

## A revisionist view of fluxionality in metal polyhydrides: the role of exchange coupling

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*Organometallics*, **1990**, 9 (10), 2643-2645 • DOI: 10.1021/om00160a005 • Publication Date (Web): 01 May 2002

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increase in  $\beta_0$  value relative to that of *p*-nitroaniline can reach a factor of 3. Comparison to a "fully conjugated" molecule with a more extended conjugation such as 4-amino-4'-nitrostilbene illustrates the role of the silicon atoms in the reduction of both maximum absorption wavelength ( $\lambda_{\text{max}} = 385$  nm instead of 430 nm in acetone) and intramolecular charge transfer (by a factor of 2 for  $\beta_0$  as compared to the EFISH-deduced value given by Oudar.<sup>8</sup> These results can be interpreted by the following model:<sup>9</sup>  $\beta = \beta_{\text{add}} + \beta_{\text{CT}}$ ;  $\beta_{\text{add}}$  is obtained by a vectorial addition of the contributions of each side group, which are considered to be independent; this addition is made with respect to the geometrical considerations of the  $sp^3$  orbitals of silicon.

(7) Cheng, A.; Tam, W. *Proc. SPIE-Int. Soc. Opt. Eng.* 1989, 61, 1187.

(8) Oudar, J. L. *J. Chem. Phys.* 1977, 67, 446.

(9) Barzoukas, M.; Josse, D.; Zyss, J.; Soula, G. Mignani, G. To be submitted for publication in *Organometallics*.

$\beta_{\text{CT}}$  is the difference between  $\beta$  and  $\beta_{\text{add}}$ . For compound **4c** the important contribution of the CT through the silicon chain is clearly pointed out. The nonlinear optical properties of compounds **4a**, **4b**, and **4c** are listed in Table I.<sup>10</sup>

The work done currently concerns the studies of the CT behavior in donor/acceptor substituted silanes and their efficiency in NLO. The results of this investigation will soon be published in a subsequent paper.

(10)  $\beta$  measurements were performed with use of the electric field induced second harmonic (EFISH) method.<sup>8</sup> The laser sources consisted of a Q-switched, mode-locked Nd<sup>III</sup>:YAG laser emitting pulse trains (duration 160 ps) at 1.34  $\mu\text{m}$  and a Q-switched Nd<sup>III</sup>:YAG laser emitting 10-ns pulses at 1.06  $\mu\text{m}$ . The second-harmonic signal was measured at 670 nm from solutions of various concentrations in acetone.

(11) Dipole moment measurements were made with use of the Hedestrand method in 1,4-dioxane: Hedestrand, G. *Z. Phys. Chem., Abt. B* 1929, 2, 428.

## A Revisionist View of Fluxionality in Metal Polyhydrides: The Role of Exchange Coupling

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Received June 4, 1990

**Summary:** A reinterpretation of the <sup>1</sup>H NMR spectra of ( $\eta\text{-C}_5\text{R}_5$ )Ru(PPh<sub>3</sub>)H<sub>3</sub> (R = H, **1**; R = Me, **2**) is proposed on the basis of new data from the <sup>1</sup>H NMR spectra of **1** and **1-d**<sub>2</sub>. A single resonance is observed in the hydride region of the <sup>1</sup>H{<sup>31</sup>P}NMR spectrum of **1** down to 190 K, consistent with previous reports. A low-temperature limiting <sup>1</sup>H NMR spectrum of the A<sub>2</sub>BX type (X = <sup>31</sup>P) was ultimately observed for **1** at 170 K. Computer simulation of the spectrum of **1** at 170 K gives a value of 900 Hz for  $J_{\text{A-B}}$ . In contrast, the <sup>1</sup>H{<sup>31</sup>P} NMR spectrum of **1-d**<sub>2</sub> at 190 K exhibits two distinct hydride resonances in the ratio 2:1, which coalesce at 210 K. From the coalescence temperature, the barrier to thermally activated hydride site exchange is  $\Delta G^\ddagger_{210} = 9.5$  kcal/mol. The exceptionally large value for  $J_{\text{A-B}}$  in **1** is attributed to a quantum-mechanical exchange process, which is effectively quenched by deuterium substitution. A similar interpretation of the previously reported spectra for **2** gives  $J_{\text{A-B}} = 290$  Hz at 180 K.

