

Tri-*tert*-butylated SubPc **1** (Scheme 1) prepared by a literature method^{5a} at ca. 50% yield and succinimidine (**2a**)⁶ or diiminoisoindoline analogues **2a–d**⁷ (ca. 7 equiv) were reacted at 80–90 °C in a mixture of *N,N*-dimethyl sulfoxide and either chlorobenzene, *o*-dichlorobenzene, 1-chloronaphthalene, or 2-chloronaphthalene (2–1:1 v/v) for 5–27 h (reaction time and solvent ratio depend mainly on the solubility of **2**). After removal of the solvent under reduced pressure, the residue was chromatographed on silica gel with methylene chloride as eluent. The blue-green fraction was collected, and this fraction was further purified by gel permeation chromatography using Bio-beads SX-8 (Bio-rad) and methylene chloride or tetrahydrofuran to give a very dark blue, shining solid in 8–20% yield depending on the system.⁸ Consistent with the structure (**3a–d**), parent ion peaks were observed at 632, 682, 732, and 782, respectively, using the fast atom bombardment technique, and **3a–d** were fully characterized by IR, NMR, and elemental analysis.⁸ The inner two pyrrole protons of these compounds generally gave three broad absorption peaks due to the presence of isomers and the difference of the attached position at fields as high as –1.7 to –4.4 ppm typical of Pcs.^{8,9}

Figure 1 shows the absorption spectra of these compounds. The spectrum of **3a** is similar to that of tribenzotetraazaporphine without peripheral substituent groups,¹⁰ and the spectrum of **3b** is typical of nonmetalated phthalocyanines.^{3a} The position of the Q-band peaks shifts to longer wavelength with the enlargement of the π -conjugated system, particularly that of the longest wavelength band, which shifts 20–30 nm (420–530 cm⁻¹) per benzene unit. The absorption coefficients (ϵ) of the Q bands decrease generally with decreasing symmetry of the molecules, i.e., **3b** > **3c** > **3d** > **3a**, while the ratio of the actual absorption intensity (the oscillator strength) at 500–800 nm is 0.75:1.00:1.03:0.88 for **3a:3b:3c:3d**. On the other hand, neither the ϵ values nor the positions of the Soret bands differ significantly among the compounds. Thus, fine tuning of the position of the intense Q band was realized by the removal or displacement of one benzene ring in Pcs.

The present method has several advantages over hitherto known mixed condensation methods. (i) The yield is relatively high. (ii) Purification is easy as column chromatography exhibits two easily separated colored bands. One is the blue fraction of the desired compound, and the other is the reddish purple fraction of unreacted **1**. (iii) No Pc analogue containing more than one **2** unit is obtained. If we collect the blue fraction in the purification process (column), it always gives Pc analogues that contain only one **2** unit.

In spite of being aromatic compounds, SubPcs are known to have a cone-shaped structure.^{5c} Such distorted bent aromatic

compounds appear structurally strained and unstable, and since structurally highly strained compounds such as cyclobutenes¹¹ and epoxides have successfully been applied in organic synthesis, this character of SubPcs appears to enable their above ring-expansion reaction to occur.

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Direct Observation and Retro-Ene Reaction of a Propargylic Diazene. Stereochemical Assignment of Monoalkyl Diazenes

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Allylic and propargylic diazenes and their rearrangement by [3,3]-sigmatropic elimination of dinitrogen (retro-ene reaction) have been invoked in numerous organic transformations.^{1,2} As rearrangement uniformly occurs under the conditions of diazene formation, these hypothetical intermediates have not previously been observed, and fundamental questions regarding their stereochemistry (*E* vs *Z*) and reactivity remain. Employing a new method for diazene generation,² we have been able to produce and study such an intermediate at low temperature and thereby address these issues of structure and mechanism, as described below.

