

**Figure 2.** Space-filling models of  $[(\text{bpy})\text{Re}^{\text{I}}(\text{CO})_3\text{NC}(\text{CH}_2)_n\text{CH}_3]^+$  showing the maximal degree of overlap between the alkyl chain and the bpy ligand. (A)  $n = 5$ ; (B)  $n = 9$ ; (C)  $n = 13$ . The view in all cases is from the top along the CN-Re axis. The bpy is at the bottom of the figure and one of the CO's is visible on the upper left.

make contact with the bpy; thus, no perturbation of the decay results. Medium-length chains can interact to varying degrees depending on the chain length. Longer chains can completely cover one bpy face.

Solvent shielding by intramolecular foldback is supported by examination of space-filling molecular models. Figure 2A shows a model for the  $n = 5$  case where the alkyl chain was folded to give maximum proximity or contact with the exposed bpy face. In this case there is little or no actual contact between the two portions, and the degree of shielding is minimal. Figure 2B shows the same view for  $n = 9$  where roughly 50% of the face is shielded from solvent contact. Finally, Figure 2C shows the  $n = 13$  case where the one bpy face is virtually completely shielded from the solvent. Further increases in  $n$  have no appreciable effect on the degree of solvent shielding of the bpy.

The changes in  $\tau$  exactly mirror the degree of solvent shielding predicted by the molecular models. For  $n \leq 5$ , there is no shielding, and  $\tau$  is independent of  $n$ . Starting around  $n$  equal 6 to 7, shielding can occur and  $\tau$  increases. For  $n \geq 13$ , 100% coverage of one face can occur and  $\tau$  is again independent of  $n$ , but at a different value than for the earlier plateau. For intermediate  $n$ 's where the degree of coverage depends on chain length,  $\tau$  varies rapidly with  $n$ . For example, at  $n = 9$ , the models show that about half of the bpy face is covered, and the  $\tau$ 's for acetonitrile and pyridine are almost exactly halfway between the unshielded and fully shielded plateaus.

If this model is correct anything that perturbs the degree of chain foldback should alter the excited-state lifetime. We reasoned that we should be able to pull the longer hydrophobic chains away from the bpy face by forming alkyl cyclodextrin (CD) inclusion complexes. The driving force for such complexation is displacement of water from the hydrophobic CD cavity.<sup>5</sup> We find that  $\alpha$ - and  $\beta$ -CD Re(I) inclusion complexes do form, and the lifetime and degree of shielding of the excited state from external quenchers varies in a manner consistent with our model.

The good correspondence between  $\tau$  and the fractional coverage of the bpy chromophore, assuming a maximal interaction of the alkyl chain, suggests a strong driving force for foldback. We would expect this driving force to depend on solvent hydrophobicity, and we do observe changes in the detailed shapes and breakpoints of the curves for different solvents, but the effect is not large. These results support a remarkably strong specific alkyl chain-bpy interaction even in such a nonpolar solvent as toluene.

In conclusion, we present evidence for an intramolecular shielding effect on excited-state properties for a transition-metal photosensitizer. This effect arises from self-foldback of long alkyl chain ligands onto the bpy chromophore, thereby shielding part or all of one bpy face from the solvent. This intramolecular hydrophobic sheath may prove useful in enhancing luminescence

properties and in controlling excited-state electron- and energy-transfer processes as well as back-electron-transfer reactions.

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### A Metal-Centered Radical-Pair Mechanism for Alkyne Hydrogenation with a Binuclear Rhodium Hydride Complex. CIDNP without Organic Radicals

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A radical pair mechanism for the hydrogenation of unsaturated substrates by mononuclear transition-metal hydrides has been demonstrated by the occurrence of chemically induced dynamic nuclear polarization (CIDNP).<sup>1-4</sup> In this mechanism, an  $\text{M}^{\bullet}, \text{R}^{\bullet}$  radical pair forms by H atom transfer, eq 1, and leads to the



observed CIDNP through singlet-triplet mixing and spin selective reactions. The reactant and product resonances in these reactions show *net* polarization which is explained by the difference in  $g$  values of the radical pair components,  $\text{M}^{\bullet}$  and  $\text{R}^{\bullet}$ .<sup>1</sup> In this paper, we report that CIDNP also occurs in the hydrogenation of alkynes by  $\text{Rh}_2\text{H}_2(\text{CO})_2(\text{dppm})_2$  (**1**)<sup>5</sup> but that the basis for CIDNP in this system is different, involving an extraordinary metal-centered biradical.<sup>6</sup>