There is currently great interest in the structure and reactivity of transition-metal polyhydride complexes. In light of the discovery of transition-metal dihydrogen complexes by Kubas<sup>1</sup> and theoretical work by Burdett and co-workers indicating that other polyhydrogen "ligands" such as H<sub>3</sub> and H<sub>4</sub> may exist,<sup>2</sup> we<sup>3</sup> and others<sup>4-6</sup> have in-

vestigated the possible role of H-H bonding interactions in transition-metal polyhydrides. While there is currently no evidence for H<sub>3</sub> or H<sub>4</sub> ligands as ground-state structures, such polyhydrogen ligands are possible intermediates in the well-studied rearrangement processes of stereochemically nonrigid or fluxional polyhydrides.<sup>7</sup>

A particularly interesting class of polyhydrides are neutral ruthenium(IV) complexes of the form ( $\eta\text{-C}_5\text{R}_5$ )Ru(L)H<sub>3</sub> (R = H, Me; L = tertiary phosphine ligand). The first such complex, ( $\eta\text{-C}_5\text{H}_5$ )Ru(PPh<sub>3</sub>)H<sub>3</sub> (**1**), was reported by Davies and co-workers in 1983.<sup>8</sup> It was reported that complex **1** exhibits a single doublet resonance in the hydride region of the <sup>1</sup>H NMR spectrum ( $^2J_{\text{H-P}} = 18$  Hz) down to 193 K, the lowest temperature reported. This observation, in conjunction with the observation of two bands in the infrared spectrum attributed to  $\nu(\text{Ru-H})$ , led to the assignment of a trigonal-bipyramidal structure, with the three hydride ligands in the equatorial plane. Subsequent work by Suzuki and co-workers<sup>9</sup> on the closely related complex ( $\eta\text{-C}_5\text{Me}_5$ )Ru(PPh<sub>3</sub>)H<sub>3</sub> (**2**) cast some doubt on this assertion, since the results of an X-ray study of **2** clearly showed that the structure is a distorted capped square pyramid, with the cyclopentadienyl ligand capping. In the case of **2**, Suzuki reports that the <sup>1</sup>H NMR spectrum

(5) Antinolo, A.; Chaudret, B.; Commenges, G.; Fajardo, M.; Jalon, F.; Morris, R. H.; Otero, A.; Schweitzer, C. T. *J. Chem. Soc., Chem. Commun.* 1988, 1210-1212.

(6) Arliguie, T.; Border, C.; Chaudret, B.; Devillers, J.; Poilblanc, R. *Organometallics* 1989, 8, 1308-1314. Large values of  $J_{\text{A-B}}$  observed in the low-temperature <sup>1</sup>H NMR spectrum of ( $\eta\text{-C}_5\text{Me}_5$ )Fe(PMe<sub>3</sub>)H<sub>3</sub> have also been attributed to exchange coupling: Paciello, R. A.; Manriquez, J. M.; Bercaw, J. E. *Organometallics* 1990, 9, 260-265.

(7) Cf.: Jesson, J. P. In *Transition Metal Hydrides*; Muetterties, E. L., Ed.; Marcel Dekker: New York, 1972; Chapter 4.

(8) Davies, S. G.; Moon, S. D.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* 1983, 1278-1279.

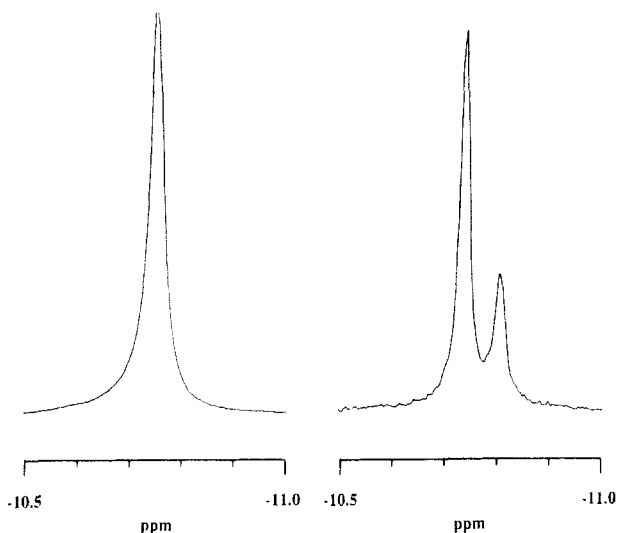
(9) Suzuki, H.; Lee, D. H.; Oshima, N.; Moro-oka, Y. *Organometallics* 1987, 6, 1569-1575.