The reaction of (3-phenyl-2-propynyl)hydrazine (**1**) with 4-methyl-1,2,4-triazoline-3,5-dione (MTAD) in tetrahydrofuran produces 1,2-propadienylbenzene (**2**) in 70% yield after chromatographic isolation.² Through the use of variable-temperature NMR spectroscopy, we have learned that two pathways operate in the formation of **2** from **1**. A sealed, evacuated NMR tube containing solid MTAD (1 equiv) layered upon a frozen solution of hydrazine **1** and vinylidene chloride (internal reference) in deoxygenated tetrahydrofuran-*d*₆ was agitated in a –100 °C bath so as to mix the thawing components and was quickly loaded into the probe of a high-field NMR spectrometer, precooled to –95 °C. Three products were formed cleanly and reproducibly: 4-methylurazole (85%), allene **2** (44%), and as evidenced by the low-field resonance at δ 15.9 ppm, the propargylic diazene **3** (40%).³ These products were stable at –95 °C, and their ratio did not vary appreciably from run to run, nor was the product distribution altered when the sample was prepared by allowing the frozen mixture to thaw within the probe (as monitored by the appearance and sharpening of the deuterium lock signal). Upon warming to –70 °C, signals for **3** underwent first-order decay ($k = (8 \pm 2) \times 10^{-5} \text{ s}^{-1}$, four determinations, $t_{1/2} = 2.5 \text{ h}$) while those for **2** grew correspondingly ($k = (7 \pm 4) \times 10^{-5} \text{ s}^{-1}$).⁴ The data

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(7) Brach, P. J.; Grammatica, S. J.; Ossanna, O. A.; Weinberger, L. J. *Heterocycl. Chem.* 1970, 7, 1403–1405. Kaplan, M. L.; Lovinger, A. J.; Reents, W. D.; Schmidt, P. H. *Mol. Cryst. Liq. Cryst.* 1984, 112, 345–358. **2d** was obtained by the reaction of ammonia gas with 2,3-dicyanoanthracene, which was obtained from 2,3-bis(dibromomethyl)naphthalene (Ried, W.; Bodem, H.; Ludwig, V.; Neidhardt, H. *Chem. Ber.* 1968, 91, 2479–2484) and fumaronitrile.

(8) The yields and analytical data of the products are as follows (reaction was carried out in a DMSO/1-chloronaphthalene 2:1 v/v mixture for **3a–c** and a 1:1 mixture for **3d**). **3a**: 13%. Anal. Calcd for C₄₀H₄₀N₈: C, 75.92; H, 6.37; N, 17.71. Found: C, 75.70; H, 6.06; N, 17.96. **3b**: 20%. Anal. Calcd for C₄₄H₄₂N₈: C, 77.39; H, 6.20; N, 16.41. Found: C, 77.07; H, 6.02; N, 16.70. **3c**: 11%. Anal. Calcd for C₄₈H₄₄N₈: C, 78.66; H, 6.05; N, 15.29. Found: C, 78.39; H, 5.87; N, 15.55. **3d**: 8%. Anal. Calcd for C₅₂H₄₆N₈: C, 79.77; H, 5.92; N, 14.31. Found: C, 79.54; H, 5.67; N, 14.64. The 500-MHz ¹H NMR data in CDCl₃ are as follows. **3a**: 8.35–9.05 (m, 9 H), 7.92–7.97 (m, 2 H), 1.76–1.87 (m, 27 H), –1.73 to –1.97 (3 br s at –1.78, –1.83, and –1.94, in total 2 H). **3b**: 8.3–9.1 (m, 8 H), 8.0–8.2 (m, 3 H), 1.81–1.92 (m, 27 H), –2.7 to –4.1 (3 br s at –2.86, –3.36, and –3.97, in total 2 H). **3c**: 7.4–9.3 (m, 15 H), 1.81–1.93 (m, 27 H), –2.35 to –3.2 (3 br s at –2.55, –2.76, and –3.03, in total 2 H). **3d**: 9.38 (s, 2 H), 7.4–9.2 (m, 15 H), 1.70–1.80 (m, 27 H), –1.8 to –4.4 (3 br s at –2.15, –3.00, and –3.36, in total 2 H).

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(3) Tsuji, T.; Kosower, E. M. *J. Am. Chem. Soc.* 1971, 93, 1992. The observation of long-range coupling between the diazenyl proton and the methylene group (⁴J_{HH} = 2.4 Hz) provides further evidence supporting structure **3**.

(4) Without proper care in purification of reagents, the decomposition of **3** to form **2** is more rapid and irreproducible, though always strictly first order in **3**. Values cited in the text were obtained with carefully purified materials and were the slowest decompositions observed. It is reasonable to propose that impurities catalyze the decomposition of **3**, perhaps by trans → cis isomerization (vide infra).

