provides a bite angle of 95–96 as discussed earlier, which causes a CAD effect. Isomerization of NiEDDA from cis-α-octahedral to cis-β-octahedral to relieve the CAD effect, like the reaction of NiEDDA with en, may be used to explain the slow rate of formation. The b term of eq 8 then represents k_d, the dissociation of an acetate arm of Ni(EDDA)(–O–N)$^-$. The dissociation of an acetate arm from Ni(EDDA)(–N–N) having a monocoordinated en species was estimated to be 7×10^2 s^{-1}. The k_d value for the dissociation of an acetate arm from Ni(EDDA)(–O–N)$^-$ having an amino acid coordinated through the acetate group will differ from k_d of Ni(EDDA)(–N–N) due to (1) the added negative charge of the coordinated acetate from the amino acid and (2) the coordination of an oxygen of the amino acid instead of a nitrogen of en. Thus, the factors of 3.1 due to charge and of 10 due to coordinated nitrogen do not apply, and k_d for the NiEDDA–amino acid systems is 23 s^{-1}. This is very close to the observed value of 44 s^{-1} seen for both systems. Further, a dissociation mechanism would predict identical k_d values for both amino acids reacting with NiEDDA, which is what is experimentally seen. The conclusion is that the NiEDDA reaction with amino acids proceeds through an isomerization mechanism.

Conclusions

The rate of formation of a ternary complex in which all metal coordination sites could be occupied by multidentate ligands involves a combination of many factors. The amount of steric hindrance that occurs as a ligand attacks an already coordinated metal varies considerably, depending on the size and geometry of the attacking ligand and the coordinated ligand. Protons on atoms in the chelate rings adjacent to open coordination sites severely limit the room at those sites as is seen by comparing the rate of reaction of Ni(trien)$^{2+}$ and NiEDDA with attacking ligands. These steric requirements may cause dissociation of an arm of the coordinated ligand in order to accommodate the attacking ligand. bpy and phen are examples of this. Thus, in some instances, there may not be enough room for complete coordination of all sites on the metal.

Further, dissociation of the coordinated ligand may not be apparent from a consideration of only the formation rate constant. Dissociation of a chelate ring can be rapid enough to not influence the formation rate, as it is with EDDA, or it may be slower than a formation reaction, as it is with Ni(trien)$^{2+}$. The stability of the ternary complex provides evidence for this.

Finally, the coordinated ligand appears to be able to decrease ring closure of the attacking ligand through distortion of the metal coordination sphere. This CAD effect may be revealed through isomerization of the complex, which, in some cases, can occur at a rate comparable to ring closure.

The complicated and variable nature of these effects has prompted the current study of other similar systems.

Registry No. en, 107-15-3; bpy, 366-18-7; phen, 66-71-7; gly, 56-40-6; sar, 107-97-1.

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Chemical Reduction of Bis[bis(diphenylphosphino)ethane]rhodium(1+), [Rh(dppe)$_2$]$^+$. Characterization of Rh(dppe)$_2$^{0} and Rh(dppe)$_2$$^-$

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The reduction of bis[bis(diphenylphosphino)ethane]rhodium(1+), [Rh(dppe)$_2$]$^+$, has been reexamined, employing a purely chemical approach. The reduction is found to proceed in two discrete single-electron steps, with initial formation of Rh(dppe)$_2$^{0}, followed by reduction to Rh(dppe)$_2$$^-$. In dry benzene, Rh(dppe)$_2$$^+$ is reduced with 1 equiv of sodium naphthalenide (NaNp) to yield an extremely air-sensitive solution that shows a strong EPR signal with coupling to four equivalent phosphorus atoms, assigned to Rh(dppe)$_2$^{0}. Further reduction with NaNp yields Rh(dppe)$_2$$^-$, characterized by NMR and by chemical quenching experiments. The fully reduced species Rh(dppe)$_2$$^-$ reacts with proton sources by acid–base chemistry to produce RhH(dppe)$_2$, while Rh(dppe)$_2$^{0} is inert to reaction with MeOH, CH_3CN, cumene, and triphenylmethane. A kinetic barrier to H atom transfer exists as shown by the lack of reaction between Rh(dppe)$_2$^{0} and Ph_3CH and between RhH(dppe)$_2$ and $Ph_3C\cdot$ radical. Through variation of solvent and temperature conditions, the intermediate d^9 Rh(0) species is found to be in equilibrium with Rh(dppe)$_2$$^+$ and Rh(dppe)$_2$$^-$. In toluene, the Rh(dppe)$_2$^{0} species is found to be fluxional on the EPR time scale.

Introduction

The electrochemical behavior of square-planar (dppe)$_2$ complexes (dppe = 1,2-bis(diphenylphosphino)ethane) of Rh and Ir has been studied by a number of research groups.[1–4] There is general agreement that the electrolysis of M(dppe)$_2$$^+$ in CH_3CN results in the formation of the metal hydride species MH(dppe)$_2$ and the overall passage of two electrons.

