philes such as F^- and OAc^- show an appreciable reactivity at sulfonyl sulfur.[2b]

The presumed transition state for reaction 1 is probably similar to that for reaction 2 shown above, with H_2O rather than NH_3 as the leaving group. The sulfur center in $(CH_3)_2SOH_2^{2+}$ is a borderline soft acid in which the reactivity order for the halides is inverted by dipolar aprotic solvents (*e.g.*, $Cl^- > Br^- > I^-$ in DMSO).[3] The relative softness of sulfur in $(CH_3)_2SNH_3^{2+}$ is greater than that in $(CH_3)_2SOH_2^{2+}$ as judged by the observed solvent effects. Even in $X_{DMSO} = 0.700$ where Cl^- is only poorly solvated, Cl^- is unreactive toward $(CH_3)_2SNH_3^{2+}$. The preference of this center for soft base nucleophiles is great enough that inversion in the reactivity order does not occur.[25] No quantitative comparison of the rates of reduction of $(CH_3)_2SO$ and $(CH_3)_2SNH_2^+$ can be made because the order with respect to $(CH_3)_2SO$ is indeterminable in DMSO solvents.[3] However, the ratio of the third-order rate constants $k_{(CH_3)_2SNH_2^+}/k_{(CH_3)_2SO} = 2800$ in $X_{DMSO} = 0.500$ indicates that iodide is more reactive at the softer sulfur center.

Acknowledgment. We are grateful to the National Science Foundation for support of this work under Grants GP-2968 and 7981.

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[25] R. G. Pearson and J. Songstad, *J. Am. Chem. Soc.*, **89**, 1827 (1967)

Hydrogen–Carbon-13 Spin–Spin Coupling in Transition Metal Hydride Complexes[1]

George M. Whitesides and G. Maglio

Contribution from the Department of Chemistry,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.
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Abstract: Analysis of the proton nmr spectra of $K_3[HIr(CN)_5]$ (**1**), $K_3[HRh(CN)_5]$ (**2**), *trans*-$[HPtCN(P(C_2H_5)_3)_2]$ (**4**), $HMn(CO)_5$ (**5**), *cis*-$HMn(CO)_4P(C_2H_5)_3$ (**6**), $Na[HW_2(CO)_{10}]$ (**7**), and $Na[HMo_2(CO)_{10}]$ (**8**) either naturally abundant or isotopically enriched in ^{13}CN or ^{13}CO has yielded values of ^1H–M–^{13}C spin-spin coupling constants for representative transition metal carbonyl and cyano hydrides. The utility of these coupling constants in structural investigations of hydride complexes of the transition metals is discussed briefly, with particular reference to compounds **2**, **5**, and **6**.

Proton nmr spectroscopy is well established as a technique of general usefulness in structural investigations of hydride complexes of the transition metals.[2] With few exceptions, metal hydride complexes are diamagnetic,[3] and the resonances due to the hydride ligands characteristically occur in a high-field region of the spectrum which contains no interfering absorptions due to solvents or to other ligands. Consequently, hydride resonances are relatively easily detected even at the low concentrations frequently required for these studies.

For the large and important class of metal hydride complexes which contain phosphines or phosphites as ligands, straightforward analysis of ^1H–^{31}P spin–spin coupling constants provides a simple and apparently reliable method for establishing the relative stereochemistry of the hydride- and phosphorus-containing ligands.[4] The determination of stereochemistry for metal hydride complexes which do *not* contain phosphorus remains a difficult problem. Although ir spectroscopy is useful in studies of metal carbonyl hydrides of appropriate symmetry, and single-crystal X-ray diffraction studies are being carried out on increasing numbers of complexes, development of alternative spectroscopic approaches to stereochemical studies of transition metal hydrides would constitute a valuable addition to the range of techniques applicable to the examination of these materials.

The work reported in this paper was initiated in the hope that ^1H–^{13}C spin-spin coupling constants could be utilized in transition metal carbonyl and cyano hydrides in a manner analogous to that with which ^1H–^{31}P coupling constants are used in metal phosphine hydrides, to provide information concerning the stereochemical arrangement of hydride and carbonyl or cyanide groups coordinated to a common metal atom. The natural abundance of ^{13}C is 1.1%; its nuclear spin is $^1/_2$. The ^1H nmr spectrum of the transition metal hydride containing carbon monoxide or cyanide ligands would thus be expected to consist of the superposition of strong resonances due to species containing only ^{12}CO or ^{12}CN ligands, and additional weaker satellite peaks due to ^1H–^{13}C spin-spin coupling in species containing one or more ^{13}C-containing ligands.[5]

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[1] Supported by the National Science Foundation, Grant GP-7266.