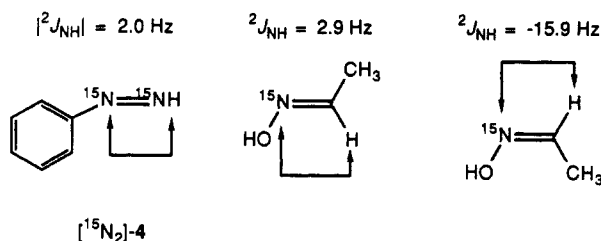
Table I. ^{15}N - ^1H Coupling Constants for Diazenes **3** and **4**

compound	$ ^1J_{\text{NH}} $, Hz	$ ^2J_{\text{NH}} $, Hz	δ H, ppm
$[^{15}\text{N}_2]$ - 3 ^a	50.8	1.8	15.9
$[^{15}\text{N}_2]$ - 4 ^a	51.6	2.0	16.1
$[^{15}\text{N}_2]$ - 4 ^b	49.4	2.0	15.5

^aNMR solvent: THF-*d*₈. ^bNMR solvent: CD₂Cl₂, data from ref 9a.

show that the formation of **2** from **1** occurs by two distinct processes: a low-temperature pathway (≤ -95 °C) and a pathway involving the apparent first-order decomposition of persistent diazene **3** at -70 °C. These observations are reasonably explained by the mechanism presented in Scheme I. It is proposed that oxidation of **1** with MTAD leads to approximately equal amounts of (*Z*)- and (*E*)-diazene **3**.⁵ In accord with the presumed requirement for cis stereochemistry in the sigmatropic elimination, the *Z* isomer rearranges at low temperature and is not observed, while the (*E*)-diazene persists, undergoing first-order decomposition at -70 °C, also to produce **2**. The latter transformation may involve rate-limiting *trans* \rightarrow *cis* isomerization of the diazene which could occur by stepwise or concerted proton-transfer reactions with a molecule other than **3**. Consistent with this notion, preliminary experiments show that 4-methylurazole catalyzes the decomposition of **3** at -70 °C, entering into the rate expression with order ~ 1 (concentration range 0.02–0.05 M). To provide further support for these mechanistic proposals, we sought independent confirmation of the stereochemistry of the persistent diazene **3**.

The stereochemistry of monoalkyldiazenes has not been subject to rigorous determination, since in no case have both *cis* and *trans* isomers of a given monosubstituted diazene been studied. Indeed, as we will demonstrate, it is unlikely that a *cis*-monoalkyldiazene has ever been observed. The most conclusive determination of stereochemistry appears to be for methyl diazene, where high-resolution gas-phase infrared spectroscopy (of both CH₃N=NH and CH₃N=ND) secured the *trans* assignment.⁶ In other work, a series of monosubstituted diazenes, prepared under conditions likely to promote *cis*-*trans* isomerization, were assigned as *trans* on the basis of thermodynamic considerations and ultraviolet absorption intensities.^{7,8} More recently, ¹H NMR spectroscopy has been used to establish stereochemistry in the first reported preparation of a *cis*-monosubstituted diazene [(*Z*)-phenyldiazene, (*Z*)-**4**].^{9a} The *cis* assignment derives from the two-bond coupling constant between the diazenyl proton and a β -¹⁵N label, employing the (*E*)- and (*Z*)-acetaldehyde oximes as a stereochemical reference.^{9a,10} As this method appeared most suitable for our



(5) This ratio may reflect the stereoselectivity of the MTAD oxidation. Alternatively, the *E* isomer could arise, in whole or in part, by a *cis* \rightarrow *trans* isomerization reaction of (*Z*)-**3** in competition with sigmatropic rearrangement. Mechanisms for the formation of **2** from **1** which do not involve (*Z*)-**3** can also be invoked.