Pilloni et al.[1] first proposed that the electrochemical reduction of the Rh(I) and Ir(I) complexes proceeds by a single two-electron reduction to the anion M(dppe)$_2$$^-$, followed by proton abstraction from the solvent to give the hydride product. Later work by Ginsberg et al.[2] and Eisenberg et al.[3] contrasted this report. These groups proposed that the path by which hydride is formed involves one-electron reduction of M(dppe)$_2$$^+$ to the d^9 intermediate M(dppe)$_2$^{0}, followed by hydrogen atom abstraction from the solvent and subsequent reduction of the solvent radical. The viability of a d^9 M(0) species received support from reports by Keim[5] describing the electrochemical preparation of Rh(0) complexes and by Hanzlik[6] reporting one-electron reductions of other Rh(I) and Ir(I) chelates.

Although agreement exists on the formation of the metal hydride MH(dppe)$_2$ and the passage of two electrons in the electrolysis as determined by coulometry, there is fundamental disagreement on the mechanism of hydride formation. Pilloni et al.[1,4] favor a single two-electron EC mechanism, while Ginsberg et al.[2] and Eisenberg et al.[3] envision the reduction proceeding via an ECE mechanism with one-electron steps for hydride formation.

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$$\text{EC:}\qquad \mathrm{M(dppe)_2^+} \xrightarrow{2e^-} \mathrm{M(dppe)_2^-}$$

$$\mathrm{M(dppe)_2^-} \xrightarrow{CH_3CN} \mathrm{MH(dppe)_2 + CH_2CN^-}$$

$$\text{ECE:}\qquad \mathrm{M(dppe)_2^+} \xrightarrow{e^-} \mathrm{M(dppe)_2^0}$$

$$\mathrm{M(dppe)_2^0} \xrightarrow{CH_3CN} \mathrm{MH(dppe)_2 + CH_2CN\cdot}$$

$$\mathrm{CH_2CN\cdot} \xrightarrow{e^-} \mathrm{CH_2CN^-}$$

In an attempt to resolve the differences in interpretation of the electrochemical data and to unequivocally identify the initial reduction products, a purely chemical approach to the reduction of $Rh(dppe)_2^+$ has been undertaken. The results of this study, which have been presented in preliminary form,[7] are described herein. These results implicate an EEC mechanism in which the two-electron-reduction product undergoes reaction with protic and not H atom sources. Recently, Pilloni et al.[8] have reported the electrochemical reductions of related d^8 Rh and Ir compounds $M(CO)L_3^+$ where L = PR_3, leading to formation of $HM(CO)L_3$. In this recent work the reductions are found to proceed in discrete one-electron steps in contrast with their observations on $M(dppe)_2^+$ and in agreement with the results of Ginsberg et al.[2] and Eisenberg et al.[3] for the $M(dppe)_2^+$ systems.

Experimental Section

Manipulations involving air-sensitive materials were carried out on a high vacuum line or in a drybox, using solvents that were purified and degassed before use.

Physical Measurements. ^1H NMR spectra were recorded on a Bruker WH 400 400-MHz instrument. Deuterated solvents were purchased from Aldrich and were purified, distilled, and degassed prior to use. EPR spectra were recorded on a Bruker ER-200 EPR spectrometer. Electronic spectra were recorded on a Perkin-Elmer Model 330 spectrophotometer using 1-cm or 1-mm quartz cells. Cooling was achieved with dry ice and acetone in a Dewar containing four quartz windows.

Preparation of $[Rh(dppe)_2]BF_4$. The literature method involving treatment of $RhCl(PPh_3)_3$ with 2 equiv of dppe was used to prepare $Rh(dppe)_2Cl$.[9] A solution of the bis(phosphine) (1.3 g, 3.4 mmol) in benzene (20 mL) is added to a refluxing solution of $RhCl(PPh_3)_3$ (1.6 g, 1.7 mmol) in benzene (75 mL) under N_2, and the solution is heated at reflux for 30 min. The yellow precipitate is filtered, washed with benzene, and air-dried; yield 1.5 g (92%). Metathesis to produce the fluoroborate salt is then carried out by dissolving a 10-fold excess of $NaBF_4$ (1.8 g, 16 mmol) in methanol/water (20 mL/8 mL). This is added to a CH_2Cl_2 (10 mL) solution of $Rh(dppe)_2Cl$ (1.5 g, 1.6 mmol), and the solution stirred for 20 min. The product $[Rh(dppe)_2]BF_4$ precipitates as a dark yellow material, which is filtered in air and recrystallized from CH_2Cl_2/ether to give bright yellow crystals, yield 1.45 g (91%).

Preparation of $RhH(dppe)_2$. The literature method involving treatment of $Rh(dppe)_2Cl$ with sodium borohydride was used to prepare the corresponding hydride.[10] A solution of $Rh(dppe)_2Cl$ (1.0 g, 1.1 mmol) in ethanol (20 mL) is treated with a solution of $NaBH_4$ (0.12 g, 3.3 mmol) in ethanol (15 mL) under nitrogen. The resulting crystalline precipitate is filtered, dried, and recrystallized from benzene/ethanol; yield 0.94 g (95%).