(1) For a recent review, see: Kubas, G. J. *Acc. Chem. Res.* 1988, 21, 120-128.

(2) Burdett, J. K.; Phillips, J. R.; Pourian, M. R.; Poliakov, M.; Turner, J. J.; Upmacis, R. *Inorg. Chem.* 1987, 26, 3054-3063.

(3) Heinekey, D. M.; Payne, N. G.; Schulte, G. *J. Am. Chem. Soc.* 1988, 110, 2303-2305.

(4) Arliguie, T.; Chaudret, B.; Devillers, J.; Poilblanc, R. *C. R. Acad. Sci., Ser. 2* 1987, 305, 1523-1526.



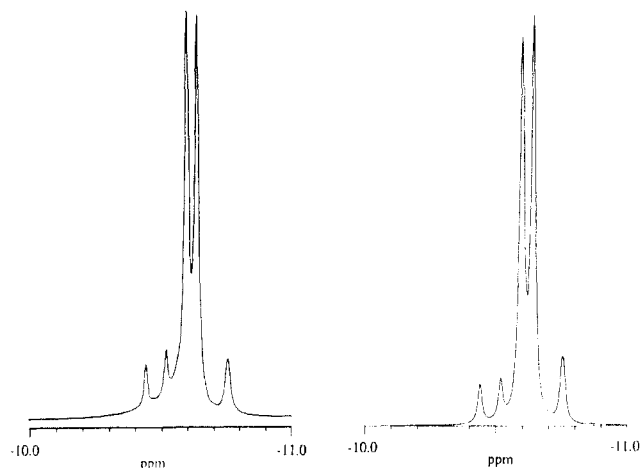
**Figure 1.**  $^1\text{H}\{^{31}\text{P}\}$  NMR spectra (490 MHz, hydride region) for **1** (left) and **1-d<sub>2</sub>** (right) at 190 K in  $\text{CD}_2\text{Cl}_2$ .

in the hydride region is a doublet at 193 K but that the signal "decoalesces" at ca. 180 K. The low-temperature spectrum was not well resolved and could not be interpreted. Thus, **1** and **2** are examples of a large class of fluxional polyhydride complexes where definitive slow-limit  $^1\text{H}$  NMR spectra have not been obtained. It has been previously assumed that such spectral data indicate that facile thermally activated site exchange is occurring in such cases.<sup>7</sup>

We have recently proposed the existence of a quantum-mechanical exchange coupling between the hydrogen nuclei in certain transition-metal polyhydride complexes.<sup>10</sup> This coupling is a manifestation of a coherent site exchange process and can be considerably larger than normal magnetic couplings arising by the Fermi contact mechanism. In general, such a large coupling will have the effect of obscuring the chemical shift difference between inequivalent hydride environments in a polyhydride complex. In practice, a very large coupling could give the same observed spectrum as facile thermally activated site exchange. Since it has been demonstrated that the coherent exchange process is effectively quenched by partial deuterium substitution,<sup>10</sup> we have investigated the  $^1\text{H}\{^{31}\text{P}\}$  NMR spectrum of **1-d<sub>2</sub>** at low temperature.

Representative  $^1\text{H}\{^{31}\text{P}\}$  spectra for **1** and **1-d<sub>2</sub>** (190 K) are shown in Figure 1. The spectrum of **1** at this temperature exhibits a single resonance in the hydride region, consistent with the observations of Davies and co-workers.<sup>8</sup> In contrast, the spectrum of **1-d<sub>2</sub>** clearly shows two signals in a 2:1 intensity ratio. At higher temperatures, the two signals coalesce. Simulation of the line shapes for this thermally activated exchange process gives  $\Delta G^*_{210} = 9.5 \text{ kcal mol}^{-1}$ .

The origin of this striking difference between **1** and **1-d<sub>2</sub>** was probed by observing the  $^1\text{H}$  NMR spectra of **1** at lower temperatures in  $\text{CDFCl}_2$  solvent.<sup>11</sup> The spectrum in the hydride region consists of a highly second order  $\text{A}_2\text{BX}$  spin system ( $\text{X} = ^{31}\text{P}$ ), with extremely large values for  $J_{\text{A-B}}$ .