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Table II. ^{15}N - ^{15}N and ^{15}N - ^{13}C Coupling Constants for Diazenes **3**–**7**

compound	$ ^1J_{\text{NN}} $, Hz	$ ^1J_{\text{NCl}} $, Hz	$ ^2J_{\text{NCl}} $, Hz
(<i>Z</i>)- 5	21.0		
(<i>Z</i>)- 6	21.0		
(<i>Z</i>)- 7	21.0	11.2 ^a	3.5 ^a
(<i>E</i>)- 5	17.0		
(<i>E</i>)- 6	17.0		
(<i>E</i>)- 7	16.1	4.2 ^a	8.0 ^a
3	17.2	5.4 ^b	8.1 ^b
4	17.2		

^aCoupling to the methyl carbon. ^bCoupling to the methylene carbon. **5** = C₆H₅N=NC(CH₃)₂CN, **6** = C₆H₅N=NC(CH₃)₂C₆H₅, **7** = C₆H₅N=NCH₃.

purposes, we prepared [¹⁵N₂]-**3** by low-temperature oxidation (as above) of appropriately labeled **1**. One- and two-bond ¹⁵N-¹H coupling constants were readily determined and proved to be essentially identical with those observed with the putative *cis*-diazene **4** (Table I). Similarly, oxidation of [¹⁵N₂]phenylhydrazine with MTAD in tetrahydrofuran-*d*₈ at -95 °C afforded a single diazene, **4** ($\sim 43\%$ yield), exhibiting essentially identical one- and two-bond coupling constants as **4** prepared in the previous study (Table I).^{9a,11} Attempts to induce isomerization of **4** by low-temperature ultraviolet irradiation led to the formation of benzene; in no instance in our studies or in earlier work has the isomeric phenyldiazene been observed. With these considerations, the fact that a *Z* stereochemical assignment for persistent diazene **3** is inconsistent with the mechanistic proposals outlined above, and given the potential poor correlation of oximes and diazenes, we have reevaluated the assignment of stereochemistry in these monoalkyldiazenes using ¹⁵N-¹⁵N and ¹⁵N-¹³C heteronuclear coupling constants for analysis and *cis*- and *trans*-dialkyldiazenes as reference materials.

Porter and co-workers observed a correlation between the magnitude of ¹⁵N-¹⁵N coupling and stereochemistry in dialkyldiazenes **5** and **6** (Table II).¹² We have confirmed and extended Porter's findings with (*E*)- and (*Z*)-[¹⁵N₂]phenylmethyldiazene (**7**).¹³ As summarized in Table II, (*Z*)-dialkyldiazenes uniformly exhibit ¹⁵N-¹⁵N couplings of 21 Hz while values for the *E* isomers fall in the range of 16–17 Hz. Analysis of [¹⁵N₂]-**3** and [¹⁵N₂]-**4** by low-temperature ¹⁵N NMR spectroscopy established $|^1J_{\text{NN}}|$ for each as 17.2 Hz, consistent with a *trans* assignment.

More compelling are the variations in magnitude of one- and two-bond ¹⁵N-¹³C coupling constants as a function of stereochemistry, as revealed by observation of the methyl carbon resonance in ¹³C NMR spectra of (*E*)- and (*Z*)-C₆H₅¹⁵N=¹⁵NCH₃ and C₆H₅¹⁴N=¹⁵NCH₃ (Table II).^{13,14} Low-temperature ¹⁵N NMR spectroscopy of triply labeled **3** (C₆H₅C¹³CH₂¹⁵N=¹⁵NH) established a close correspondence in one- and two-bond ¹⁵N-¹³C coupling constants for **3** and (*E*)-**7**, but not (*Z*)-**7**. The data presented strongly support the assignment of *E* stereochemistry for diazenes **3** and **4** in this study and suggest that earlier reports describing (*Z*)-monoalkyldiazenes are likely in error.⁹

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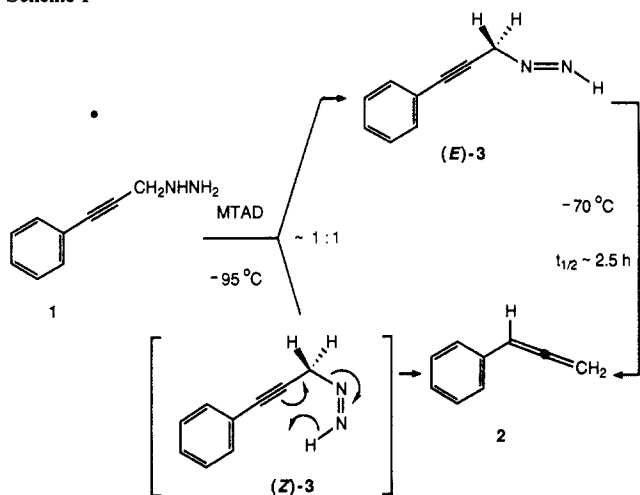
(11) At least three other non-diazene, hydrazine-derived components are present in the mixture. Analysis of the reaction products from low-temperature oxidation of [¹⁵N₂]-phenylhydrazine by ¹⁵N NMR spectroscopy shows that at least two of these arise by coupling of two or more molecules of phenylhydrazine.