Preparation of $Rh(dppe)_2^-$. The chemical reductions of $Rh(dppe)_2^+$ were carried out in THF, benzene, and toluene solvents at concentrations of 2–8 mM. Sodium and sodium naphthalenide (NaNp) were used as reducing agents. All reductions were carried out under N_2 or under vacuum. In a typical reduction, 2 equiv of a NaNp/THF solution is added to a 5 mM solution of $[Rh(dppe)_2]BF_4$ (0.01 g, 0.01 mmol in 2 mL solvent), followed by stirring at room temperature for 20 min in a dry box. The solution is then transferred to an NMR tube, and the solvent is removed under vacuum. The NMR solvent is then distilled into the NMR tube over the red/brown residue, and the tube is flame sealed.

Quenching of $Rh(dppe)_2^-$ with CH_3OH. A sample of $[Rh(dppe)_2]BF_4$ (0.01 g, 0.01 mmol) in benzene (2.0 mL) is reduced with 2 equiv of NaNp, producing a red/brown solution. Solvent is removed under vacuum and C_6D_6 distilled in. One equivalent of CH_3OH is vacuum transferred to the solution, causing an immediate change from red/brown to orange. The sample is flame sealed in an NMR tube and characterized.

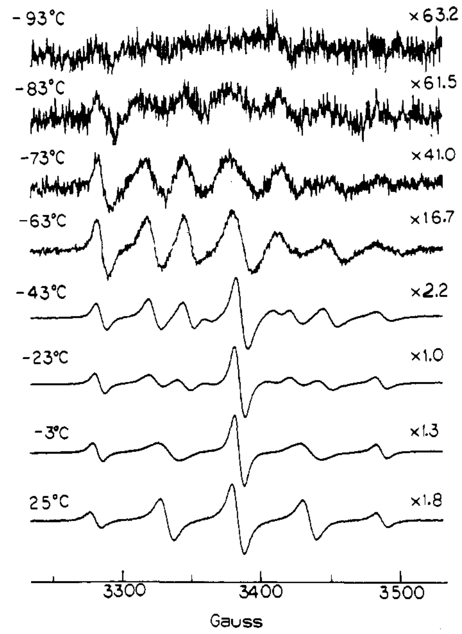

Figure 1. Variable-temperature EPR spectra of equilibrium 1 in toluene. A scale factor for each spectrum is shown on the right and has been normalized to the most intense signal at −23 °C.

Quenching of $Rh(dppe)_2^-$ with CH_3CN. This was carried out analogously to the quenching with CH_3OH.

Preparation of $Rh(dppe)_2^0$ by Reduction of $Rh(dppe)_2^+$. $[Rh(dppe)_2]BF_4$ (0.01 g, 0.01 mmol) in benzene (2.0 mL) is reduced with 1 equiv of NaNp, producing a blue solution. After stirring for 20 min at room temperature in a drybox, the solution is transferred to an EPR sample tube and flame sealed under vacuum.

Preparation of $Rh(dppe)_2^0$ by Comproportionation. A solution of $Rh(dppe)_2^-$ is prepared by treating 0.01 g of $[Rh(dppe)_2]BF_4$ in THF (2.0 mL) with 2 equiv of NaNp. An additional 0.01 g of $[Rh(dppe)_2]BF_4$ is then added to the red/brown solution, and the solution remains red/brown. The THF is removed under vacuum, and benzene is then distilled in, producing a blue $Rh(dppe)_2^0$ solution.

Quenching Experiments Attempted with $Rh(dppe)_2^0$. A sample of $[Rh(dppe)_2]BF_4$ (0.01 g, 0.01 mmol) in benzene (2.0 mL) is reduced with 1 equiv of NaNp, producing a blue solution. Methanol or acetonitrile (1–5 equiv) is vacuum transferred into the solution, or 1–5 equiv of triphenylmethane or cumene in benzene is added. The solution is allowed to stir under N_2 for up to 6 h. The solution is transferred to an NMR tube, and the solvent is removed under vacuum. The NMR solvent is then distilled into the NMR tube, and the tube is flame sealed.

Results and Discussion

Reductions in Benzene and Toluene. The reduction of $Rh(dppe)_2^+$ to $Rh(dppe)_2^0$ is achieved by addition of 1 equiv of NaNp to a 5 mM solution of $[Rh(dppe)_2]BF_4$. The resulting deep blue solution that arises from addition of NaNp to the yellow solution of $Rh(dppe)_2^+$ exhibits a symmetrical five-line EPR signal with phosphorus coupling $\langle A \rangle = 52G$ and $\langle g \rangle = 2.027$ (see Figure 1, 25 °C spectrum). Rhodium hyperfine structure is not observed, as is consistent with other Rh(0) species.[11,12] The blue color and radical signal persist up to several days under N_2 or under vacuum. The only other rhodium-containing product observed is $RhH(dppe)_2$[13] as determined by ^1H NMR spectroscopy, at concentrations of 5–20% of the initial $[Rh(dppe)_2]BF_4$ concentration.

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(13) The amount of $RhH(dppe)_2$ appears to arise from impurities in the solvent, as the amount of hydride remains constant throughout each lot of purified solvent and varies when a new lot of solvent is introduced.

