis*-$RuH_2(DMPE)_2$ (*cis*-**3**) acquired at ambient temperature in THF-d_8 (Figure 1a) consists of two apparent triplet resonances (splitting *ca.* 22 Hz), due to the two sets of two magnetically nonequivalent phosphorus nuclei of the *cis* isomer in an AA'XX' spin system. The hydride region of the ^1H NMR spectrum (Figure 1b) of this compound at ambient temperature shows an apparent doublet of quartets, due to splitting arising from three similar $^2J_{PH(cis)}$ couplings (*ca.* 24 Hz) and one $^2J_{PH(trans)}$ coupling (*ca.* 76 Hz). In the $^{31}P\{^1H\}$ NMR spectrum (Figure 1a) of *trans*-$RuH_2(DMPE)_2$ (*trans*-**3**), the equivalent phosphorus nuclei resonate at lower field than the phosphorus resonances of its *cis* isomer. In the ^1H NMR spectrum, the *trans*-dihydride resonates at higher field than the *cis*-dihydride, and gives rise to a quintet with $^2J_{PH(cis)}$ coupling of about 21 Hz.

The exchange between the *cis*- and *trans*-$RuH_2(DMPE)_2$ can be detected in the ^{31}P NMR spectrum by saturation transfer. Selective saturation (using a DANTE sequence[11]) of the downfield ^{31}P resonance for the *cis*-dihydride resulted in 30% decrease in the intensity of the ^{31}P resonance for the *trans* isomer at 323 K, and this puts an upper limit of approximately 0.1 s^{-1} on the rate of *cis*/*trans* isomerization.

Reaction of $RuH_2(DMPE)_2$ (3) with Alcohols. As with $FeH_2(DMPE)_2$ and other iron complexes containing bidentate alkylphosphine ligands,[3] dihydride **3** is protonated by methanol (pK_a *ca.* 15.2) and ethanol (pK_a *ca.* 15.8).

(i) Protonation of $RuH_2(DMPE)_2$ in Methanol Solution. Dissolution of $RuH_2(DMPE)_2$ in methanol affords a mixture containing two products in the ratio of approximately 2:1. The

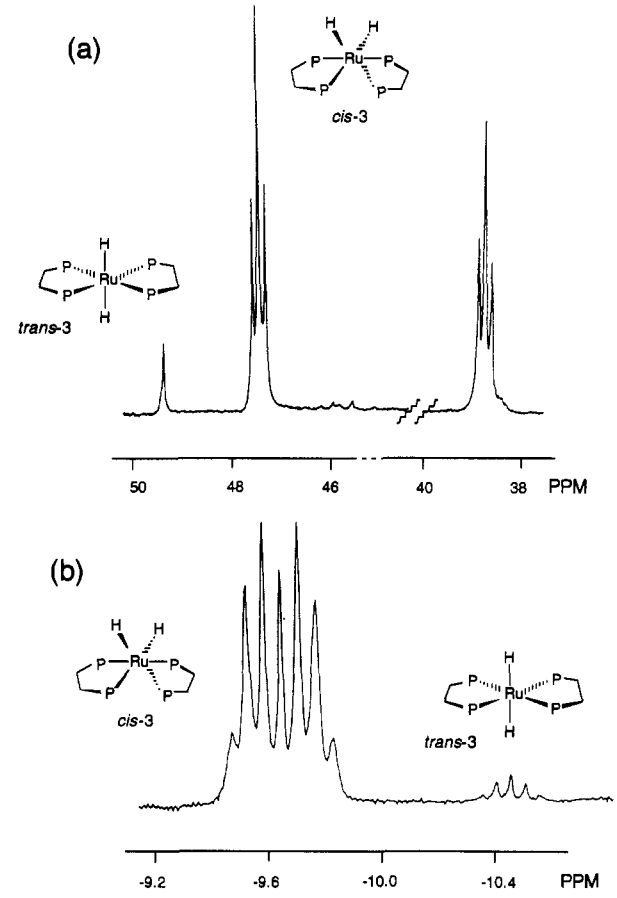


Figure 1. (a) $^{31}P\{^1H\}$ NMR spectrum (162.0 MHz) of $RuH_2(DMPE)_2$ (**3**) in THF-d_8 at 300 K. (b) Hydride region of 400-MHz ^1H NMR spectrum of $RuH_2(DMPE)_2$ (**3**) in THF-d_8 at 300 K.

products are in equilibrium, and the ratio of products in solution changes with temperature.

The major product was identified as *trans*-$[RuH(H_2)(DMPE)_2]^+$ (**4**) by NMR spectroscopy. The $^{31}P\{^1H\}$ NMR spectrum (162 MHz) of *trans*-$[RuH(H_2)(DMPE)_2]^+$ (**4**) (Figure 2) consists of a broad singlet at 40.3 ppm due to the four equivalent phosphorus nuclei. The hydride region of the ^1H NMR spectrum of **4** consists of a broad two-proton singlet at *ca.* −7 ppm ($W_{1/2}$ = 40 Hz at 250 K in methanol) and a one-proton quintet at *ca.* −13 ppm ($^2J_{PH(cis)}$ = 20.8 Hz). The broadened singlet is attributed to the protons of the η^2-H_2 bound to Ru; the quintet resonance is attributed to the σ-bound Ru–H proton, coupled to four equivalent phosphorus nuclei.

The minor *trans*-ruthenium hydride which has a ^{31}P resonance at 42.1 ppm in the ^{31}P NMR spectrum in neat methanol is attributed to the complex $[RuH(DMPE)_2]^+$ (**6**). Evacuation of the space above a methanol sample of dihydride **3** caused a 50% decrease in the concentration of the molecular hydrogen complex and a 100% increase in the intensity of the ^{31}P resonance at 42.1 ppm. Introduction of hydrogen gas (1 atm) into the evacuated sample caused an increase in the concentration of the molecular hydrogen complex and an almost complete disappearance of the resonance at 42.1 ppm. This set of observations is consistent with a mechanism where the molecular hydrogen complex *trans*-$[RuH(\eta^2\text{-}H_2)(DMPE)_2]^+$ easily (and reversibly) loses H_2 to form a five-coordinate species $[RuH(DMPE)_2]^+$, possibly stabilized by the methanol solvent (Scheme 3) or by agostic interactions. Puerta *et al.*[8b] have recently spectroscopically and chemically characterized $[Ru(dippe)_2H]^+$ [dippe = 1,2-bis(diisopropylphosphino)ethane], and Saburi *et al.*[12] have characterized 5-coordinate ruthenium hydrides $[Ru(diop)_2H]^+$ and $[Ru(dppb)_2H]^+$ [diop =

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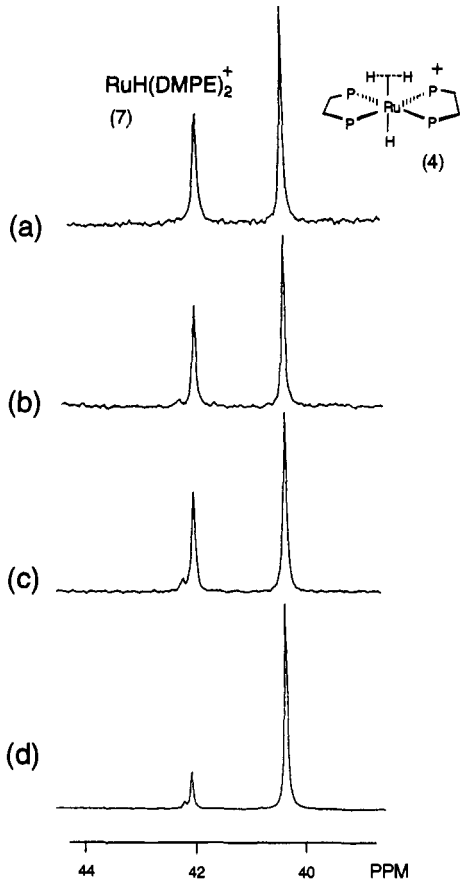
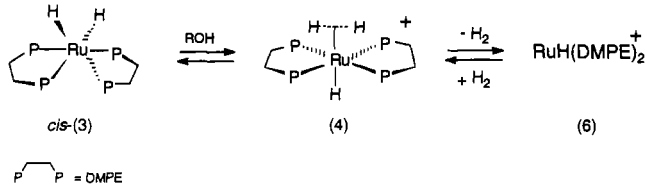


Figure 2. $^{31}P\{^1H\}$ NMR spectra (162.0 MHz) of a mixture of *trans*-$[RuH(\eta^2\text{-}H_2)(DMPE)_2]^+$ (**4**) and $[RuH(DMPE)_2]^+$ (**6**), generated by reaction of $RuH_2(DMPE)_2$ (**3**) with neat methanol, acquired at (a) 298 K (b) 270 K, (c) 245 K, and (d) 220 K.

Scheme 3



2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)-butane); dppb = 1,4-bis(diphenylphosphino)butane], where the electron-deficient metal center is stabilized by agostic interactions with C–H bonds from the ligand backbone.

Reducing the pressure above the sample (*i.e.* removing hydrogen gas from the equilibrium) causes a shift in the equilibrium to the side of $[RuH(DMPE)_2]^+$, and conversely, increasing the concentration of hydrogen gas pushes the equilibrium toward the molecular hydrogen complex *trans*-$[RuH(\eta^2\text{-}H_2)(DMPE)_2]^+$.