Complex **1** reacts rapidly with  $\text{PhC}\equiv\text{CH}$  in  $\text{C}_6\text{D}_6$  under  $\text{H}_2$  to give  $\sim 1$  equiv of styrene and an intense blue complex, **2**, which

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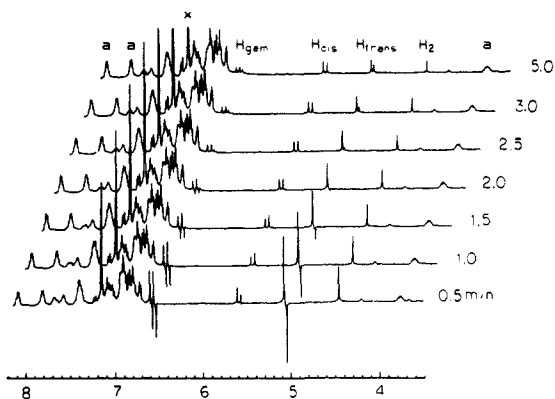
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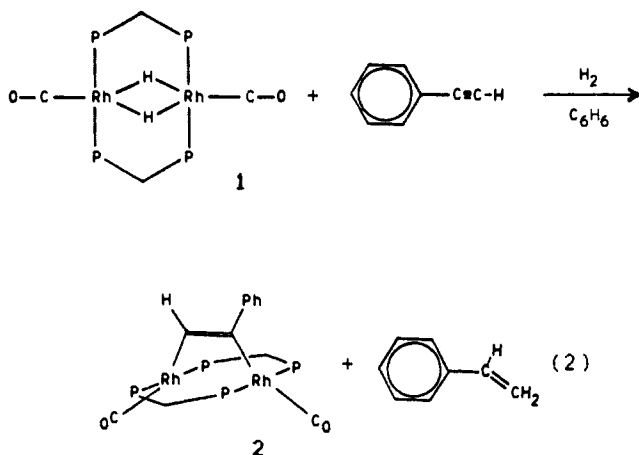
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**Figure 1.**  $^1\text{H}$  NMR spectra at 400 MHz for the reaction of  $\text{Rh}_2\text{H}_2(\text{CO})_2(\text{dppm})_2$  (**1**) with  $\text{PhC}\equiv\text{CH}$  in  $\text{C}_6\text{D}_6$  under  $\text{H}_2$  during the first 5 min of reaction. The resonances labeled (a) are due to the product complex **2**. The peak (x) which is truncated in the later spectra is due to benzene- $d_5$ .

shows NMR resonances characteristic of an unsymmetrical alkene-bridged A-frame structure, eq 2.<sup>7</sup> Complex **2** slowly converts

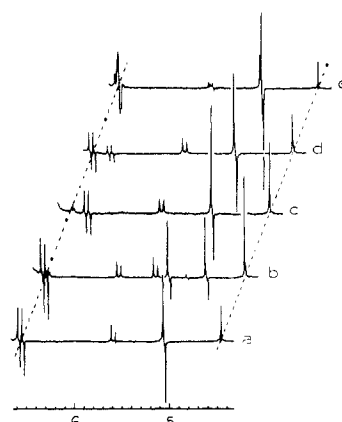


to the more stable isomer containing a  $\mu_2, \eta^2$ -alkyne bridge which has been reported previously along with the isomeric vinylidene complex  $\text{Rh}_2(\mu\text{-C}=\text{CHPh})(\text{CO})_2(\text{dppm})_2$ .<sup>8</sup> The addition of hydrogen to  $\text{PhC}\equiv\text{CH}$  in (2) is predominantly cis as evidenced by relative amounts of isotopomers formed when using either **1** +  $\text{PhC}\equiv\text{CD}$  under  $\text{H}_2$  or  $\text{Rh}_2\text{D}_2(\text{CO})_2(\text{dppm})_2$ , **1**- $d_2$ , +  $\text{PhC}\equiv\text{CH}$  under  $\text{D}_2$ . Reaction similar to (2) occurs with a variety of alkynes including  $\text{MeC}\equiv\text{CH}$ ,  $t\text{-BuC}\equiv\text{CH}$ ,  $\text{EtOC}\equiv\text{CH}$ ,  $\text{HC}\equiv\text{CCOOMe}$ ,  $\text{HC}\equiv\text{CCH}_2\text{OH}$ , and  $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{OH}$ , leading in each case to formation of the corresponding olefin and an intensely colored complex analogous to **2**.