Table I. NMR Spectral Data for Rhodium dppe Complexes

		^{1}H NMR			
solvent	complex	δ(methylene)[c]	δ(*o*-Ph)[c]	δ(hydride)	^{31}P NMR[a]
C_6D_6	$Rh(dppe)_2^+$	1.86[d]	7.34		
	$RhH(dppe)_2$	2.09	7.48	−10.20 (quint of d; J_{P-H} = 17.9 Hz, J_{Rh-H} = 10.4 Hz)	57.0 (d, J_{Rh-P} = 149 Hz)
	$Rh(dppe)_2^-$	2.32	7.65		57.4 (d, J_{Rh-P} = 183 Hz)
THF-d_8	$Rh(dppe)_2^+$	2.26	7.34		55.0 (d, J_{Rh-P} = 132 Hz)[b]
	$RhHndppe)_2$	2.15	7.34	−10.56 (quint of d; J_{P-H} = 17.8 Hz, J_{Rh-P} = 10.4 Hz)	53.3 (d, J_{Rh-P} = 143 Hz)[b]
	$Rh(dppe)_2^-$	1.85[e]	7.44		58.8 (d, J_{Rh-P} = 193 Hz)[b]

[a] Recorded on a Bruker WH-400 at 162 MHz. [b] ^{31}P NMR spectra recorded in THF containing 20% C_6D_6. [c] Resonances appear as multiplets with unresolved coupling. [d] Chemical shift is concentration dependent and is given at 0.75 mM. [e] Chemical shift is temperature dependent and is given at 22 °C.

The electronic spectrum of the initial yellow $Rh(dppe)_2^+$ solution in benzene exhibits bands at 315 and 408 nm, while the blue solution produced upon addition of 1 equiv of NaNp shows a broad band at 615 nm and a trace of the band at 408 nm.[14]

Further reduction of the blue $Rh(dppe)_2^0$ species, or reduction of $[Rh(dppe)_2]BF_4$ with 2 or more equiv of NaNp, produces a red/brown solution that lacks an EPR signal and exhibits new NMR resonances in addition to those for $RhH(dppe)_2$.[13] The new ^{1}H NMR resonances in the phenyl and methylene regions of the spectrum (δ 7.65 and 2.32) are analogous to those for $Rh(dppe)_2^+$ and $RhH(dppe)_2$, though shifted downfield (see Table I). The ^{31}P NMR spectrum consists of a doublet at δ 57.4 (J_{P-Rh} = 183 Hz) and the doublet due to $RhH(dppe)_2$ at δ 57.0 (J_{P-Rh} = 149 Hz). The new resonance is assigned to the anionic species $Rh(dppe)_2^-$. The NMR data for the three rhodium-containing species $[Rh(dppe)_2]BF_4$, $Rh(dppe)_2^-$, and $RhH(dppe)_2$ are given in Table I.

Addition of 1 equiv of $Rh(dppe)_2^+$ to a benzene solution of the red/brown anion $Rh(dppe)_2^-$ causes a gradual equilibration to the blue $Rh(dppe)_2^0$ species. This change may be followed by NMR and EPR spectroscopies, and it is clear that the comproportionation equilibrium lies to the right in eq 1, favoring $Rh(dppe)_2^0$ formation in benzene.

$$Rh(dppe)_2^- + Rh(dppe)_2^+ \rightleftarrows 2Rh(dppe)_2^0 \tag{1}$$

The reactivity of each of the reduction products was examined with methanol and acetonitrile as substrates. In large-scale and sealed-tube experiments, $Rh(dppe)_2^-$ is prepared from the corresponding cation and 1 equivalent of methanol is added. The red/brown benzene solution turns pale orange upon shaking or stirring at room temperature, and clean conversion of the anion to $RhH(dppe)_2$ is observed. In the ^{1}H NMR spectrum, the phenyl and methylene resonances due to the anion $Rh(dppe)_2^-$ (δ 7.65 and 2.32) disappear and are replaced by peaks due to $RhH(dppe)_2$ (δ 7.48, 2.09, and −10.2). Similarly, treatment of $Rh(dppe)_2^-$ in benzene with 1–5 equiv of acetonitrile also quenches the anion to hydride, but at a rate much slower than with methanol. Reaction of the anion with MeOH occurs in less than 1 min, while reaction of $Rh(dppe)_2^-$ with MeCN in benzene takes more than 2 h to form $RhH(dppe)_2$.

While the anion is converted cleanly to hydride in the presence of MeOH or MeCN, $Rh(dppe)_2^0$ is found not to react with these substrates. The blue Rh(0) solution, produced in benzene by addition of 1 equiv of NaNp to $[Rh(dppe)_2]BF_4$, is unaffected when 1–5 equiv of MeOH is added at room temperature. The solution of $Rh(dppe)_2^0$ remains blue, and no additional $RhH(dppe)_2$[13] is observed in the ^{1}H NMR spectrum of the sample. Similarly, treatment of $Rh(dppe)_2^0$ with acetonitrile causes no change in the blue solution, nor any additional formation of $RhH(dppe)_2$.[13] It thus appears that the reactive species in these examples is the anion $Rh(dppe)_2^-$, which reacts with MeOH and MeCN by acid–base chemistry.