A number of five-coordinate ruthenium(II) hydrides have been reported[2a 8d,13] previously to be reasonably stable species. Five-coordinate ruthenium(II) hydrides having bidentate phosphine ligands arranged in a *trans* geometry are known to give rise to hydride resonances in ^1H NMR spectra at characteristically high field (*ca.* –22 ppm).[8d] In this work, the species resonating at 42.1 ppm in the ^{31}P NMR spectrum has a hydride at very high field ($\delta(^1H)$ –25.9 ppm).

The ratio of the concentration of the molecular hydrogen complex **4** to other species in the methanol solution decreases with an increase in temperature from 220 to 300 K. At 230 K, approximately 70% of the mixture is the molecular hydrogen

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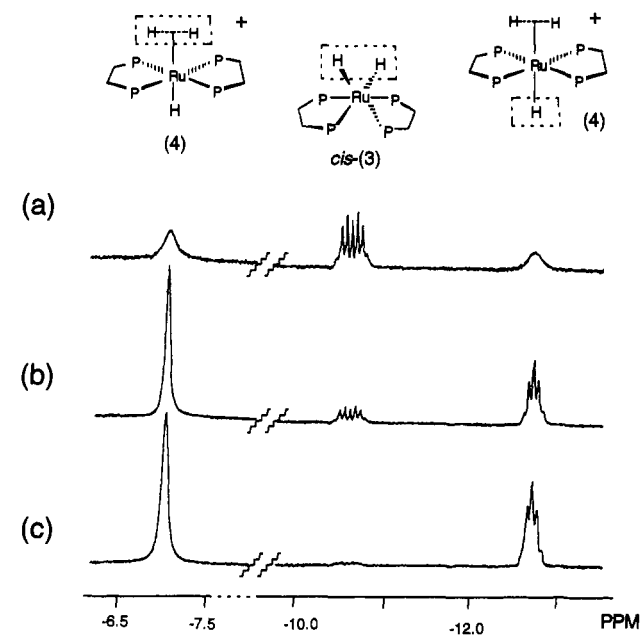


Figure 3. High-field region of the ^1H NMR spectrum (400.1 MHz) of a solution of $RuH_2(DMPE)_2$ (**3**) (41 mM in ethanol) at (a) 285 K, (b) 260 K, and (c) 235 K.

complex. At 300 K, hydride exchange among the methanol solvent, the molecular hydrogen complex **4**, and the five-coordinate complex **6** is observed on the NMR time scale by saturation transfer.

(ii) Protonation of $RuH_2(DMPE)_2$ in Ethanol Solution. In ethanol, the protonation of the dihydride **3** to form the trihydride **4** is reversible and the equilibrium is temperature-dependent. The equilibrium between dihydride **3** and trihydride **4** favors the formation of the dihydride at room temperature, while the molecular hydrogen complex dominates at temperatures below 260 K (Figure 3). At 285 K, the ratio of **3**:**4** in ethanol is approximately 3:5 for a 41 mM solution (with respect to ruthenium). The temperature dependence of the equilibrium constant for the reaction

$$RuH_2(DMPE)_2 + H^+ \rightleftharpoons RuH(H_2)(DMPE)_2^+$$

(determined by simple integration of the ^{31}P NMR spectra) affords $\Delta H = -(25.12 \pm 0.06)$ kJ mol^{-1} and $\Delta S = -(83.2 \pm 1.7)$ J mol^{-1} K^{-1}.

Besides dihydride **3** and the molecular hydrogen complex **4**, the five-coordinate $[RuH(DMPE)_2]^+$ was also present but only as a minor product. At temperatures above 260 K, the ^{31}P resonance of *trans*-$[RuH(H_2)(DMPE)_2]^+$ is broadened due to exchange with $[RuH(DMPE)_2]^+$. At 315 K, the exchange is sufficiently rapid that the resonance of $[RuH(DMPE)_2]^+$ coalesces with the resonance of the molecular hydrogen complex to give a single broad peak at *ca.* 41 ppm in the ^{31}P spectrum, just above the baseline. The two triplet ^{31}P resonances for the *cis*-dihydride, however, are sharp even at 315 K, suggesting that any exchange between *cis*-**3** and **4** is slow on the NMR time scale at this temperature.

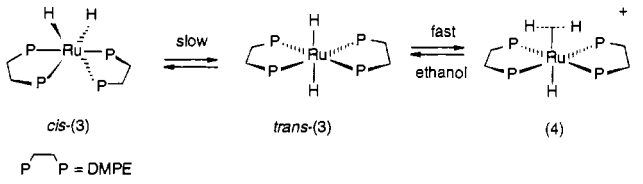
The singlet resonance for the *trans*-dihydride *trans*-**3** is unobservable in the ^{31}P NMR spectrum in ethanol solution. However, at 270 K, saturation at approximately δ 46 ppm in the ^{31}P spectrum (*i.e.* at the chemical shift expected for *trans*-**3**) causes a significant decrease in the intensity of the signal in the ^{31}P resonance for the molecular hydrogen complex **4**. There is no measurable change in the intensity of the resonance of **4** when the signal for *cis*-**3** is saturated. This result indicates the *trans*-dihydride reacts reversibly (and rapidly on the NMR time scale) with the protic solvent. The reaction of *trans*-**3** to form the

Table 1. T_1 Values[a] of η^2-H_2 and Terminal Hydride Ligands for *trans*-[RuH(η^2-H_2)(DMPE)$_2$]$^+$ in Ethanol (Measured by the Inversion-Recovery Method)

	T_1, ms	
temp, K	Ru(η^2-H_2)	Ru–H
200	25.6 ± 0.9	489 ± 12
230	16.1 ± 0.4	594 ± 7

[a] Measured at 400.13 MHz.

Scheme 4



molecular hydrogen complex **4** occurs much more rapidly than the exchange between the *cis* and *trans* isomers of **3**, possibly because *trans*-**3** has the correct stereochemistry for formation of **4** and little ligand reorganization is required (Scheme 4).

The ruthenium dihydrides are only partially protonated by ethanol or methanol when the alcohol is present only as a minor component of a dilute aprotic solution, and this reflects the poor acidity of the alcohol. The observed tendancy for the ruthenium dihydride to protonate in neat methanol and ethanol solvents probably arises because these solvents can support and stabilize the ionic products formed on protonation. This rationalization is consistent with the lesser degree of protonation observed with ethanol as solvent compared to methanol, and with alcohols of lower dielectric constant the protonation/deprotonation equilibrium probably lies well to the side of the uncharged metal dihydride.

NMR Evidence for η^2-Coordination of Dihydrogen in *trans*-[RuH(η^2-H_2)(DMPE)$_2$]$^+$. NMR spectroscopy has been used extensively to study molecular hydrogen complexes in solution.[14] It has been consistently found that the coordinated H_2 ligand has a relatively short T_1 (longitudinal relaxation time) since the proximity of the H atoms in the η^2 ligand lead to efficient dipole–dipole relaxation. The T_1 values of the η^2-H_2 and the hydride ligands of *trans*-[RuH(H_2)(DMPE)$_2$]$^+$ (**4**) were determined (using an inversion–recovery method) at 200 and 230 K in ethanol solution (Table 1).

At 200 and 230 K, T_1 values measured at 400 MHz for the η^2-H_2 ligand are 25.6 and 16.1 ms, respectively. These values satisfy the accepted "T_1 criterion" for "nonclassical" (or η^2 bound) hydrides,[14] and they are comparable to those reported for [*trans*-RuH(H_2)(DEPE)$_2$]$^+$BPh$_4^-$.[8c] The corresponding T_1 values measured for the σ-bound hydride ligand in **4** are 489 and 594 ms at 200 and 230 K, respectively, and these values are comparable to those reported for other "classical" metal hydrides.[1]

Evidence for the presence of an intact H–H bond in η^2-H_2 is provided by the facile formation of the H–D isotopomer. Dropwise addition of CH_3OH to a CD_3OD solution of $RuH_2(DMPE)_2$ (*i.e.* a solution of *trans*-[RuD(D_2)(DMPE)$_2$]$^+$ (**4**-d_3)) successively exchanges the ruthenium-bound deuterides for hydrogen. The high-field region of the $^1H\{^{31}P\}$ NMR spectrum acquired after CH_3OH was added (Figure 4b) exhibits signals in the two regions expected (i) for the protons in the η^2-bound H_2 (or H–D) at about −7 ppm and (ii) for σ-bound metal hydrides. After addition of the first drop of CH_3OH, the spectrum contains an intense 1:1:1 triplet ($^1J_{HD}$ = 32.2 Hz) at −7 ppm with a smaller doublet of triplets shifted 30 Hz to high field of the large triplet. The more