In all of these reactions, CIDNP is seen as shown in Figure 1 for eq 2. The most striking aspects of the observed CIDNP of Figure 1 are the strong absorption/emission (A/E) multiplet effect of the trans proton ( $\delta$  5.06;  $J_{\text{HH}} = 11$ , 1 Hz) of the product styrene, the unusual A/E/A/E multiplet effect of the geminal proton ( $\delta$  6.57;  $J_{\text{HH}} = 18$ , 11 Hz), a weak and variable multiplet effect in the cis proton resonance ( $\delta$  5.59;  $J_{\text{HH}} = 18$ , 1 Hz), and the absence of a net effect. Also seen is the resonance for dissolved  $\text{H}_2$  ( $\delta$  4.42) which shows an initial intensity 3 times greater than its long-term value. The reaction between  $\text{EtOC}\equiv\text{CH}$  and **1** produces completely analogous CIDNP results with little polarization of the

(7) Typically, 10 mg (0.01 mmol) of **1** is dissolved in 0.5 mL of  $\text{C}_6\text{D}_6$  under  $\text{H}_2$  in an NMR tube sealed with a septum. Addition of  $\text{PhCCH}$  (3  $\mu\text{L}$ , 0.03 mmol) by syringe is followed immediately by placement in the probe of a Bruker WH-400 400-MHz NMR spectrometer. Spectroscopic data for **2**:  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ ) - $\text{CH}_2$ - region:  $\delta$  3.77 (m, 2 H), 2.64 (m, 2 H) with a geminal coupling  $J_{\text{HH}}$  of 12 Hz.  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  23.0 (m) and 26.4 (m).  $^{13}\text{C}\{^1\text{H}\}$  NMR for alkyne carbons: 150.1 (m, width  $\sim$ 70 Hz,  $\text{PhCCH}$ ) and 174.1 (m, width  $\sim$ 70 Hz,  $\text{PhCCH}$ ) with assignments made by using specifically labeled  $\text{PhCCH}$ .

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**Figure 2.**  $^1\text{H}$  NMR spectra at 400 MHz showing CIDNP of the styrene resonances for eq 2 under  $\text{H}_2$ . (a) **1** +  $\text{PhC}\equiv\text{CH}$ ; (b) **1** +  $\text{PhC}\equiv^{13}\text{CH}$ ; (c) **1** +  $\text{Ph}^{13}\text{C}\equiv\text{CH}$ ; (d) **1** +  $\text{PhC}\equiv\text{CH}$  +  $\text{Ph}^{13}\text{C}\equiv\text{CH}$ ; (e) **1** +  $\text{PhC}\equiv\text{CD}$ .

cis proton resonance of the product olefin. In the reaction of **1** with other alkynes, the cis proton resonance shows different degrees of polarization, while the trans and geminal protons exhibit strong multiplet effects similar to those of Figure 1. These results indicate that a radical pair mechanism is followed in the hydrogenation of alkyne by **1**, and  $\Delta g$  of the radical pair must be near zero to explain the absence of net effects in the observed CIDNP.<sup>9-12</sup> We can thus rule out a mechanism based on a  $\text{M}^{\cdot}\text{R}^{\cdot}$  radical pair similar to that invoked in previous studies using mononuclear transition-metal hydrides.<sup>1-4</sup>