The observation that $Rh(dppe)_2^0$ is inert toward MeOH and MeCN prompted attempts at reacting the radical with more conventional hydrogen atom sources. After preparation of $Rh(dppe)_2^0$ in benzene, up to 5 equiv of triphenylmethane or cumene were added and no changes were observed in either the ^{1}H or EPR spectra. No additional hydride was formed,[13] the signal and intensity of $Rh(dppe)_2^0$ remained unchanged, and no organic free-radical products were detected.

Interestingly, no reaction was observed to take place between $RhH(dppe)_2$ and $Ph_3C\cdot$. A solution of the trityl radical was prepared in THF,[15] and up to 5 equiv was added to an orange THF solution of $RhH(dppe)_2$. No Ph_3CH was observed in the ^{1}H NMR spectrum, and the intensity of the rhodium hydride resonance (δ −10.2) remained unchanged.

It is likely that steric factors account for the observation that neither reaction 2 nor 3 occurs. Both $Rh(dppe)_2^0$ and triphenylmethane are sterically bulky, and it is reasonable to assume that they are unable to approach each other near enough to effect hydrogen atom transfer.

$$Rh(dppe)_2^0 + Ph_3CH \rightarrow \text{no reaction} \tag{2}$$

$$RhH(dppe)_2 + Ph_3C\cdot \rightarrow \text{no reaction} \tag{3}$$

With the isolation and characterization of each reduction product, it seems clear that the full reduction of $[Rh(dppe)_2]BF_4$ proceeds by two single-electron steps, with intermediate formation of $Rh(dppe)_2^0$. This also represents the first isolation and EPR characterization of $Rh(dppe)_2^0$ and NMR characterization of $Rh(dppe)_2^-$. These observations support the notion of reduction of $[Rh(dppe)_2]BF_4$ proceeding by sequential one-electron steps and speak against the notion of a single two-electron reduction. The implication inherent in a single two-electron-reduction mechanism is that the single-electron-reduction product, in this case $Rh(dppe)_2^0$, is more easily reduced than the cation, which in turn implies that the radical should readily disproportionate to cation and anion, $Rh(dppe)_2^+$ and $Rh(dppe)_2^-$. This is not observed in benzene at room temperature. In fact the opposite appears true. While the $Rh(dppe)_2^0$ radical is in equilibrium with $Rh(dppe)_2^+$ and $Rh(dppe)_2^-$, it seems clear that the equilibrium (1) lies well to the right in benzene at room temperature.

Reductions in THF. Changing the solvent from benzene to THF significantly affects the position of equilibrium 1. Addition of 2 equiv of NaNp to a THF solution of $[Rh(dppe)_2]BF_4$ produces the red/brown anion, identified by its methylene resonance in the ^{1}H NMR spectrum (δ 1.85 (CH_2) in THF-d_8) which may be quenched with methanol or acetonitrile to yield $RhH(dppe)_2$ (δ 2.15 (CH_2) in THF-d_8). These observations are analogous to those seen in benzene with these substrates. As in benzene, quenching of the anion $Rh(dppe)_2^-$ in THF is rapid with methanol (less than 1 min) and considerably slower with acetonitrile (several hours).

The reduction of $[Rh(dppe)_2]BF_4$ in THF upon addition of 1 equiv of reducing agent, however, differs from the reduction in benzene. Upon addition of 1 equiv of NaNp to $[Rh(dppe)_2]BF_4$ in THF, the yellow solution becomes red/brown in color, not blue as in benzene solvent. The red/brown THF solution exhibits a strong band at 408 nm with a shoulder at 462 nm and no band at 615 nm, in contrast with that observed for the blue benzene

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(14) Although the ^{1}H NMR spectrum reveals the presence of $RhH(dppe)_2$, the absorption at 398 nm for $RhH(dppe)_2$ is not clearly seen, as it may be buried under a more intense absorption.

(15) Trityl radical $Ph_3C\cdot$ was prepared according to: Zieger, H. E.; Angres, I.; Maresca, L. *J. Am. Chem. Soc.* **1973**, *95*, 8201.

solution of $\mathrm{Rh(dppe)_2^0}$ at room temperature. The only ^{1}H NMR resonances observed in THF are those due to $\mathrm{RhH(dppe)_2}$.[13]

An EPR signal is observed for $\mathrm{Rh(dppe)_2^0}$ in THF although it is weaker in intensity than is found in the blue benzene solution of $\mathrm{Rh(dppe)_2^0}$. Area calculations reveal the intensity of $\mathrm{Rh(dppe)_2^0}$ in THF to be only 20% the intensity of $\mathrm{Rh(dppe)_2^0}$ in benzene or toluene. Absolute intensity measurements of the $\mathrm{Rh(dppe)_2^0}$ signal in each solvent were made by employing Tempol (4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxy) radical as a concentration standard and determining the area under each absorption curve.[16] These measurements indicate the presence of 83% $\mathrm{Rh(dppe)_2^0}$ in a blue toluene solution and 17% $\mathrm{Rh(dppe)_2^0}$ in a red/brown THF solution.[17]

It is clear from electronic and EPR spectroscopic results that equilibrium 1 is significantly influenced by solvent. The ^{1}H NMR data also indicate that the equilibrium is rapid on the NMR time scale, as neither $\mathrm{Rh(dppe)_2^+}$ or $\mathrm{Rh(dppe)_2^-}$ is observed by NMR spectroscopy at room temperature in THF.