[2] Reviews: (a) A. P. Ginsburg, *Transition Metal Chem.*, 1, 111 (1965); (b) M. L. H. Green and D. J. Jones, *Advan. Inorg. Chem. Radiochem.*, 7, 146 (1965).

[3] The reported paramagnetic hydrides are $Cp_4Ti_2H_2$: H. Brintzinger, *J. Amer. Chem. Soc.*, **88**, 4305, 4307 (1966); $Li_3[Cr_2H_3(C_6H_5)_6]$, F. Hein and R. Weiss, *Naturwiss.*, **46**, 321 (1959).

[4] A *trans* H–M–P stereochemistry is normally characterized by J(H,P) of 80–160 Hz, while a *cis* stereochemistry results in J(H,P) of 10–40 Hz.[2]

[5] The analysis of ^{13}C satellites has been extensively exploited in determination of ^1H–^{13}C coupling constants in organic molecules.[6] To our knowledge, the only such coupling reported for a metal hydride has been the *cis* coupling (*vide infra*) of $[HW_2(CO)_{10}]^-$.[7]

[6] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Oxford, 1966, p 1011 *ff*.

[7] R. G. Hayter, *J. Amer. Chem. Soc.*, **88**, 4376 (1966).

Table I. ^1H–^{13}C Spin-Spin Coupling Constants (Hz) in Transition Metal Hydrides

	Compound	Solvent	Chem shift[a]	*trans* $J(^1H,^{13}C)$	*cis* $J(^1H,^{13}C)$	$J(^1H,M)$	$J(^1H,^{31}P)$
1	$K_3[HIr(CN)_5]$	H_2O	14.37	37.2	5.7		
2	$K_3[HRh(CN)_5]$	H_2O	10.61	56.2	5.7	12.6	
3	$K_3[HCo(CN)_5]$	H_2O	12.65				
4	*trans*-$[HPtCN(P(C_2H_5)_3)_2]$	$CHCl_3$	8.13	41.9		798.0	15.6
5	$HMn(CO)_5$	$(C_2H_5)_2O$	7.73	7.0	14.0		
6	*cis*-$HMn(CO)_4P(C_6H_5)_3$	$(C_2H_5)_2O$	6.43	5.2	15.7[b] 12.1[c]		34.0
7	$Na[HW_2(CO)_{10}]$	THF	12.58	4.3	3.5	42.1	
8	$Na[HMo_2(CO)_{10}]$	CH_3OH	12.15	. . .[d]	4.3		

[a] Chemical shifts are expressed in ppm upfield from TMS. [b] Coupling to the carbonyl group *cis* to the $P(C_6H_5)_3$ ligand. [c] Coupling to the carbonyl group *trans* to the $P(C_6H_5)_3$ ligand. [d] The value of this coupling constant is either 4.3 Hz or $\lesssim$3.0 Hz. See the text for discussion of this point.

It has been found that the relative magnitudes of *cis* and *trans* ^1H-M-^{13}C coupling constants in representative octahedral carbonyl hydrides are similar. Thus, these couplings will probably be of only limited usefulness as absolute stereochemical probes. The differences between *cis* and *trans* ^1H–^{13}C couplings in the two cyano hydrides examined are larger; the absolute magnitudes of these coupling constants may be of greater utility in stereochemical investigations. However, regardless of the usefulness of ^1H-M-^{13}C coupling constants as absolute stereochemical probes, the data collected in these studies demonstrate that ^1H–^{13}C coupling constants can be of use in the solution of structural problems which require differentiation between structures containing different numbers of distinct carbonyl or cyanide groups.