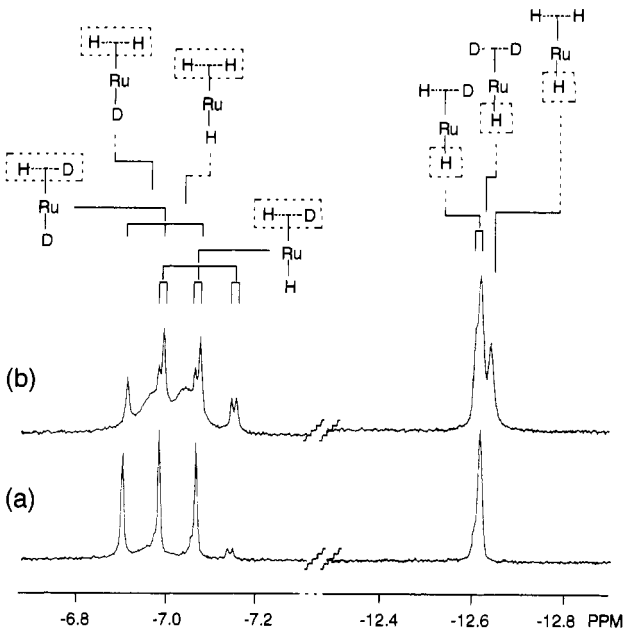


Figure 4. Hydride region of the $^1H\{^{31}P\}$ NMR spectra (400.1 MHz, 250 K) of *trans*-[RuD(η^2-D_2)(DMPE)$_2$]$^+$ (**4**-d_3) in neat CD_3OD (a) after addition of *ca.* 5 μL of CH_3OH and (b) after addition of 60 μL of CH_3OH.

intense 1:1:1 triplet (Figure 4a) is due to *trans*-[RuD(η^2-HD)(DMPE)$_2$]$^+$, which is the isotopomer formed initially by intermolecular exchange of **4**-d_3 with CH_3OH. The minor signal is due to *trans*-[RuH(η^2-HD)(DMPE)$_2$]$^+$ and the smaller (doublet) splitting (4.5 Hz) in this signal arises from coupling of the ^1H of the η^2-HD to the σ-bound hydride, across the ruthenium center. The origin of all splittings has been confirmed by decoupling experiments. Coupling of the ^1H nuclei of η^2-H_2 to other ligands bound to a metal is usually not observed because of the rapid relaxation of the nuclei in the η^2-H_2 group. However in the η^2-HD isotopomers, relaxation of ^1H in the η^2-HD group is substantially slowed compared to the η^2-H_2 compound and the signals are sharper and better resolved. The magnitude of the observed $^1J_{HD}$ coupling falls within the range of values reported so far for η^2-HD ligands in other molecular hydrogen complexes[1,15] and is very similar to those reported for *trans*-[RuH(HD)(DEPE)$_2$]$^+$BPh$_4^-$ measured under similar conditions.[8c] The coupling constant $^1J_{HD}$ varies little from the H/η^2-HD species to the D/η^2-HD species. The presence of a large $^1J_{HD}$ coupling in the η^2-HD complexes is characteristic of the "loose" η^2 type coordination of the dihydrogen ligand in **4**, and this is probably due to the poor σ-bonding and π-back-bonding nature of ruthenium. The observed chemical shift difference (30 Hz) between the *trans*-deuteride (*i.e.* D/η^2-HD) and the *trans*-hydride (*i.e.* H/η^2-HD) is in the expected upfield direction.[16]

Three overlapping σ-bonded hydride resonances were observed at approximately −12.6 ppm throughout the course of protonation, and their assignments are shown in Figure 4. The relative intensities of the signals from the σ-bonded hydrides change systematically as expected as the proportion of CH_3OH in the CD_3OD solution increases. One of the resonances shows coupling to η^2-HD, and this confirms its assignment as that from *trans*-[RuH(η^2-HD)(DMPE)$_2$]$^+$. The three σ-bonded hydride resonances have very similar chemical shifts but do not fall in a monotonic sequence. The resonance of the σ-H of the η^2-HD/σ-H isotopomer appears to lower field, and that of the η^2-H_2/σ-H isotopomer, at highest field.

(14) See for example: (a) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95. (b) Hamilton, D. G. *J. Am. Chem. Soc.* **1988**, *110*, 4126 and references therein. (c) Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J. *J. Am. Chem. Soc.* **1991**, *113*, 4173. (d) Kubas, G. J.; Ryan, R. R.; Wroblewski, D. *J. Am. Chem. Soc.* **1986**, *108*, 1339.

(15) Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299.

(16) Crabtree, R. H.; Habib, A. *Inorg. Chem.* **1986**, *25*, 3698.

(17) Johnson, C. K. *ORTEP: A Thermal Ellipsoid Plotting Program*; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

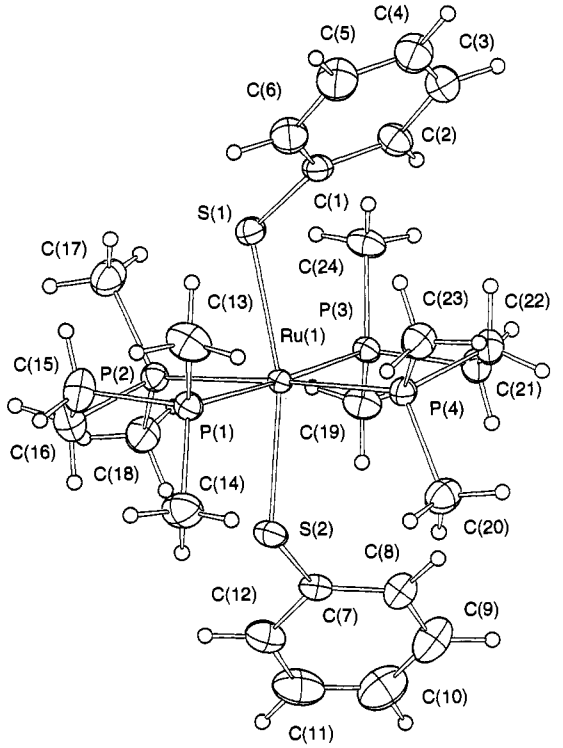
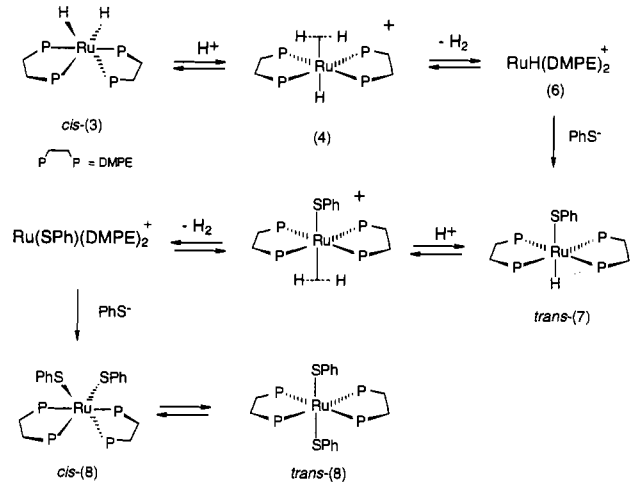


Figure 5. View of *trans*-Ru(SPh)$_2$(DMPE)$_2$ (*trans*-**8**) giving the atom numbering. Ellipsoids are drawn at the 30% probability level.[17]

Scheme 5



The two broad resonances (δ –7.15 and –6.97) which form among the 1:1:1 triplets are due to *trans*-[RuD(η^2-H$_2$)(DMPE)$_2$]$^+$ and *trans*-[RuH(η^2-H$_2$)(DMPE)$_2$]$^+$. At 250 K, all five isotopomers containing at least one metal-coordinated proton (*i.e.* D/η^2-H$_2$, H/η^2-D$_2$, D/η^2-HD, H/η^2-HD, and H/η^2-H$_2$) are observable in the ^{1}H NMR spectrum.

Reactions of RuH$_2$(DMPE)$_2$ with Thiols. The facile substitution of the η^2-bound dihydrogen in *trans*-[FeH(η^2-H$_2$)(DMPE)$_2$]$^+$ for thiolate ions has been demonstrated,[4] and similar behavior was anticipated for the ruthenium analogue.

Thiophenol. Treatment of RuH$_2$(DMPE)$_2$ (**3**) (30 mM in THF) with thiophenol (2 equiv) at 240 K resulted in the formation of the molecular hydrogen complex *trans*-[RuH(η^2-H$_2$)(DMPE)$_2$]$^+$ (**4**) and *trans*-RuH(SPh)(DMPE)$_2$ (*trans*-**7**) (δ(^{31}P{^{1}H}) 42.3 ppm; δ(^{1}H) Ru–H –18.33 ppm, qu, $^2J_{HP}$ = 21.5 Hz) within 10 min. *trans*-RuH$_2$(DMPE)$_2$ (*trans*-**3**) was protonated more rapidly than the corresponding *cis* isomer, as indicated by its effectively complete disappearance from the ^{31}P NMR spectrum within minutes of mixing the reactants. The rapid reaction of *trans*-**3** is consistent with the mechanism (Scheme 4) where the *trans*-isomer is preferentially protonated and the *cis*-isomer reacts only slowly by initial isomerization to the *trans*-isomer. Under the experimental conditions, the molecular hydrogen complex **4** was stable at temperatures below 270 K. Above 270 K, *trans*-[RuH(η^2-H$_2$)(DMPE)$_2$]$^+$ rapidly loses dihydrogen gas (δ(^{1}H) 4.4 ppm), and after 1 hour at 280 K, the yellow complex *trans*-RuH(SPh)(DMPE)$_2$ (*trans*-**7**) is the predominant species (>90%) present in the reaction mixture. The corresponding *cis*-ruthenium thiolate hydride was never observed during the course of reaction, and this contrasts with the observed formation of *cis*-FeH(SPh)(DMPE)$_2$ from *cis*-FeH$_2$(DMPE)$_2$ via *trans*-[FeH(η^2-H$_2$)(DMPE)$_2$]$^+$ under similar conditions.[4]

On further reaction at room temperature, the bright yellow compound *cis*-Ru(SPh)$_2$(DMPE)$_2$ (*cis*-**8**) was formed and was identified and characterized by ^{31}P, ^{1}H, and ^{13}C NMR spectroscopy. The *cis*-ruthenium dithiolate complex is likely to be formed via protonation of the thiolate hydride, *trans*-**7**, followed by loss of the η^2-H$_2$ ligand and attack by a thiophenolate ion. After 1 week at room temperature, the sample contains a mixture of *cis*- and *trans*-Ru(SPh)$_2$(DMPE)$_2$ in the ratio of *ca.* 2:1. *cis*-**8** is both the kinetic and thermodynamic product of the second substitution reaction (Scheme 5).