The change in the position of equilibrium 1 is also evidenced by chemical quenching experiments. A solution of $\mathrm{Rh(dppe)_2^+}$ in THF is reduced with 1 equiv of reducing agent to produce a red/brown solution. Upon addition of 1 equiv of methanol at room temperature, the solution becomes orange and the ^{1}H NMR spectrum reveals formation of $\mathrm{RhH(dppe)_2}$ and $\mathrm{Rh(dppe)_2^+}$ in a 1:1 ratio by NMR integration. Two possibilities exist to explain this result (eq 4 and 5). Since the reaction of $\mathrm{Rh(dppe)_2^0}$ with

$$\mathrm{Rh(dppe)_2^+ + Rh(dppe)_2^- + S\text{–}H \rightarrow RhH(dppe)_2 + S^- + Rh(dppe)_2^+} \quad (4)$$

$$\mathrm{Rh(dppe)_2^0 + S\text{–}H \rightarrow RhH(dppe)_2 + S\cdot \xrightarrow{Rh(dppe)_2^0} S^- + Rh(dppe)_2^+} \quad (5)$$

methanol does not proceed in benzene to form $\mathrm{RhH(dppe)_2}$, eq 5 seems unlikely. Equation 4 is more reasonable, with reaction to form $\mathrm{RhH(dppe)_2}$ proceeding through $\mathrm{Rh(dppe)_2^-}$. Thus, the reduction of $\mathrm{Rh(dppe)_2^+}$ in THF with 1 equiv of reducing agent produces species corresponding to disproportionation of $\mathrm{Rh(dppe)_2^0}$, with equilibrium 1 now lying to the left.

The equilibrium between $\mathrm{Rh(dppe)_2^0}$ and the disproportionated species $\mathrm{Rh(dppe)_2^+}$ and $\mathrm{Rh(dppe)_2^-}$ (eq 1) is both shifted and slowed down by lowering the temperature of the solution. Examination of the ^{31}P NMR spectrum of the single-electron-reduction product in THF shows only peaks due to $\mathrm{RhH(dppe)_2}$[13] at room temperature. At 0 °C, two broad doublets begin to grow in, and as the temperature is lowered to −60 °C, the peaks increase in intensity and become much sharper (see Figure 2). These two doublets are assigned to $\mathrm{Rh(dppe)_2^+}$ and $\mathrm{Rh(dppe)_2^-}$, on the basis of comparison with independently prepared samples of these species. This behavior is reversible, as subsequent warming of the sample results in disappearance of the doublets. The same temperature-dependent behavior may be followed by ^{1}H NMR spectroscopy in THF-d_8 by monitoring the methylene resonances.

As the appearance of $\mathrm{Rh(dppe)_2^+}$ and $\mathrm{Rh(dppe)_2^-}$ may be followed by variable-temperature NMR spectroscopy, the disappearance of $\mathrm{Rh(dppe)_2^0}$ may be followed by VT EPR. The one-electron reduction in toluene gives results that are identical with those found in benzene. At room temperature the blue toluene solution of $\mathrm{Rh(dppe)_2^0}$ exhibits the expected five-line symmetrical EPR signal. As the temperature is lowered from 25 to −23 °C, the intensity of the $\mathrm{Rh(dppe)_2^0}$ EPR signal increases linearly as $1/T$ (K). However, upon further cooling, the intensity of the radical signal decreases dramatically as is shown in Figure 1. At −90 °C the EPR signal is virtually gone. Subsequent warming of the sample regenerates the original $\mathrm{Rh(dppe)_2^0}$ signal at the original intensity.[18]

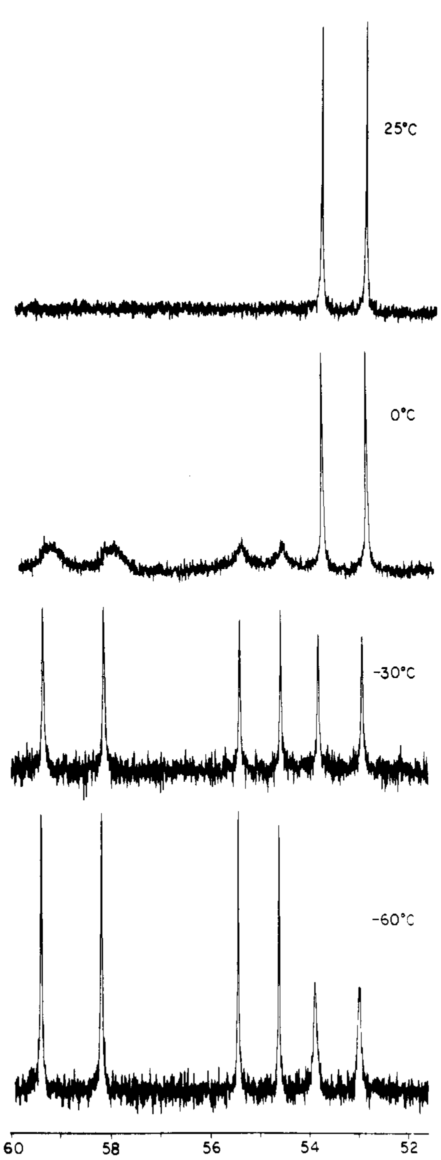

Figure 2. Variable-temperature ^{31}P NMR spectra of equilibrium 1 plus $\mathrm{RhH(dppe)_2}$ in THF with 20% $\mathrm{C_6D_6}$.