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Scheme 1



Given the proposed formation of (Z)-3 in oxidation of **1** with MTAD and the modest yield of (E)-4 in oxidation of phenylhydrazine, it is tempting to speculate that (Z)-4 was produced in the latter reaction but is quite unstable in solution, even at $-95\text{ }^{\circ}\text{C}$.¹¹ This must certainly be the case for (Z)-3, were it produced, where ΔG^{\ddagger} for the proposed sigmatropic elimination can be estimated to be $<12\text{ kcal/mol}$ at $-95\text{ }^{\circ}\text{C}$.

Acknowledgment. We are grateful to Professor John D. Roberts for discussions concerning ^{15}N NMR spectroscopy and to Dr. David R. Wheeler for assistance with high-vacuum techniques. This research was generously supported by the National Science Foundation, the David and Lucile Packard Foundation, and the following industrial sponsors: Monsanto Company, Rohm & Haas Company, Eli Lilly and Company, and Hoffman-La Roche Inc.

Supplementary Material Available: A low-temperature NMR spectrum of **2** and **3** and a plot of the first-order decomposition of **3** at $-70\text{ }^{\circ}\text{C}$ (1 page). Ordering information is given on any current masthead page.

Kinetics by High-Pressure Nuclear Magnetic Resonance: Reversible Hydrogen Binding in $(\eta^2\text{-H}_2)\text{Cr}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_{11})_3]_2$

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High-pressure NMR is a powerful technique for studying a variety of important systems.¹ Molecular hydrogen complexes

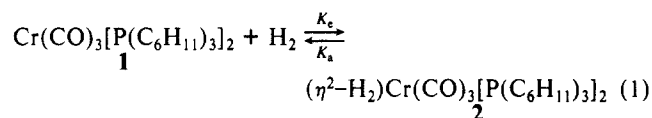
(1) (a) Heaton, B. T.; Jones, J.; Eguchi, T.; Hoffman, G. A. *J. Chem. Soc., Chem. Commun.* **1981**, 331. (b) Heaton, B. T.; Strona, L.; Jonas, J.; Eguchi, T.; Hoffman, G. A. *J. Chem. Soc., Dalton Trans.* **1982**, 1159. (c) Roe, D. C. *J. Magn. Reson.* **1985**, *63*, 388. (d) Krusic, P. J.; Jones, D. J.; Roe, D. C. *Organometallics* **1986**, *5*, 456. (e) Roe, D. C. *Organometallics* **1987**, *6*, 942. (f) Horváth, I. T.; Kastrup, R. V.; Oswald, A. A.; Mozeleski, E. J. *Catal. Lett.* **1989**, *2*, 85. (g) Millar, J. M.; Kastrup, R. V.; Harris, S.; Horváth, I. T. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 194.

Table I^a

pressure, psi	temp, $^{\circ}\text{C}$	R_{BF}	$T_{1\text{F}}$, ms	$T_{1\text{B}}$, ms	$T_{1\text{F}}^{\text{a}}$, ms	$T_{1\text{B}}^{\text{a}}$, ms	K_{e} , s^{-1}
150 H_2	-33	0.49	121	10.8	1450	9	23.0 ± 2.0
150 H_2	-41	0.56	330	10.0	1450	11	5.0 ± 0.5
150 H_2	-52	0.58	780	16.0	1450	13.5	1.1 ± 0.1
150 H_2	-61	0.60	1080	16.9	1450	18	0.6 ± 0.15
413 H_2	-42	0.14	806	9.8	1450	10	4.0 ± 0.5
800 H_2	-24	0.16	139	17.3	1450	9	62.5 ± 2.5
800 H_2	-35	0.15	465	9.5	1450	9.8	10.0 ± 1.0
800 H_2	-43	0.15	711	9.9	1450	9.8	5.0 ± 0.5
800 H_2	-50	0.26	895	10.1	1450	11	1.9 ± 0.2
800 H_2	-59	0.19	1146	16.0	1450	16	1.0 ± 0.1