Orange crystals (plates) of *trans*-Ru(SPh)$_2$(DMPE)$_2$ (*trans*-**8**) suitable for X-ray diffraction studies were obtained by slow evaporation of a toluene solution. A view of the neutral complex *trans*-Ru(SPh)$_2$(DMPE)$_2$ is shown in Figure 5. The crystallographic data are summarized in Table 2. Bond lengths and angles are given in Tables 3 and 4, respectively.

In the structure of *trans*-Ru(SPh)$_2$(DMPE)$_2$ (*trans*-**8**), the benzenethiolate ligands are mutually *trans* (Chart 1); however, there are considerable deviations from an idealized octahedral geometry. This is most obvious in the S–Ru–S angle, which is 165.6°. The asymmetry arises primarily from interactions between the phenyl groups and the phosphine ligands. In the crystal, the phenyl groups are both disposed toward the same phosphine and therefore both S atoms are deflected toward the other phosphine. The molecule has approximate C_2 symmetry with the axis bisecting the C–C bonds of the phosphine ligands and passing through the Ru atom. The Ru–P bond lengths (2.334 Å on average) are substantially longer than the corresponding Fe–P bonds to Fe(II) (2.19 Å) in *trans*-Fe(SPh)$_2$(DMPE)$_2$.[4]

Table 2. Crystal Data for *trans*-Ru(SPh)$_2$(DMPE)$_2$ (*trans*-**8**)

space group	$P2_1/a$	empirical formula	$C_{24}H_{42}RuP_4S_2$
a, Å	15.035(3)	Z	4
b, Å	9.881(3)	abs coeff, cm^{-1}	9.01
β, deg	97.51(2)	temp, °C	21
c, Å	19.604(4)	λ, Å	0.710 69
V, Å^3	2887(1)	$R(F_o)^a$	0.029
fw	619.70	$R_w{}^a$	0.031
D_{calc}, g cm^{-3}	1.426		

^{a} $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $R_w = \Sigma(w^{1/2}||F_o| - |F_c||)/\Sigma w^{1/2}|F_o|$.

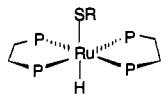
Table 3. Bond Lengths (Å) for *trans*-Ru(SPh)$_2$(DMPE)$_2$ (*trans*-**8**)

S(1)–Ru(1)	2.472(1)	S(2)–Ru(1)	2.466(1)
P(1)–Ru(1)	2.360(1)	P(2)–Ru(1)	2.338(1)
P(3)–Ru(1)	2.327(1)	P(4)–Ru(1)	2.310(1)
C(1)–S(1)	1.768(4)	C(7)–S(2)	1.765(4)
C(13)–P(1)	1.823(4)	C(14)–P(1)	1.820(4)
C(15)–P(1)	1.831(5)	C(16)–P(2)	1.844(4)
C(17)–P(2)	1.818(4)	C(18)–P(2)	1.824(4)
C(19)–P(3)	1.830(4)	C(21)–P(3)	1.843(4)
C(24)–P(3)	1.822(4)	C(20)–P(4)	1.828(4)
C(22)–P(4)	1.843(4)	C(23)–P(4)	1.818(4)
C(2)–C(1)	1.392(6)	C(6)–C(1)	1.395(6)
C(3)–C(2)	1.365(6)	C(4)–C(3)	1.382(7)
C(5)–C(4)	1.364(7)	C(6)–C(5)	1.377(6)
C(8)–C(7)	1.387(6)	C(12)–C(7)	1.388(6)
C(9)–C(8)	1.370(7)	C(10)–C(9)	1.348(8)
C(11)–C(10)	1.374(9)	C(12)–C(11)	1.383(7)
C(16)–C(15)	1.508(6)	C(22)–C(21)	1.529(6)

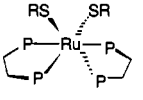
Table 4. Bond Angles (deg) for *trans*-$Ru(SPh)_2(DMPE)_2$ (*trans*-**8**)

S(2)–Ru(1)–S(1)	165.6(0)	P(1)–Ru(1)–S(1)	85.1(0)
P(1)–Ru(1)–S(2)	83.9(0)	P(2)–Ru(1)–S(1)	84.6(0)
P(2)–Ru(1)–S(2)	84.9(0)	P(2)–Ru(1)–P(1)	83.7(0)
P(3)–Ru(1)–S(1)	92.1(0)	P(3)–Ru(1)–S(2)	98.7(0)
P(3)–Ru(1)–P(1)	177.2(0)	P(3)–Ru(1)–P(2)	95.7(0)
P(4)–Ru(1)–S(1)	98.0(0)	P(4)–Ru(1)–S(2)	92.5(0)
P(4)–Ru(1)–P(1)	96.4(0)	P(4)–Ru(1)–P(2)	177.3(0)
P(4)–Ru(1)–P(3)	84.4(0)	C(1)–S(1)–Ru(1)	122.3(1)
C(7)–S(2)–Ru(1)	123.8(1)	C(13)–P(1)–Ru(1)	122.9(2)
C(14)–P(1)–Ru(1)	120.0(2)	C(14)–P(1)–C(13)	99.8(2)
C(15)–P(1)–Ru(1)	107.6(2)	C(15)–P(1)–C(13)	101.3(2)
C(15)–P(1)–C(14)	102.1(2)	C(16)–P(2)–Ru(1)	107.6(1)
C(17)–P(2)–Ru(1)	120.3(2)	C(17)–P(2)–C(16)	101.6(2)
C(18)–P(2)–Ru(1)	121.6(2)	C(18)–P(2)–C(16)	102.2(2)
C(18)–P(2)–C(17)	100.4(2)	C(19)–P(3)–Ru(1)	123.8(1)
C(21)–P(3)–Ru(1)	109.3(1)	C(21)–P(3)–C(19)	102.1(2)
C(24)–P(3)–Ru(1)	118.2(1)	C(24)–P(3)–C(19)	97.3(2)
C(24)–P(3)–C(21)	103.2(2)	C(20)–P(4)–Ru(1)	118.4(2)
C(22)–P(4)–Ru(1)	109.1(1)	C(22)–P(4)–C(20)	102.4(2)
C(23)–P(4)–Ru(1)	122.7(2)	C(23)–P(4)–C(20)	99.2(2)
C(23)–P(4)–C(22)	102.2(2)	C(2)–C(1)–S(1)	123.7(3)
C(6)–C(1)–S(1)	119.8(3)	C(6)–C(1)–C(2)	116.2(4)
C(3)–C(2)–C(1)	122.2(4)	C(4)–C(3)–C(2)	120.5(5)
C(5)–C(4)–C(3)	118.5(5)	C(6)–C(5)–C(4)	121.2(5)
C(5)–C(6)–C(1)	121.4(5)	C(8)–C(7)–S(2)	124.3(4)
C(12)–C(7)–S(2)	119.1(4)	C(12)–C(7)–C(8)	116.2(4)
C(9)–C(8)–C(7)	122.1(5)	C(10)–C(9)–C(8)	120.6(6)
C(11)–C(10)–C(9)	119.6(6)	C(12)–C(11)–C(10)	120.0(6)
C(11)–C(12)–C(7)	121.5(5)	C(16)–C(15)–P(1)	110.6(3)
C(15)–C(16)–P(2)	109.1(3)	C(22)–C(21)–P(3)	111.0(3)
C(21)–C(22)–P(4)	110.8(3)		

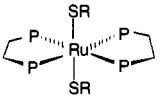
Chart 1



trans-(7) R = Ph
trans-(9) R = $CH_3CH_2CH_2$-
trans-(10) R = *t*-butyl-
trans-(11) R = $HSCH_2CH_2CH_2$-
trans-(12) R = 3-HS-C_6H_4-
trans-(14) R = $HOCH_2CH_2$-



cis-(8) R = Ph
cis-(13) R = 3-HS-C_6H_4-
cis-(15) R = $HOCH_2CH_2$-



trans-(8) R = Ph

Propanethiol. Substitution of *cis*-$RuH_2(DMPE)_2$ is slower with propanethiol than with thiophenol, presumably due to its lower acidity.[18] In THF solution, addition of propanethiol (2 equiv) to **3** does not produce the molecular hydrogen complex **4** in a concentration that can be detected by NMR spectroscopy. No reaction with propanethiol is observed at temperatures below 270 K. At 270 K, the resonance of *trans*-$RuH_2(DMPE)_2$ vanished immediately from the ^{31}P NMR spectrum on addition of the thiol. At 300 K, the resonances of *cis*-$RuH_2(DMPE)_2$ disappeared from the ^{31}P NMR spectrum and a new *trans* hydride was formed ($\delta(^{31}P\{^1H\})$ (THF, 300 K) 43.2 ppm; $\delta(^1H)$ (THF, 300 K) Ru–H −16.73 ppm, qu, $^2J_{cisPH}$ = 22 Hz). The NMR spectrum of the *trans* hydride was consistent with the formulation *trans*-$RuH(SCH_2CH_2CH_3)(DMPE)_2$ (*trans*-**9**) and was formed in quantitative yield after standing of the mixture for 2 h at room temperature. No *cis*-monothiolate hydride or any dithiolate complexes was detected even after 10 days at room temperature, suggesting that isomerization of *trans*-**9** and further substitution of *trans*-**9** with thiolate ion are both slow processes.