Figure 1 also reveals that significant changes in the EPR pattern occur as a function of temperature. At −3 °C, an alternating line width effect is observed,[19] and at −43 °C the spectrum shows hyperfine coupling from two sets of two equivalent P nuclei with $\langle A \rangle$ values of 37.5 and 63.2 G. The $\mathrm{Rh(dppe)_2^0}$ species is thus found to be fluxional on the EPR time scale. Below −43 °C the spectrum shows further change as the signal intensity decreases. The spectra at or below −43 °C exhibit anisotropic broadening as the tumbling rate decreases, yielding patterns in which individual line widths vary with nuclear spin state.[20] A detailed EPR study of the fluxional behavior of $\mathrm{Rh(dppe)_2^0}$ and related compounds will be reported separately.[21]

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(16) For details of EPR intensity measurements, see: Wertz, J. E.; Bolton, J. R. "Electron Spin Resonance: Elementary Theory and Practical Applications"; McGraw-Hill: New York, 1972; pp 450–464.

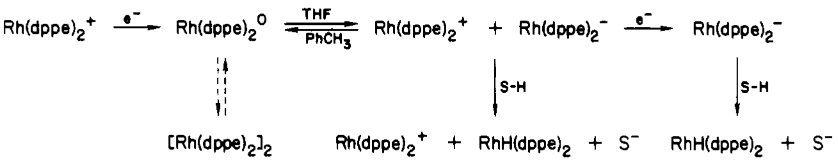
(17) These figures are for a solution that is 6 mM in rhodium as determined by further reduction of $\mathrm{Rh(dppe)_2^0}$ to $\mathrm{Rh(dppe)_2^-}$ and quenching of the anion with methanol to form $\mathrm{RhH(dppe)_2}$. The solvents were removed under vacuum; $\mathrm{C_6D_6}$ was added to the orange solid, followed by addition of 0.007 mmol of methanol. The concentration of $\mathrm{RhH(dppe)_2}$ was then determined with methanol as an internal integration standard.

(18) For comparison, EPR spectra of the galvinoxyl radical (4-[[3,5-bis(1,1-dimethylethyl)-4-oxo-2,5-cyclohexadien-1-ylidene]methyl]-2,6-bis(1,1-dimethylethyl)phenoxy) were recorded from room temperature to −90 °C, and the signal increased linearly with $1/T$ throughout that temperature range. We thereby rule out the disappearance of the $\mathrm{Rh(dppe)_2^0}$ signal as an instrument artifact.

(19) Sullivan, P. D.; Bolton, J. R. *Adv. Magn. Reson.* **1970**, *4*, 39.

(20) Carrington, A.; McLachlan, A. D. "Introduction to Magnetic Resonance"; Harper and Row: New York, 1967; pp 197–199 Chasteen, N. D.; Hanna, M. W.; *J. Phys. Chem.* **1972**, *76*, 3951 and references therein.

Scheme I



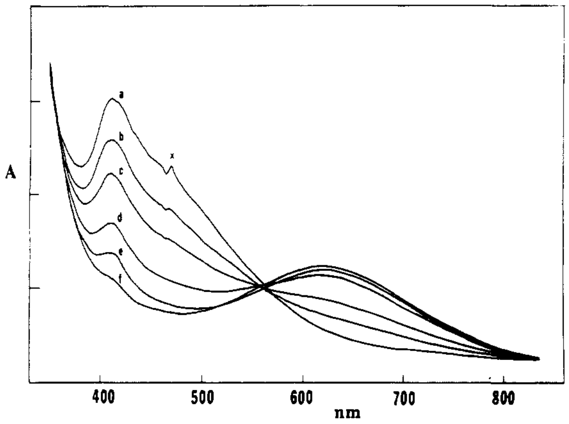


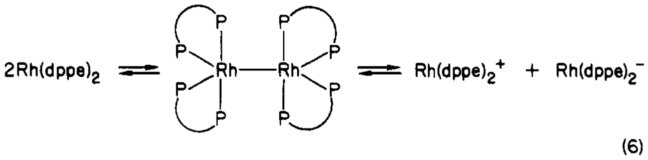
Figure 3. Variable-temperature electronic spectra of equilibrium 1 in toluene: (a) −90 °C; (b) −78 °C; (c) −66 °C; (d) −48 °C; (e) −25 °C; (f) 25 °C. × is believed to be an instrument artifact.

The low-temperature behavior of the single-electron-reduction product can also be followed by electronic spectroscopy. The blue $Rh(dppe)_2^0$ toluene solution at 25 °C exhibits a broad band at 615 nm and a trace of a band at 408 nm, presumably due to the starting complex $[Rh(dppe)_2]$ BF_4. As the temperature is lowered to −90 °C, the solution becomes red/brown in color and the 615-nm absorption loses intensity while the one at 408 nm grows in, confirming the notion of disproportionation at low temperature (see Figure 3). The anion $Rh(dppe)_2^-$, which exhibits a broad band at 425 nm, is not directly observed at low temperature. However, the absorption at 408 nm is significantly broader than is observed for pure $Rh(dppe)_2^+$, suggesting that the anion absorption is buried under the 408-nm band and not resolved.