In order to probe the basis of CIDNP in eq 2, a series of labeling experiments was performed, the results of which are shown in Figure 2. Trace 2a corresponds to the initial spectrum seen in Figure 1. When either  $\text{PhC}\equiv^{13}\text{CH}$  or  $\text{Ph}^{13}\text{C}\equiv\text{CH}$  is used as the alkyne in (2), large coupling is seen between the  $^{13}\text{C}$  nucleus and the styrene proton(s) attached to it, but as shown in spectra b and c of Figure 2, no polarization occurs in the CIDNP due to  $^{13}\text{C}$  hyperfine. Spectrum b, Figure 2, also exhibits particular enhancement of the  $\text{H}_2$  absorption and a very slight net effect of the styrene trans and geminal resonances. In Figure 2c the downfield half of the  $^{13}\text{C}$ -coupled geminal resonance at  $\delta$  6.57 is obscured by aromatic proton resonances, while from Figure 2d a value of 155 Hz is obtained for the  $^1J_{\text{CH}}$  coupling by using a mixture of  $\text{Ph}^{13}\text{C}\equiv\text{CH}$  and  $\text{PhC}\equiv\text{CH}$  in eq 2. Spectrum c, Figure 2, also shows a small resonance at  $\delta$  6.52 due to the  $\mu_2, \eta^2$ -alkyne bridged complex<sup>7</sup> which grows in slowly.

Deuterium labeling reveals a strong multiplet effect in the trans and geminal protons when  $\text{PhC}\equiv\text{CD}$  is reacted with **1** (spectrum e) and no CIDNP when  $\text{PhC}\equiv\text{CH}$  reacts with **1**- $d_2$ . In the reaction leading to Figure 2e, a small amount of  $\text{PhC}\equiv\text{CH}$  which is present accounts for the cis resonance at  $\delta$  5.59 and confirms an isotope shift of the trans resonance at  $\delta$  5.06. The major conclusions from these labeling studies are the following: (1) no polarization occurs for  $^1\text{H}$  and  $^{13}\text{C}$  nuclei which are part of the alkyne substrate throughout the course of the reaction, and (2) the only styrene protons showing polarization are those which originated on the binuclear complex  $\text{Rh}_2\text{H}_2(\text{CO})_2(\text{dppm})_2$  (**1**).

Both the absence of polarization due to  $^{13}\text{C}$  hyperfine in spectra b-d, Figure 2, and the cis addition of hydrogen to  $\text{PhC}\equiv\text{CH}$  argue strongly against styrenyl radicals as components of the radical pair responsible for the CIDNP effect. This conclusion is further supported by the fact that efforts to block CIDNP by trapping styrenyl radicals with dihydroanthracene, 1,4-cyclohexadiene, and cumene have been unsuccessful. Moreover, when **1**- $d_2$  and  $\text{PhC}\equiv\text{CD}$  are reacted in the presence of a 20-fold excess of

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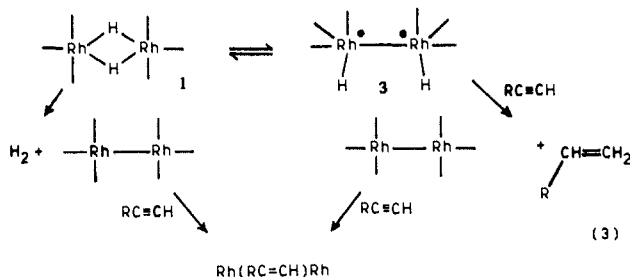
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cumene, no styrene containing olefinic protons is observed.

The results of our experiments lead us to the inescapable conclusion that the radical pair responsible for CIDNP in the reaction of **1** with alkynes must be a metal-centered biradical (MCBR). The major polarizations we see only occur in the hydrogens originally on **1**. For a pure multiplet effect,  $\Delta g$  of the radical pair must be zero, but a radical pair based on styrenyl radicals is totally inconsistent with experiment. We therefore propose that **1** rapidly and reversibly forms a biradical isomer **3** which undergoes singlet-triplet mixing and spin-selective reaction to produce CIDNP. The "singlet" reaction channel of **3** is recombination to **1**, whereas the escape or "triplet" channel corresponds to reaction with  $\text{RC}\equiv\text{CH}$ , as shown in eq 3.<sup>13</sup> Application



of Kaptein's rule for multiplet effects based on this analysis leads to the prediction of A/E polarization of the geminal and trans resonances in accord with our observations.<sup>14</sup> That the addition of  $\text{H}_2$  to the alkyne occurs with predominantly cis stereochemistry and very little or no net effect indicates that the biradical **3** transfers its H atoms to  $\text{RC}\equiv\text{CH}$  in an essentially concerted manner.