Although the molecular hydrogen complex was not detected by NMR spectroscopy, hydrogen gas was observed in the ^1H NMR spectrum ($\delta(^1H)$ 4.45 ppm). This suggests the formation of a complex of molecular hydrogen *trans*-$[RuH(H_2)(DMPE)_2]^+$ in solution, as the intermediate leading directly to *trans*-**9**. In a less polar solvent such as toluene, the thiolate hydride *trans*-**9** was formed more slowly. This further supports a reaction mechanism which involves polar intermediates. In toluene, only the monosubstituted product, propanethiolate hydride *trans*-**9**, was formed even when excess (5 equiv) propanethiol was used. The reaction was complete overnight at room temperature, and *trans*-**9** was isolated as a white solid.

***tert*-Butyl Mercaptan.** Reaction of dihydride **3** with *tert*-butyl mercaptan proceeded in a similar manner to the reaction with propanethiol except that the bright yellow complex *trans*-$RuH(SCMe_3)(DMPE)_2$ (*trans*-**10**) was formed at a lower temperature (250 K). At 300 K, *trans*-**10** was formed in >95% yield (by NMR) within 20 min of mixing the reactants. The monothiolate hydride *trans*-**10** failed to undergo a second substitution in the presence of excess thiol, even after 5 days at room temperature.

1,3-Propanedithiol. The reaction of $RuH_2(DMPE)_2$ (25 mM in THF) with 1,3-propanedithiol (2 equiv) in THF solution afforded the *trans*-monothiolate hydride *trans*-$RuH(SCH_2CH_2CH_2SH)(DMPE)_2$ (*trans*-**11**) in quantitative yield (by NMR) within 0.5 h at room temperature. No reaction was observed at temperatures below 270 K. *trans*-**11** was first observed in the ^{31}P NMR spectrum at 270 K, but the reaction was slow at this temperature. As with other reactions with alkanethiols, the molecular hydrogen complex **4** did not accumulate to a concentration detectable by NMR spectroscopy. Further substitution of the initially formed thiolate hydride did not occur even after 10 days at room temperature. Although iron cyclic dithiametallacycles $Fe(SCH_2CH_2S)(DMPE)_2$ and $Fe(SCH_2CH_2CH_2S)(DMPE)_2$ are readily formed by reaction of $FeH_2(DMPE)_2$ with ethanedithiol or 1,3-propanedithiol,[4] analogous cyclic products are not formed from $RuH_2(DMPE)_2$, and this may be due to the conformational stability of ruthenium DMPE complexes compared to the iron analogues. A *trans* to *cis* isomerization of the metal phosphine skeleton is necessary to form the dithiametallocycles, and this may be a comparatively difficult process for DMPE complexes of ruthenium.

1,3-Benzenedithiol. The molecular hydrogen complex **4** was formed immediately and quantitatively when 1,3-benzenedithiol (2 equiv) was added to $RuH_2(DMPE)_2$ (**3**) at 250 K. *trans*-$RuH(m\text{-}SC_6H_4SH)(DMPE)_2$ (*trans*-**12**) was formed in small quantity (*ca.* 20% of the total mixture) at this temperature ($\delta(^{31}P\{^1H\})$ (THF, 270 K) 42.3 ppm; $\delta(^1H)$ (THF, 270 K) Ru–H −18.31 ppm, qu, $^2J_{cisPH}$ = 21.8 Hz). When the temperature was raised to 270 K, substitution of the η^2-H_2 ligand for thiolate was complete and *trans*-**12** was the only product present in the mixture. At room temperature, the ruthenium-bound hydride in *trans*-**12** underwent exchange with free thiol, as indicated by broadening of the hydride resonance and the resonance for free thiol in the ^1H NMR spectrum. A second substitution with the aromatic dithiol afforded the dithiolate complex *cis*-$Ru(m\text{-}SC_6H_4SH)_2(DMPE)_2$ (*cis*-**13**). After 2 days at room temperature, an equilibrium mixture containing *trans*-**12** and *cis*-**13** in the ratio of 2:5 was obtained. There was no evidence for the formation of a cyclic compound $Ru(m\text{-}SC_6H_4S)(DMPE)_2$.

2-Mercaptoethanol. 2-Mercaptoethanol (0.7 equiv) was reacted with $RuH_2(DMPE)_2$ (**3**) (62 mM in benzene-d_6) at 300 K. After 40 min, a symmetrical *trans* hydride was formed. No change in the product mixture was observed even after 2 weeks at room temperature. Although 2-mercaptoethanol could react either via the thiol or hydroxyl functional groups, $^{13}C\{^{31}P\}$ and $^{13}C\{^1H\}$ NMR spectroscopic data indicated that the attack was via sulfur; *i.e.*, $RuH(SCH_2CH_2OH)(DMPE)_2$ was formed as the sole reaction product. The carbon atom directly attached to the sulfur atom shows coupling to the four equivalent phosphorus nuclei and has a chemical shift similar to that of the corresponding carbon atom in *trans*-$RuH(SCH_2CH_2CH_3)(DMPE)_2$ (*trans*-**9**). Moreover, no reaction was obtained when dihydride **3** was treated with $HOCH_2CH_2SCH_2CH_3$ (5 equiv) in THF-d_8 even after 1 week at room temperature. The *trans* hydride observed in solution

(18) Crampton, M. R. *The Chemistry of the Thiol Group, Part 1*; Patai, S., Ed.; John Wiley and Sons: London, 1974; pp 379–415.

Table 5. Selected ^1H and ^{31}P NMR Data[a] for $RuH_2(DMPE)_2$, $RuH(SR)(DMPE)_2$, and $Ru(SR)_2(DMPE)_2$ Complexes

complex	$\delta(^1H)$[b] Ru–H	$^2J_{HP}$, Hz	$\delta(^{31}P\{^1H\})$[b]
cis-$RuH_2(DMPE)_2$[c] (*cis*-**3**)	−9.60	apparent dq (doublet splitting = 60.0 Hz, quartet splitting = 20.5 Hz)	38.3, 47.3 (apparent triplets; splitting = 21.5 Hz)
trans-$RuH_2(DMPE)_2$[c] (*trans*-**3**)	−10.50	20.7	49.1
trans-$[RuH(\eta^2\text{-}H_2)(DMPE)_2]^+$[d] (**4**)	−7.0 (Ru–(η^2-H_2))	*e*	40.3
	−12.89 (Ru–H)	20.8	
trans-$RuH(SPh)(DMPE)_2$ (*trans*-**7**)	−18.33	21.9	42.6
cis-$Ru(SPh)_2(DMPE)_2$ (*cis*-**8**)	*f*	*f*	31.8, 37.6 (apparent triplets, splitting = 22.1 Hz)
trans-$Ru(SPh)_2(DMPE)_2$ (*trans*-**8**)	*f*	*f*	35.6
trans-$RuH(SCH_2CH_2CH_3)(DMPE)_2$ (*trans*-**9**)	−16.73	22.0	43.2
trans-$RuH(SCMe_3)(DMPE)_2$ (*trans*-**10**)	−18.0	22.7	40.2
trans-$RuH(SCH_2CH_2CH_2SH)(DMPE)_2$ (*trans*-**11**)	−16.81	21.8	43.0
trans-$RuH(m\text{-}SC_6H_4SH)(DMPE)_2$ (*trans*-**12**)	−18.31	21.8	42.3
cis-$Ru(m\text{-}SC_6H_4SH)_2(DMPE)_2$ (*cis*-**13**)	*f*	*f*	32.0, 37.8 (apparent triplets, splitting = 22.4 Hz)
trans-$RuH(SCH_2CH_2OH)(DMPE)_2$ (*trans*-**14**)	−16.84[c]	22.1	42.4[c]
cis-$Ru(SCH_2CH_2OH)_2(DMPE)_2$ (*cis*-**15**)	*f*	*f*	34.2, 37.7[g] (apparent triplets, splitting = 22.1 Hz)

[a] ^1H NMR (400 MHz) and ^{13}P NMR (162 MHz) were obtained with a Bruker AMX 400 NMR spectrometer. ^1H chemical shifts were measured relative to internal residual solvent resonances. ^{31}P chemical shifts were measured relative to external, neat trimethyl phosphite (taken as 140.85 ppm) at the temperature quoted. [b] THF solvent, 300 K. [c] Benzene-d_6, 300 K. [d] THF, 250 K. [e] Not measured. [f] Not applicable. [g] Toluene-d_8, 300 K.

with $HSCH_2CH_2OH$ was identified as *trans*-$RuH(SCH_2CH_2OH)(DMPE)_2$ (*trans*-**14**).