**Figure 2.** Experimental (left) and calculated (right)  $^1\text{H}$  NMR spectra (490 MHz) for **1** at 170 K in  $\text{CDFCl}_2$ . Parameters for the calculation are  $\delta_{\text{A}} = -10.55 \text{ ppm}$ ,  $\delta_{\text{B}} = -10.75 \text{ ppm}$ ,  $J_{\text{A-B}} = 900 \text{ Hz}$ ,  $J_{\text{A-P}} = 29.5 \text{ Hz}$ , and  $J_{\text{B-P}} = 4 \text{ Hz}$ .

The observations are exemplified by the spectrum at 170 K (Figure 2), which was fit computationally to values of  $\delta_{\text{A}} = -10.55 \text{ ppm}$ ,  $\delta_{\text{B}} = -10.75 \text{ ppm}$ ,  $J_{\text{A-B}} = 900 \text{ Hz}$ ,  $J_{\text{A-P}} = 29.5 \text{ Hz}$ , and  $J_{\text{B-P}} = 4 \text{ Hz}$ . While the chemical shift parameters and H-P coupling constants are reliably fit, the value obtained for  $J_{\text{A-B}}$  is somewhat approximate, since the weak outer lines of the spectrum were not located and the portion of the spectrum that was observable is relatively insensitive to variation in  $J_{\text{A-B}}$ . The value of 900 Hz should be regarded as a minimum, since lower values give poorer fits, while the input of higher values of  $J_{\text{A-B}}$  gives calculated spectra that are essentially indistinguishable from the one shown in the figure. The observation of a single resonance for **1** at slightly higher temperatures is explicable in terms of a small chemical shift difference (0.2 ppm) between the two hydride environments, a very large coupling constant, and a slight line broadening due to slow thermally activated exchange of the A and B hydride environments.

The NMR observations reported by Suzuki and co-workers<sup>9</sup> for  $(\eta\text{-C}_5\text{Me}_5)\text{Ru}(\text{PPh}_3)\text{H}_3$  (**2**) can now be interpreted in terms of similar large couplings. The reported low-temperature (190 K)  $^1\text{H}$  NMR spectra for **2** can be simulated as an  $\text{A}_2\text{BX}$  spin system ( $\text{X} = ^{31}\text{P}$ ) with  $\delta_{\text{A}} = -10.23 \text{ ppm}$ ,  $\delta_{\text{B}} = -10.29 \text{ ppm}$ ,  $J_{\text{A-B}} = 290 \text{ Hz}$ ,  $J_{\text{A-P}} = 28 \text{ Hz}$ , and  $J_{\text{B-P}} = 4 \text{ Hz}$ .

Similar observations on the related complexes  $(\eta\text{-C}_5\text{Me}_5)\text{Ru}(\text{PR}_3)\text{H}_3$  ( $\text{R} = \text{CHMe}_2, \text{Cy}$ ) have been reported by Chaudret and co-workers.<sup>6</sup> In these cases, low-temperature  $^1\text{H}$  NMR spectra were well resolved and could be fit as  $\text{A}_2\text{BX}$  spin systems with  $J_{\text{A-B}}$  values of up to 131 Hz. It seems likely that these large couplings are also the result of a coherent exchange process, rather than any bonding interactions between the hydride ligands. We have previously observed<sup>3,10</sup> that the magnitude of the exchange coupling in cationic iridium trihydride complexes of the form  $([\eta\text{-C}_5\text{H}_5]\text{Ir}(\text{L})\text{H}_3]^+$  is inversely proportional to the basicity of the ligand L. A similar effect is observed in the neutral ruthenium complexes considered here. For the complexes  $(\eta\text{-C}_5\text{Me}_5)\text{Ru}(\text{PR}_3)\text{H}_3$ ,  $J_{\text{A-B}}$  increases from ca. 60–130 Hz<sup>6</sup> for  $\text{R} = \text{CHMe}_2$  and  $\text{Cy}$  to the 290 Hz noted above for the  $\text{R} = \text{Ph}$  derivative (complex **2**). Permethylation of the cyclopentadienyl ligand (**2** versus **1**) leads to a substantial decrease in the exchange coupling (290 Hz for **2** versus 900 Hz for **1**).