To our knowledge this is the first example of CIDNP based on a metal-centered biradical. Our CIDNP results may be compared with those of Closs and Kaptein for organic biradicals in which singlet-triplet mixing occurs by either a spin-sorting mechanism as is seen in the present study or by  $T_1$ -S mixing which leads to emission effects exclusively.<sup>15</sup> The latter is dominant when the exchange integral  $J$ , which reflects the singlet-triplet splitting, is large and comparable to the Zeeman splitting; our results suggest that in the case of **3**,  $J$  is relatively small. Further experimental and theoretical work on biradicals such as **3** is needed.

While the present study is the first to recognize the MCBR for producing CIDNP, one other report involving a polynuclear transition-metal organometallic compound shows similar effects.<sup>16</sup> Specifically, Bergman et al. find multiplet effects in the hydrogenolysis of  $\text{Co}_3(\text{CO})_9(\mu_3\text{-CCH}_2\text{-}t\text{-Bu})$  to give  $t\text{-BuCHCH}_2$  with polarization only in the protons originating from  $\text{H}_2$ .<sup>16</sup> We think that that reaction may also proceed via a metal-centered biradical, and we suggest that MCBR mechanisms which are difficult to detect may occur more commonly in reactions involving polynuclear transition-metal hydrides.

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(13) Complex **1** undergoes facile loss of  $\text{H}_2$  in the absence of other reagents.<sup>5</sup> This loss of  $\text{H}_2$ , seen in the present study when reaction 2 is done under  $\text{N}_2$  with lower resultant yields of styrene, is not necessary to explain the observed multiplet effects. However, in some experiments, significant enhancement of  $\text{H}_2$  absorption is detected. This result cannot be explained by **3** and suggests the possibility of a second metal-centered biradical such as one with both H's on a single Rh center prior to  $\text{H}_2$  reductive elimination. This observation is under continuing study.

(14) The A/E phase of the multiplet effect is determined from Kaptein's rule<sup>11</sup> assuming a singlet precursor, escape or triplet products, a positive spin-spin coupling constant, and the fact that the coupled nuclei are on different radical centers of the MCBR.

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**Registry No.** **1**, 91759-40-9; **2**, 80846-11-3;  $\text{PhC}\equiv\text{CH}$ , 536-74-3;  $\text{MeC}\equiv\text{CH}$ , 74-99-7;  $t\text{-BuC}\equiv\text{CH}$ , 917-92-0;  $\text{EtC}\equiv\text{CH}$ , 107-00-6;  $\text{HC}\equiv\text{CCOOMe}$ , 922-67-8;  $\text{HC}\equiv\text{CCH}_2\text{OH}$ , 107-19-7;  $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{OH}$ , 764-01-2.

### Hydrido Methylidene, Hydrido Vinylidene, Hydrido Oxo, and Hydrido Formaldehyde Derivatives of Bis(pentamethylcyclopentadienyl)tantalum

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Transition-metal complexes of the general class  $\text{L}_n\text{M}(\text{H})(=\text{X})$  ( $\text{X} = \text{CH}_2$ ;  $\text{C} = \text{CH}_2$ ,  $\text{O}$ ) are of interest as models for reactive intermediates in a variety of catalytic processes. Hydrido alkylidene complexes, generated by a 1,2-hydrogen shift from metal alkyls, have been postulated to play an important role in the metathesis and polymerization of olefins,<sup>1</sup> while surface-bound vinylidene species have been detected<sup>2</sup> and recently proposed to account for linear/branched hydrocarbon distributions in Fischer-Tropsch synthesis.<sup>3</sup> The third member of the class described here,  $\text{L}_n\text{M}(\text{H})(=\text{O})$ , is of fundamental importance in reactions involving  $\text{H}_2\text{O}$ ,  $\text{O}_2$ , or peroxides. Although an example of an oxo hydride has not previously been reported, several oxo alkyl species have been characterized recently.<sup>4</sup>

We have described the preparation of a number of permethyltantalocene derivatives and commented on the remarkable stability conferred by two pentamethylcyclopentadienyl ligands.<sup>5</sup> This important facet and a general reluctance for permethylmetallocene derivatives to undergo oligomerization processes have allowed us to prepare and investigate the reaction chemistry of a number of monomeric hydrido derivatives of general formula,

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