In toluene-d_8, addition of excess 2-mercaptoethanol (4 equiv with respect to ruthenium) to $RuH_2(DMPE)_2$ (**3**) (20 mM) at 230 K immediately converted the dihydride (both *cis* and *trans* isomers) into *trans*-$[RuH(\eta^2\text{-}H_2)(DMPE)_2]^+$ (**4**) with only a very minor amount of the *trans*-monothiolate hydride *trans*-**14** being formed. When the yellow reaction mixture was warmed to 260 K, *trans*-**14** was the only product present in the mixture by NMR spectroscopy. On standing of the reaction mixture overnight at room temperature, a symmetrical *cis* compound was formed which was present in equal concentration with *trans*-**14**. After 2 days at room temperature, the *trans*-monothiolate hydride had reacted completely and the symmetrical *cis* compound was formed in quantitative yield (by NMR). The *cis* compound was identified by ^1H and ^{13}C NMR spectroscopy as *cis*-$Ru(SCH_2CH_2OH)_2(DMPE)_2$ (*cis*-**15**) and is probably formed via protonation of *trans*-**14** followed by substitution with a thiolate ion. Protonation of the ruthenium-bound hydride in *trans*-**14** by the pendant OH group in its thiolate ligand was never observed directly, nor was the formation of any alkoxy-substituted ruthenium complex.

General Properties of $RuH(SR)(DMPE)_2$ and $Ru(SR)_2(DMPE)_2$ Complexes. All thiolate hydrides and dithiolate complexes studied are neutral, diamagnetic compounds, which are soluble in THF, benzene, and toluene. These complexes are generally pale yellow in color and oxygen-sensitive. For all the thiolate hydrides studied, only the *trans* stereoisomer is observed in solution under the experimental conditions. In the ^1H NMR spectra of the *trans*-thiolate hydrides, the ruthenium-bound protons appear characteristically in the range −16 to −18 ppm with a quintet splitting ($^2J_{HP}$) of about 22 Hz. In the ^{31}P NMR spectra of the *trans*-thiolate hydride complexes, the four equivalent ^{31}P nuclei of the DMPE ligands resonate at about 43 ppm.

In the ^{31}P spectrum, the *cis*-dithiolates studied give rise to two apparent triplets in the region 30–40 ppm with splittings of approximately 22 Hz (Table 5).

Conclusion

$RuH_2(DMPE)_2$ can be synthesized in good yield from *trans*-$RuCl_2(DMPE)_2$ by reduction with sodium metal and 2-propanol. Similar to the corresponding Fe complex, $RuH_2(DMPE)_2$ is basic and can be protonated by weak organic acids such as alcohols and thiols to give complexes of molecular hydrogen. The weakly bound η^2-H_2 ligand in these molecular hydrogen complexes can be displaced readily (for example by thiolates) to form new hydride complexes in high yield and high purity. In methanol solution, a previously unreported five-coordinate ruthenium(II) complex, $[RuH(DMPE)_2]^+$, exists in equilibrium with the molecular hydrogen complex.

Experimental Section

Unless otherwise stated, all manipulations were carried out using standard Schlenk or vacuum line techniques or in a Vacuum Atmospheres drybox under argon (CIG-HYTEC, >99.99%). Ruthenium trichloride trihydrate was obtained from Aldrich Chemicals and used without further purification. Propanethiol (Aldrich), thiophenol (Merck), 1,3-propanedithiol (BDH), 1,3-benzenedithiol (Aldrich), and 2-mercaptoethanol (Fluka) were obtained commercially and distilled before use. THF was distilled from sodium benzophenone ketyl under nitrogen. Benzene was distilled and deoxygenated (by three freeze–pump–thaw cycles) before use. Absolute ethanol and AR grade methanol were dried by distillation from the magnesium alkoxide under nitrogen. All other solvents were distilled and deoxygenated before use. Deuterated solvents (Aldrich) were obtained commercially and used without further purification.

^1H, ^{31}P, and ^{13}C NMR spectra were obtained with a Bruker AMX 400 NMR spectrometer at 400.1, 162.0, and 100.6 MHz, respectively. Chemical shifts refer to room-temperature conditions unless specified otherwise. In the presentation of NMR data, chemical shifts (δ) are in ppm, the downfield direction being positive. ^{31}P chemical shifts were measured relative to external neat $P(OMe)_3$, taken as 140.85 ppm at the temperature quoted. ^1H and ^{13}C chemical shifts were measured relative to internal residual solvent resonances. Uncertainties in chemical shifts are typically ±0.01 ppm for ^1H and ±0.1 ppm for ^{13}C and ^{31}P. For variable-temperature spectra, the temperatures quoted are approximate (±3 K).

Microanalyses were performed by the Australian Microanalytical Service, National Analytical Laboratories Pty. Ltd., Ferntree Gully, Victoria.

Crystallography. Cell constants were determined by a least-squares fit to the θ values of 25 independent reflections, measured and refined on an Enraf-Nonius CAD4-F diffractometer with a graphite monochromator. The crystallographic data are summarized in Table 2. Data were reduced and Lorentz, polarization, and absorption corrections were applied using the Enraf-Nonius Structure Determination Package.[19] The structure of *trans*-**8** was solved by direct methods with the SHELXS-86 program.[20] All non-hydrogen atoms were refined anisotropically. H atoms were included at calculated sites (C–H = 0.97 Å) with group isotropic thermal parameters. Full-matrix least-squares refinement was carried out using the program SHELX-76.[21] Scattering factors and

(19) Enraf-Nonius Structure Determination Package, Enraf Nonius, Delft, The Netherlands, 1985.
(20) Sheldrick, G. M. SHELXS-86. *Crystallographic Computing 3*; Sheldrick, G. M., Kueger, C., Goddard, R., Eds.; Oxford University Press: Oxford, U.K., 1985; pp 175–189.
(21) Sheldrick, G. M. *SHELX-76: A Program for X-Ray Crystal Structure Determination*; University of Cambridge: Cambridge, England, 1976.

anomalous dispersion corrections for Ru were taken from ref 22, and for all others the values supplied in SHELX-76 were used. The atomic nomenclature is defined in Figure 5.[17] Full tables of bond lengths and angles and listings of atom coordinates, thermal parameters, and details of least-squares planes calculations have been deposited as supplementary material.

Preparation of $RuH_2(DMPE)_2$ (3). *trans*-$RuCl_2(DMPE)_2$ (**5**) was prepared by following the procedure recommended by Chatt and Hayter.[23] A solution of *trans*-$RuCl_2(DMPE)_2$ (**5**) (0.24 g, 0.50 mmol) in 2-propanol/THF (2:98 v/v, 30 mL) was stirred for 0.5 h under nitrogen. Sodium metal (2 g) was added, H_2 gas was evolved from the solution, and the color of the reaction mixture changed immediately to pale yellow. After being stirred for 1 h, the solvent was removed under vacuum. The residue was extracted into *n*-pentane (30 mL). The extract was filtered and dried, and the solvent was removed under vacuum. Sublimation of the dried residue at 70 °C/10^{-3} mm onto a cold finger (−78 °C) afforded $RuH_2(DMPE)_2$ (**3**) as a white powder (0.106 g, 53%). In benzene solution, an isomeric mixture of *cis*- and *trans*-$RuH_2(DMPE)_2$ exists in the ratio of 24:1. λ_{max} (*n*-pentane): 209 (ϵ, 4600) nm. Anal. Calcd for $C_{12}H_{34}P_4Ru$: C, 35.73; H, 8.50. Found: C, 35.7; H, 8.6. *cis*-$RuH_2(DMPE)_2$ (*cis*-**3**): ^{1}H NMR (benzene-d_6, 300 K) δ 1.01 (d, 6H, 2 × PCH_3), 1.18 (s, 6H, 2 × PCH_3), 1.30 (d, 6H, 2 × PCH_3), 1.36 (s, 6H, 2 × PCH_3), 1.56 (s, 6H, 2 × PCH_3), 1.33–1.39 (br m, 8H, 2 × PCH_2CH_2P), −9.60 (m, 2 × Ru–*H*); ^{31}P{^{1}H} NMR (benzene-d_6, 300 K) δ 38.3 (apparent triplet, 2P, splitting = 21.5 Hz), 47.3 (apparent triplet, 2P, splitting = 21.5 Hz); ^{13}C{^{1}H,^{31}P} NMR (benzene-d_6, 300 K) δ 23.1 (2 × PCH$_3$), 23.2 (2 × PCH$_3$), 27.4 (2 × PCH$_3$), 27.9 (2 × PCH$_3$), 33.1 (2 × PCH$_2$-CH$_2$P), 35.2 (2 × PCH$_2$CH$_2$P). *trans*-$RuH_2(DMPE)_2$ (*trans*-**3**): ^{1}H NMR (benzene-d_6, 300 K) δ −10.5 (qu, $^2J_{HP}$ = 16.5 Hz, 2 × Ru–*H*); ^{31}P{^{1}H} NMR (benzene-d_6, 300 K) δ 49.1 (s); ^{13}C{^{1}H,^{31}P} NMR (benzene-d_6, 300 K) δ 25.8 (PCH$_3$), 33.4 (PCH$_2$–).

Preparation of *trans*-$[RuH(H_2)(DMPE)_2]^+$ (4) in Methanol or Ethanol. $RuH_2(DMPE)_2$ (**3**) (10 mg, 0.025 mmol) was dissolved in dry ethanol or methanol (0.6 mL). The color of the sample changed from colorless to pale yellow immediately. The solution was cooled immediately below 210 K. ^{1}H and ^{31}P NMR spectra were acquired at different temperatures between 210 and 300 K. Concentrations of various species were obtained by integration of their corresponding ^{31}P NMR resonances. Thermodynamic parameters (ΔH and ΔS) were obtained from the equilibrium concentration ratios for various species in solution at different temperatures. T_1 values for the η^2-H_2 resonance and the terminal hydride resonance were measured in ethanol at 200 and 230 K using the inversion-recovery method. *trans*-$[RuH(H_2)(DMPE)_2]^+$ (**4**): ^{1}H (THF-d_8, 250 K) δ 1.36 (br s, 12H, 4 × PCH_3), 1.48 (br s, 12H, 4 × PCH_3), 1.55–1.70 (br m, 8H, 2 × PCH_2CH_2P), −7.0 (br s, 2H, Ru–H_2), −12.89 (qu, 1H, $^2J_{HP}$ = 20.8 Hz, Ru–*H*).