As mentioned above, many polyhydride complexes exhibit only one resonance for the hydride ligands in the  $^1\text{H}$  NMR spectrum at all accessible temperatures. The results

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(11)  $\text{CDFCl}_2$  was prepared from  $\text{CDCl}_3$  by the published procedure: Siegel, J. S.; Anet, F. A. *J. Org. Chem.* **1988**, *53*, 2689–2630. It was found that purification of the product by stirring over  $\text{CaH}_2$  was necessary to remove impurities which reacted with **1**.

reported here clearly demonstrate that this observation does not necessarily imply that rapid thermally activated exchange processes are operative. A large coupling between two or more hydrides caused by a coherent exchange process can give spectra that are easily mistaken for the fast-limit spectra of a highly fluxional molecule. Such a situation is readily revealed by deuterium substitution, which quenches the quantum-mechanical process and

allows the thermal exchange process to be clearly observed and quantified. We are continuing to investigate additional examples of this phenomenon.

**Acknowledgment.** We thank the National Science Foundation (Grant CHE-8814191) for support of this research and Johnson Matthey Inc. for a generous loan of ruthenium trichloride.

## Stannadesulfurization of a Bis(diethyldithiocarbamato)tungsten(II) Complex: Formation of an (Aminocarbyne)tungsten Complex

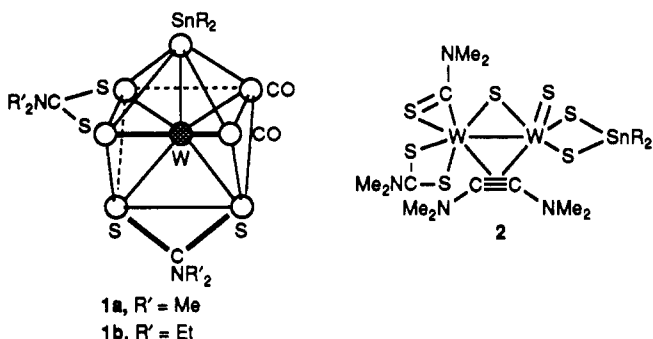
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School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, England

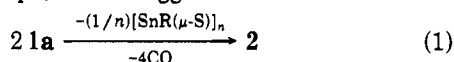
Received June 12, 1990

**Summary:** The crystalline, blue, diamagnetic complex  $[(W(\eta^2-S_2CNET_2)_2)(\mu-CNET_2)(\mu-S)(\mu-S_2CNET_2)(\mu-S_2SnR_2)]$  ( $W, W$ ) (**3**) was obtained by heating  $[W(CO)_2(\eta^2-S_2CNET_2)_2(SnR_2)]$  ( $R = CH(SiMe_3)_2$ ) under reflux in benzene: single-crystal X-ray data on **3** confirm its structure and show that (i) the carbyne ligand  $CNET_2$  symmetrically bridges the two W atoms, (ii) the  $W_2(\mu-CNET_2)$ -containing fragment  $W_2CN(C_{\infty}H_2)$  is planar, (iii) the W-S distances range from 2.30 to 2.61 Å, and (iv) the W-W distance is short, 2.614 (2) Å.

Reactions that form or break a C-C<sup>1</sup> or C-S<sup>2</sup> bond are important in organometallic chemistry. We recently reported that such processes are involved in the thermal stannadesulfurization of the new stannylene-tungsten(II) complex  $[W(CO)_2(\eta^2-S_2CNR'_2)_2(SnR_2)]$  ( $R = CH(SiMe_3)_2$ ,  $R' = Me$ ; **1a**), yielding  $[SnR_2(\mu-S)]_n$  and the ditungsten-tin



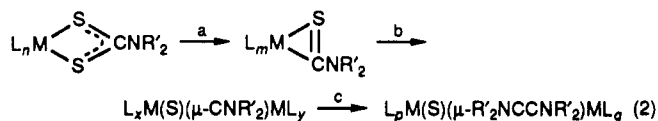
cluster **2**, featuring the diaminoalkyne ligand  $Me_2NCCNMe_2$  (eq 1).<sup>3</sup> We suggested that the latter had



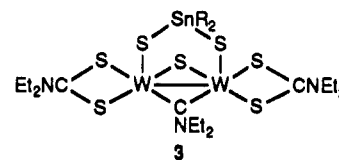
been formed by the coupling of coordinated aminocarbyne ligands  $C(NMe_2)$  of an intermediate along the reaction pathway (eq 2c, R' = Me).<sup>3</sup>

Although the internal oxidative addition of one dithiocarbamate C-S bond to tungsten is well-known (eq 2a),<sup>3,4</sup> cleavage of the remaining C-S bond, the carbyne-forming step (eq 2b), had not previously been unambiguously demonstrated.<sup>5</sup>

We now report the spectroscopic characterization and a single-crystal X-ray diffraction study of the product obtained from thermolysis of  $[W(CO)_2(\eta^2-S_2CNET_2)_2(SnR_2)]$  (**1b**). These results unequivocally establish the postulated double desulfurization of a coordinated dithiocarbamate (eq 2a,b).