The blue color in toluene, which appears to represent the highest concentration of radical, changes reversibly to red/brown with lowering of temperature. Furthermore, while the blue solution is inert toward a variety of quenching agents, the low-temperature red/brown species does react with methanol. To $Rh(dppe)_2^+$ in toluene (10 mM) is added 1 equiv of NaNp to produce a $Rh(dppe)_2^0$ solution. The blue solution is cooled to −70 °C and becomes red/brown. Upon addition of 1–5 equiv of methanol at low temperature, the solution becomes orange over a period of hours (2–3 h) and the ^1H NMR spectrum reveals formation of $RhH(dppe)_2$ and $Rh(dppe)_2^+$. Low-temperature quenching of the fully reduced $Rh(dppe)_2^-$ anion with methanol produces $RhH(dppe)_2$ over a 1-h period. Parallel experiments without cooling the blue radical solution produced no additional rhodium hydride or $Rh(dppe)_2^+$.

The blue ⇄ red/brown color change and observation of disproportionated species are also concentration dependent. A sufficiently dilute solution (2 mM) of $Rh(dppe)_2^0$ will remain blue at −90 °C. However, as the concentration of $Rh(dppe)_2^0$ is increased, there is an increase in the temperature at which one observes the blue to red/brown color change and the formation of $Rh(dppe)_2^+$ and $Rh(dppe)_2^-$.

Low-temperature studies have helped establish the reversible formation of $Rh(dppe)_2^+$ and $Rh(dppe)_2^-$ from $Rh(dppe)_2^0$. While the process occurs in both THF and toluene (and presumably benzene), the position of equilibrium 1 is different in each solvent. There also exists the possibility that in nonpolar solvents the radical $Rh(dppe)_2^0$ is actually in equilibrium with a dimeric species $[Rh(dppe)_2]_2$, rather than with $Rh(dppe)_2^+$ and $Rh(dppe)_2^-$ directly, as shown in equation 6. Dimeric products arising from



(6)

$Rh(chel)_2^0$ where chel= 2,2′-bipyridyl and 1,10-phenanthroline have been considered in the reduction of other $Rh(chel)_2^+$ complexes,[12] and Pilloni et al.[8] have identified $[Rh(CO)(PPh_3)_2(Sol)]_2$ where Sol= DME, arising from $Rh(CO)(PPh_3)_3^0$ in the reduction of $Rh(CO)(PPh_3)_3^+$. Other 17-electron species, $Mn(CO)_3(PR_3)_2$, $Mn(CO)_4PR_3$, and $Re(CO)_3(P(OR)_3)_2$, for example, have been generated by one-electron oxidation of the corresponding anion and have been shown to undergo dimerization.[22] In the case of $Rh(dppe)_2^0$ there is no evidence to support or refute a dimeric species at this time. However, even if a dimer does exist, it seems clear that the reaction chemistry that is observed results from the anion $Rh(dppe)_2^-$ and not directly from $Rh(dppe)_2^0$ or $[Rh(dppe)_2]_2$.

Conclusion

On the basis of chemical and spectroscopic data, the reduction of $[Rh(dppe)_2]BF_4$ has been established to proceed in two discrete single-electron steps, with initial formation of $Rh(dppe)_2^0$ and subsequent reduction to $Rh(dppe)_2^-$. The formation of $RhH(dppe)_2$ appears to proceed through the anion via acid–base chemistry. Each rhodium-containing reduction product was isolable and characterized spectroscopically. The fully reduced species $Rh(dppe)_2^-$ is reactive toward proton sources, while the intermediate d^9 radical reduction product $Rh(dppe)_2^0$ is inert toward a variety of substrates and appears to be too sterically crowded to react with even reactive hydrogen atom donors.

Through variation of solvent and temperature conditions, it was determined that $Rh(dppe)_2^0$ is in equilibrium with the disproportionation products $Rh(dppe)_2^+$ and $Rh(dppe)_2^-$. The blue radical species is favored in benzene or toluene at room temperature, while in a potentially coordinating solvent such as THF disproportionation products appear to predominate. The equilibrium between $Rh(dppe)_2^0$ and $Rh(dppe)_2^+$ and $Rh(dppe)_2^-$ is concentration dependent and shifts more toward the ionic species at lower temperatures.

The reduction mechanism for $[Rh(dppe)_2]BF_4$ and observed chemistry are summarized in Scheme I.

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Registry No. $[Rh(dppe)_2]BF_4$, 53450-79-6; $Rh(dppe)_2Cl$, 14874-99-8; $Rh(dppe)_2^-$, 95979-66-1; $Rh(dppe)_2^0$, 65521-62-2; $RhH(dppe)_2$, 29189-87-5.

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(21) Kunin, A.; Mueller, K.; Greiner, S.; Henderson, T.; Kreilick, R.; Eisenberg, R., to be submitted for publication.

(22) Armstead, J. A.; Cox, D. J.; Davis, R. *J. Organomet. Chem.* **1982**, *236*, 213.