^a R_{BF} is the ratio of concentrations of bound hydrogen to dissolved hydrogen. $T_{1\text{F}}$ and $T_{1\text{B}}$ are the "apparent" T_1 's, i.e., the time constants obtained by fitting the inversion recovery data to a single exponential. $T_{1\text{F}}^{\text{a}}$ and $T_{1\text{B}}^{\text{a}}$ are the T_1 's calculated in the hypothetical absence of exchange. Error limits for K_{e} 's were estimated by determining the range for which the variance between calculated and experimental inversion recovery data differed by $\leq 1\%$.

are important intermediates for homogeneous catalytic hydrogenation reactions, and numerous examples have been prepared and characterized under ambient conditions.² Since several hydrogenation catalyst systems are used above atmospheric H_2 pressure,³ studies of the behavior of molecular hydrogen complexes under pressure are of great interest. Although it has been shown by high-pressure IR that $\text{Cr}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_{11})_3]_2$ (**1**) reversibly binds H_2 under pressure (eq 1), the coordination mode of the added H_2



could not be established.⁴ We report that the reversible reaction of **1** with H_2 results in the formation of $(\eta^2\text{-H}_2)\text{Cr}(\text{CO})_3[\text{P}(\text{C}_6\text{H}_{11})_3]_2$ (**2**) (eq 1) and the elimination of the side-on coordinated hydrogen, $\eta^2\text{-H}_2$, from **2** has an activation energy of $12.7 \pm 1.0\text{ kcal/mol}$ and is independent of the H_2 pressure.

It has been shown that equilibrium **1** is shifted to **2** above 300 psi of H_2 pressure at $25\text{ }^{\circ}\text{C}$.⁴ Accordingly, when a purple solution of **1** in d_8 -toluene is charged with 400 psi of H_2 at room temperature, the color immediately changes to bright yellow.⁵ ^{31}P NMR shows nearly quantitative reaction, as the resonance of **1** at 63.6 ppm is replaced with a new singlet at 73.5 ppm for **2**.⁶ ^1H NMR at room temperature shows the resonances of the $\text{P}(\text{C}_6\text{H}_{11})_3$ ligands and a broad peak at 4.5 ppm for the dissolved H_2 . The latter indicates exchange between dissolved and coordinated H_2 , and this resonance sharpens upon cooling to $-60\text{ }^{\circ}\text{C}$ as expected. Below $-10\text{ }^{\circ}\text{C}$ a new broad singlet appears at -7.2 ppm , which broadens further upon cooling to $-60\text{ }^{\circ}\text{C}$, suggesting the presence of an $\eta^2\text{-H}_2$ in **2**.⁷ This assignment is also supported by the short T_1 minimum ($\leq 10\text{ ms}$) of the $\eta^2\text{-H}_2$.⁷ No evidence was found for the formation of a classical dihydride species from **2**.

The rate of $\eta^2\text{-H}_2$ elimination from **2** was determined by analysis of ^1H inversion recovery experiments performed in which both the bound and dissolved H_2 were inverted (Figure 1). This is not a generally applicable method for obtaining rate information but works in this case since the recovery from inversion is quite

(2) (a) Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120. (b) Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95.

(3) James, B. R. *Homogeneous Hydrogenation*; Wiley: New York, 1973.

(4) Gonzalez, A. A.; Mukerjee, S. L.; Chou, S.-J.; Kai, Z.; Hoff, C. D. *J. Am. Chem. Soc.* **1988**, *110*, 4419.

(5) (a) Measurements were made on a 7.05-T commercial instrument using d_8 -toluene solutions of **1** (6 mmol/L) in high-pressure NMR tubes described previously,^{1c} and all temperatures were measured by using a methanol standard.^{5b} (b) Van Geet, A. L. *Anal. Chem.* **1968**, *40*, 2227.

(6) In addition, a small ^{31}P resonance at 67.1 ppm was found in nearly all cases due to $\text{Cr}(\text{CO})_4[\text{P}(\text{C}_6\text{H}_{11})_3]_2$, which does not coordinate H_2 under pressure. In separate experiments we have found that its presence has no effect on the T_1 of dissolved and/or coordinated hydrogen and, therefore, does not interfere with T_1 measurements in any way.

(7) Hamilton, D. G.; Crabtree, R. H. *J. Am. Chem. Soc.* **1988**, *110*, 4126.