When a benzene solution of  $[W(CO)_2(\eta^2-S_2CNET_2)_2(SnR_2)]$  (**1b**)<sup>6</sup> was heated under reflux, a color change from yellow to dark blue occurred. From the reaction mixture, a blue crystalline solid (**3**) of empirical formula  $C_{34}H_{78}N_4S_9Si_4SnW_2$  was isolated after chromatography on Florisil.<sup>7</sup> The <sup>1</sup>H NMR spectrum showed (i) resonances



(4) (a) Ricard, L.; Estienne, J.; Weiss, R. *Inorg. Chem.* **1973**, *12*, 2182. (b) Herrick, R. S.; Nieter-Burgmayer, S. J.; Templeton, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 2599. (c) Mayr, A.; McDermott, G. A.; Dorries, A. M.; Holder, A. K.; Fultz, W. C.; Rheingold, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 310.

(5) Such a transformation has been proposed to account for the photochemical reaction of  $[W(\eta^2-PhCCH)(\eta^2-S_2CNMe_2)_2]$  with PhCCH to yield a complex containing the  $[\eta^5-C_5H_5Ph_2(NMe_2)]^-$  ligand: Morrow, J. R.; Templeton, J. L.; Bandy, J. A.; Bannister, C.; Prout, C. K. *Inorg. Chem.* **1986**, *25*, 1923.

(6)  $[W(CO)_2(\eta^2-S_2CNET_2)_2(SnR_2)]$  (**1b**) was prepared by the 1:1 reaction of  $SnR_2$  with  $[W(CO)_3(\eta^2-S_2CNET_2)_2]$  (75%, after column chromatography on a Florisil support and elution with  $n-C_6H_{14}$ ). IR (Nujol):  $\nu(CO)$  1981 (s) and 1894 (s),  $\nu(CN)$  1510 (m) and 1500 (m),  $\rho(SiCSi)$  840 (s)  $cm^{-1}$ . <sup>1</sup>H NMR ( $C_6D_6$ , 303 K):  $\delta$  3.49 (q, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 2 H,  $NCH_2CH_3$ ), 3.34 (q, <sup>3</sup>J<sub>HH</sub> = 7.4 Hz, 2 H,  $NCH_2CH_3$ ), 3.02 (q, <sup>3</sup>J<sub>HH</sub> = 6.8 Hz, 4 H,  $NCH_2CH_3$ ), 0.76 (complex m, 14 H,  $NCH_2CH_3$  and  $C(H)Si_2$ ), 0.45 (br s, 36 H,  $Si(CH_3)_3$ ). <sup>13</sup>C NMR ( $C_6D_6$ , 303 K):  $\delta$  223.0 (<sup>1</sup>J<sub>WC</sub> = 135 Hz, CO), 209.7 and 203.5 ( $S_2CN<$ ), 52.3, 50.2, and 44.0 ( $NCH_2CH_3$ ), 17.7 ( $C(H)Si_2$ ), 12.3, 12.1, and 11.9 ( $NCH_2CH_3$ ), 5.2 and 4.9 ( $Si(CH_3)_3$ ). <sup>119</sup>Sn NMR ( $C_6D_6$ , 303 K):  $\delta$  174.1. Mass spectrum (FAB; m/z (assignment)): 946 ((M - CO)<sup>+</sup>), 931 ((M - CO - CH<sub>3</sub>)<sup>+</sup>), 9.18 ((M - 2CO)<sup>+</sup>). Anal. Calcd for  $C_{34}H_{78}N_4O_2S_4Si_4SnW$ : C, 32.1; H, 6.01; N, 2.88. Found: C, 31.7; H, 5.55; N, 3.06.

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<sup>†</sup> Present address: Olin Chemicals Research, 350 Knotter Drive, P.O. Box 536, Cheshire, CT 06410-0586.

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(3) Hitchcock, P. B.; Lappert, M. F.; McGeary, M. J. *J. Am. Chem. Soc.* **1990**, *112*, 5658.