Measurement of the One-Bond H-D Coupling Constant in the η^2-HD Ligand of Molecular Hydrogen Complex. $RuH_2(DMPE)_2$ (**3**) (8 mg) was dissolved in CD_3OD (0.6 mL), and the solution was cooled to below 210 K. One drop (*ca.* 0.01 mL) of CH_3OH was added at this temperature, and any change was monitored by ^{1}H{^{31}P} and ^{31}P{^{1}H} NMR spectroscopy at 235 K. More CH_3OH was added in a dropwise fashion and the change was monitored by NMR spectroscopy similarly until *trans*-$[RuH(\eta^2\text{-}H_2)(DMPE)_2]^+$ (**4**) was obtained.

Identification of the Five-Coordinate $[RuH(DMPE)_2]^+$ Complex 6. $RuH_2(DMPE)_2$ (**3**) (3 mg, 7.4 μmol) was dissolved in neat methanol (0.7 mL) in an NMR tube fitted with a concentric Teflon valve (Young's catalogue no. NMR/5). ^{31}P and ^{1}H (with solvent suppression) NMR spectra were acquired at 220 K for control. The NMR tube was attached to a vacuum line, and the sample was degassed by three freeze–pump–thaw cycles. ^{31}P and ^{1}H NMR spectra were again acquired at 220 K to probe any change in the composition of the mixture. The NMR tube was attached to a vacuum line which was then evacuated and re-filled with hydrogen gas (1 atm). The valve was opened while the sample was frozen in a liquid-nitrogen bath. The valve was closed, and the sample was thawed and shaken vigorously to facilitate dissolution of the hydrogen gas in solution. Any change to the sample was monitored by ^{31}P and ^{1}H NMR spectroscopy at 220 K.

Reaction of $RuH_2(DMPE)_2$ with Alkane- and Arenethiols. General Procedure. Typically, a neat thiol solution (2 equiv with respect to Ru) was added (via gastight syringe) to a solution of $RuH_2(DMPE)_2$ (**3**) (*ca.* 10 mg) in oxygen-free THF-d_8 (0.5-0.7 mL) at temperatures below 210 K. The reaction was monitored by ^{31}P and ^{1}H NMR spectroscopy as the sample was warmed slowly to room temperature.

Thiophenol. At 240 K, $RuH_2(DMPE)_2$ (**3**) was completely protonated by thiophenol to give *trans*-$[RuH(H_2)(DMPE)_2]^+$ (**4**) and *trans*-$RuH(SPh)(DMPE)_2$ (*trans*-**7**). After 1 h at 280 K, the reaction to form *trans*-$[RuH(SPh)(DMPE)_2]$ was more than 90% complete. The sample was left to stand at 270 K overnight. The THF solvent was removed under vacuum. The yellow residue obtained was identified as *cis*-$Ru(SPh)_2(DMPE)_2$ (*cis*-**8**). After 1 week at room temperature, an equilibrium mixture of *cis*-$Ru(SPh)_2(DMPE)_2$ and *trans*-$Ru(SPh)_2(DMPE)_2$ was obtained in the ratio of 2:1. *trans*-$Ru(SPh)_2(DMPE)_2$ (*trans*-**8**) crystallized from toluene over a period of 10 days as yellow plates, and crystals obtained in this way were suitable for X-ray crystallography. *cis*-$Ru(SPh)_2(DMPE)_2$ (*cis*-**8**): ^{1}H NMR (THF-d_8, 300 K) δ 0.92 (m, 6H, 2 × PCH_3), 1.04 (m, 6H, 2 × PCH_3), 1.17 (d, 6H, 2 × PCH_3), 1.67 (d, 6H, 2 × PCH_3), 1.3–1.45 (br m, 4H, 2 × PCH_2–), 1.45–1.62 (br m, 4H, 2 × PCH_2–), 6.68 (m, 1H, Ar H_{para}), 6.73 (m, 2H, Ar H_{meta}), 7.7 (m, 2H, Ar H_{ortho}); ^{31}P{^{1}H} NMR (THF-d_8, 300 K) δ 31.9 (apparent triplet, splitting = 22.1 Hz), 37.6 (apparent triplet, splitting = 22.1 Hz); ^{13}C{^{1}H} NMR (THF-d_8, 300 K) δ 11.5 (2 × PCH$_3$), 17.9 (2 × PCH$_3$), 18.4 (2 × PCH$_3$), 21.8 (2 × PCH$_3$), 32.1 (2 × PCH$_2$CH$_2$P), 128.7 (Ar C_{para}), 128.9 (Ar C_{meta}), 130.5 (Ar C_{ortho}), 153.6 (Ar C_{ipso}). *trans*-$Ru(SPh)_2(DMPE)_2$ (*trans*-**8**): ^{1}H{^{31}P} NMR (THF-d_8, 300 K) δ 1.34 (s, 12H, 4 × PCH_3), 2.45 (s, 12H, 4 × PCH_3), 1.66–1.82 (br m, 8H, 2 × PCH_2CH_2P), 7.21 (m, 4H, Ar H_{ortho}), 7.15 (m, 4H, Ar H_{meta}), 6.68 (m, 2H, Ar H_{para}); ^{13}C{^{1}H} NMR (THF-d_8, 300 K) δ 15.9 (4 × PCH$_3$), 19.7 (4 × PCH$_3$), 31.1 (2 × PCH$_2$CH$_2$P), 123.5 (Ar C_{para}), 128.4 (Ar C_{meta}), 129.6 (Ar C_{ortho}), 152.5 (Ar C_{ipso}); ^{31}P{^{1}H} NMR (THF-d_8, 300 K) δ 35.6 (s).

Propanethiol. No reaction was observed between propanethiol and $RuH_2(DMPE)_2$ (**3**) at temperatures below 300 K. At room temperature, *trans*-$RuH(SCH_2CH_2CH_3)(DMPE)_2$ appeared at low concentration after 10 min. The reaction to form *trans*-$RuH(SCH_2CH_2CH_3)(DMPE)_2$ (*trans*-**9**) was complete after standing of the mixture overnight at room temperature. A single phosphorus-containing product was obtained. The reaction mixture was stripped of solvent, and the residue was recrystallized from benzene-d_6 to give *trans*-$RuH(SCH_2CH_2CH_3)(DMPE)_2$ as a white air-sensitive crystalline solid (95%) which decomposed without melting at 189–190 °C. *trans*-$RuH(SCH_2CH_2CH_3)(DMPE)_2$ (*trans*-**9**): ^{1}H NMR (benzene-d_6, 300 K) δ 0.91 (s, 12H, 4 × PCH_3), 1.23 (s, 12H, 4 × PCH_3), 0.95–1.08 (m, 4H, 4 × PC*H*H–), 1.22–1.40 (m, 4H, 4 × PCH*H*–), 2.06 (t, 2H, –SCH_2CH$_2$CH$_3$), 1.67 (m, 2H, –SCH$_2$CH_2CH$_3$), 0.93 (t, 3H, –SCH$_2$CH$_2$CH_3), −16.73 (qu, 1H, $^2J_{cisPH}$ = 22 Hz, Ru–*H*); ^{13}C{^{1}H,^{31}P} NMR (benzene-d_6, 300 K) δ 15.7 (4 × PCH$_3$), 16.3 (–SCH$_2$-CH$_2$CH$_3$), 25.7 (–SCH$_2$CH$_2$CH$_3$), 31.2 (4 × PCH$_3$), 32.3 (–SCH$_2$CH$_2$-CH$_3$), 38.3 (4 × PCH$_2$–); ^{31}P{^{1}H} NMR (THF-d_8, 300 K) δ 43.2 (s).

***tert*-Butyl Mercaptan.** $RuH_2(DMPE)_2$ (**3**) (8 mg, 20 μmol) was dissolved in THF (0.6 mL) with a few drops of THF-d_8 added. *tert*-Butyl mercaptan (5 μL, 2 equiv) was added at 220 K. The color of the reaction mixture changed immediately from colorless to bright yellow. After warming of the reaction mixture to room temperature, the reaction to form *trans*-$RuH(SCMe_3)(DMPE)_2$ was complete (>95% by NMR). *trans*-$RuH(SCMe_3)(DMPE)_2$ (*trans*-**10**): ^{1}H{^{31}P} NMR (benzene-d_6, 300 K) δ 1.24 (s, 12H, 4 × PCH_3), 1.62 (s, 12H, 4 × PCH_3), 1.59 (s, 9H, 3 × CH_3), 1.15–1.28 (br m, 4H, 4 × PC*H*H–), 1.65–1.80 (br m, 4H, 4 × PCH*H*–), −18.0 (qu, 1H, $^2J_{cisPH}$ = 22.7 Hz, Ru–*H*); ^{13}C{^{1}H} NMR (benzene-d_6, 300 K) δ 15.7 (4 × PCH$_3$), 24.3 (4 × PCH$_3$), 30.4 (3 × CH$_3$), 37.3 (2 × PCH$_2$CH$_2$P), 66.4 (–SCMe$_3$); ^{31}P{^{1}H} NMR (THF, 300 K) δ 40.2 (s). Attempted recrystallization from benzene resulted in decomposition to a black solid which was not further characterized.

1,3-Propanedithiol. No reaction was observed between 1,3-propanedithiol and $RuH_2(DMPE)_2$ (**3**) at temperatures below 270 K. At 270 K *trans*-$RuH(SCH_2CH_2CH_2SH)(DMPE)_2$ (*trans*-**11**) appeared at low concentration after 10 min. The reaction to form *trans*-$RuH(SCH_2CH_2CH_2SH)(DMPE)_2$ (*trans*-**11**) was complete after standing the mixture for 1 h at room temperature. The reaction mixture was stripped of solvent under vacuum, and the residue was recrystallized from benzene-d_6 to give *trans*-$RuH(SCH_2CH_2CH_2SH)(DMPE)_2$ as a pale yellow air-sensitive solid (90%). *trans*-$RuH(SCH_2CH_2CH_2SH)(DMPE)_2$ (*trans*-**11**): ^{1}H{^{31}P} NMR (THF-d_8, 300 K) δ 1.26 (s, 12H, 4 × PCH_3), 1.40 (s, 12H, 4 × PCH_3), 1.52–1.67 (m, 8H, 2 × PCH_2CH_2P), 2.53 (t, 1H, –SCH$_2$CH$_2$CH$_2$S*H*), 1.99 (t, 2H, –SCH_2CH$_2$CH$_2$SH), 1.75 (qu, 2H, –SCH$_2$CH_2CH$_2$SH), 1.57 (m, 2H, –SCH$_2$CH$_2$CH_2SH), −16.81 (qu, 1H, $^2J_{cisPH}$ = 21.8 Hz, Ru–*H*); ^{13}C{^{1}H,^{31}P} NMR (benzene-d_6, 300 K) δ 14.6 (4 × PCH$_3$), 23.9 (4 × PCH$_3$), 29.0 (RuSCH$_2$CH$_2$–), 30.6

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(23) Chatt, J.; Hayter, R. G. *J. Chem. Soc.* **1961**, 896.

(RuSCH$_2$-), 31.9 (4 × PCH$_2$–), 39.3 (–CH$_2$SH); ^{31}P{^{1}H} NMR (THF-d_8, 300 K) δ 43.0 (s).

1,3-Benzenedithiol. At 250 K, the molecular hydrogen complex **4** formed immediately and quantitatively as 1,3-benzenedithiol was mixed with RuH$_2$(DMPE)$_2$. At 270 K, the molecular hydrogen complex **4** reacted further to give *trans*-RuH(*m*-SC$_6$H$_4$SH)(DMPE)$_2$ (*trans*-**12**) rapidly and quantitatively. At room temperature, *trans*-**12** underwent further substitution to give the dithiolate compound *cis*-Ru(*m*-SC$_6$H$_4$SH)$_2$(DMPE)$_2$ (*cis*-**13**). After 2 days at room temperature, the reaction mixture contained *trans*-RuH(*m*-SC$_6$H$_4$SH)(DMPE)$_2$ and *cis*-Ru(*m*-SC$_6$H$_4$SH)$_2$(DMPE)$_2$ in the ratio of 2:5, respectively. *trans*-RuH(*m*-SC$_6$H$_4$SH)(DMPE)$_2$ (*trans*-**12**): ^{1}H{^{31}P} NMR (THF-d_8, 300 K) δ 1.26 (s, 12H, 4 × PC*H*$_3$), 1.32 (s, 12H, 4 × PC*H*$_3$), 1.40–1.51 (m, 4H, 4 × PC*H*H–), 1.63–1.78 (m, 4H, 4 × PCH*H*–), –18.31 (qu, 1H, $^2J_{cis\mathrm{PH}}$ = 21.8 Hz, Ru–*H*), 2.61 (br s, 1H, –S*H*), 7.11 (t, 1H, J_{meta} = 1.65 Hz, Ar *H*), 6.49 (t, 1H, J_{ortho} = 7.5 Hz, Ar *H*), 6.90 (dt, 1H, J_{ortho} = 7.5 Hz, J_{meta} = 1.6 Hz, Ar *H*), 6.89 (dt, 1H, J_{ortho} = 7.5 Hz, J_{meta} = 1.6 Hz, Ar *H*); ^{31}P{^{1}H} NMR (THF-d_8, 300 K) δ 42.3 (s). *cis*-Ru(*m*-SC$_6$H$_4$SH)$_2$(DMPE)$_2$ (*cis*-**12**): ^{1}H NMR (THF-d_8, 300 K) δ 1.08 (m, 6H, 2 × PC*H*$_3$), 1.12 (m, 6H, 2 × PC*H*$_3$), 1.21 (d, 6H, 2 × PC*H*$_3$), 1.64 (d, 6H, 2 × C*H*$_3$), 1.38–1.42 (br m, 4H, 4 × PC*H*H–), 1.51–1.68 (m, 4H, 4 × PCH*H*–), 4.24 (br s, 2H, 2 × –S*H*), 7.57 (br s, 2H, Ar *H*), 7.39 (dt, 2H, J_{meta} = 1.65 Hz, J_{ortho} = 5.1 Hz, Ar *H*), 6.62 (dd, 4 H, J_{ortho} = 5.1 Hz, J_{meta} = 1.65 Hz, Ar *H*); ^{31}P{^{1}H} NMR (THF-d_8, 300 K) δ 32.0 (apparent triplet, splitting = 22.4 Hz), 37.8 (apparent triplet, splitting = 22.4 Hz).

2-Mercaptoethanol. RuH$_2$(DMPE)$_2$ (**3**) (5 mg, 12 μmol) was dissolved in toluene-d_8 (0.6 mL) and cooled to 220 K. 2-Mercaptoethanol (4 μL, 4 equiv) was added at this temperature. The mixture was warmed slowly to room temperature, and the progress of reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy. At 280 K, the yellow reaction mixture contained *trans*-RuH(SCH$_2$CH$_2$OH)(DMPE)$_2$ (*trans*-**11**) as the sole product. *trans*-RuH(SCH$_2$CH$_2$OH)(DMPE)$_2$ (*trans*-**11**): ^{1}H{^{31}P} NMR (benzene-d_6, 300 K) δ 1.35 (s, 12H, 4 × PC*H*$_3$), 1.44 (m, 4H, 4 × PC*H*H–), 1.65 (s 12H, 4 × PC*H*$_3$), 1.75 (m, 4H, 4 × PCH*H*–), 2.74 (t, 2H, RuSCH$_2$–), 4.11 (t, 2H, RuSCH$_2$C*H*$_2$–), 4.70 (br s, 1H, –O*H*), –16.84 (qu, 1H, $^2J_{\mathrm{HP}}$ = 22.1 Hz, Ru–*H*); ^{13}C{^{1}H,^{31}P} NMR (benzene-d_6, 300 K) δ 14.6 (4 × PCH$_3$), 23.6 (4 × PCH$_3$), 36.9 (4 × PCH$_2$–), 30.4 (RuSCH$_2$–), 62.7 (–CH$_2$OH); ^{31}P{^{1}H} NMR (benzene-d_6, 300 K) δ 42.4 (s). The toluene mixture was left at room temperature for 2 days. *trans*-**11** reacted completely to give the dithiolate complex *cis*-Ru(SCH$_2$CH$_2$OH)$_2$(DMPE)$_2$ (*cis*-**15**) as the sole product. Evaporation of the solvent under vacuum followed by recrystallization of the residue from toluene afforded *cis*-Ru(SCH$_2$CH$_2$OH)$_2$(DMPE)$_2$ as a pale yellow gummy solid. *cis*-Ru(SCH$_2$CH$_2$OH)$_2$(DMPE)$_2$ (*cis*-**15**): ^{1}H NMR (toluene-d_8, 300 K) δ 0.50 (d, 6H, 2 × PC*H*$_3$), 0.85 (s, 6 H, 2 × PC*H*$_3$), 1.03 (d, 6H, 2 × PC*H*$_3$), 1.28 (s, 6H, 2 × PC*H*$_3$), 0.96–1.24 (br m, 8H, 4 × PC*H*$_2$–), 3.58 (br t, 4H, J = 5.6 Hz, 2 × RuSCH$_2$C*H*$_2$OH), 2.44 (m, 4H, 2 × RuSC*H*$_2$–), 4.27 (br s, 2H, 2 × O*H*); ^{13}C{^{1}H} NMR (toluene-d_8, 300 K) δ 13.1 (2 × PCH$_3$), 16.1 (2 × PCH$_3$), 17.9 (2 × PCH$_3$), 21.0 (2 × PCH$_3$), 29.4 (2 × RuSCH$_2$–), 33.6 (2 × PCH$_2$–), 34.6 (2 × PCH$_2$–), 65.8 (2 × RuSCH$_2$CH$_2$OH); ^{31}P{^{1}H} NMR (toluene-d_8, 300 K) δ 34.2 (apparent triplet, splitting = 22.1 Hz), 37.7 (apparent triplet, splitting = 22.1 Hz).

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Supplementary Material Available: Tables listing crystal data, thermal parameters, non-hydrogen positional parameters, hydrogen atom thermal and positional parameters, and details of least-squares plane calculations for *trans*-**8** (5 pages). Ordering information is given on any current masthead page.