Results

$[HIr(CN)_5]^{3-}$, $[HRh(CN)_5]^{3-}$, and $[HCo(CN)_5]^{3-}$. The time-averaged nmr spectrum of a saturated aqueous solution of $K_3[HIr(CN)_5]$[8] (**1**) containing ^{13}C in natural abundance consists of a sharp signal at 14.37 ppm upfield from tetramethylsilane flanked by two symmetrical pairs of satellites having relative intensity 4:1. The separation between the components of the more intense satellite doublet is 5.7 Hz; the separation between the components of the less intense doublet is 37.2 Hz. The $[HIr(CN)_5]^{3-}$ ion almost certainly has C_{4v} symmetry,[2,9,10] with the hydride occupying a normal octahedral coordination site. Assuming this geometry, the intense central line in the observed spectrum can immediately be assigned to $[HIr(^{12}CN)_5]^{3-}$ present in ~94.2% abundance. The more intense of the doublets can be assigned as ^{13}C satellites due to the 4.4% of naturally abundant $[HIr(^{13}CN)(^{12}CN)_4]^{3-}$ containing H and ^{13}CN *cis* to one another, and the less intense doublets to the 1.1% of this ion having a *trans* H-Ir-^{13}CN geometry. In samples of **1** containing only naturally abundant ^{13}C, $[HIr(^{13}CN)_2(^{12}CN)_3]^{3-}$ will be present only to the extent of approximately 0.3% and will not make an appreciable contribution to the spectrum.

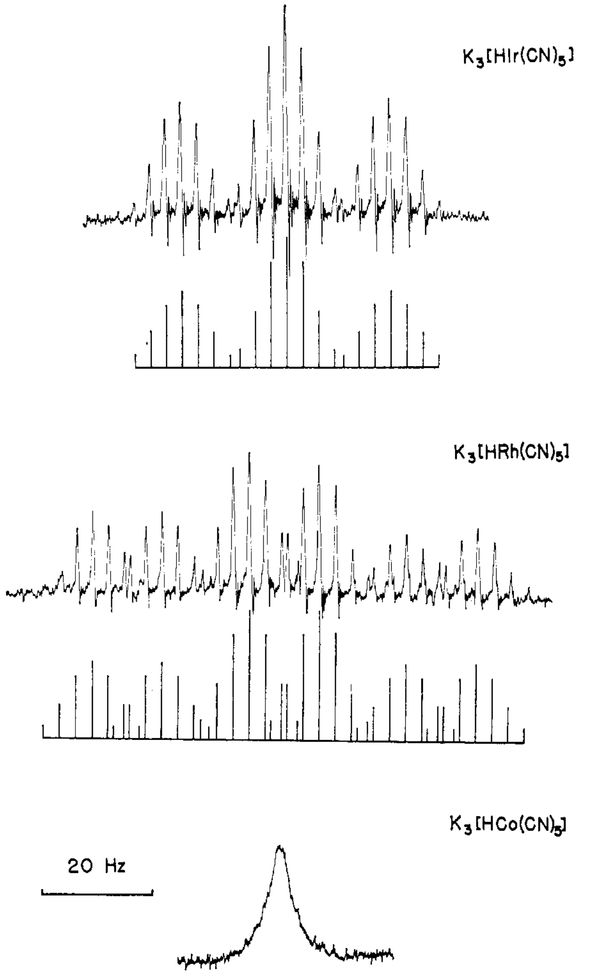

Figure 1. Observed and calculated ^1H nmr spectrum of ~55% ^{13}CN-enriched $[HIr(CN)_5]^{3-}$, $[HRh(CN)_5]^{3-}$, and $[HCo(CN)_5]^{3-}$ in water at 60 MHz. The theoretical spectra were calculated using the coupling constants of Table I.

These coupling constant assignments were confirmed by examination of the proton nmr spectrum of **1** prepared[8] using potassium cyanide enriched to the extent of 50–60% in ^{13}C. This spectrum is shown in Figure 1, together with the spectrum calculated assuming a statistical distribution of the labeled cyanide among one axial and four equivalent radical positions of an octahedral **1**, and the ^1H–^{13}C spin–spin coupling constants listed in Table I.

Analogous ^1H–^{13}C coupling constants in $K_3[HRh(CN)_5]$ (**2**) (Table I) could also be obtained from the

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(8) K. Krogmann and W. Binder, *Angew. Chem. Intern. Ed. Engl.*, 6, 881 (1967).

(9) All presently available evidence indicates that a hydride ion occupies a normal site in the coordination sphere of a metal, rather than burrowing into the metal electron cloud: *cf.* J. A. Ibers, *Ann. Rev. Phys. Chem.*, 16, 389 (1965); R. J. Doedens and L. F. Dahl, *J. Amer. Chem. Soc.*, 87, 2576 (1965).

(10) L. L. Lohr and W. N. Lipscomb, *Inorg. Chem.*, 3, 22 (1964), have obtained satisfactory agreement between the observed value of the chemical shift of the hydride of $[HCo(CN)_5]^{3-}$ and that calculated assuming an octahedral structure.

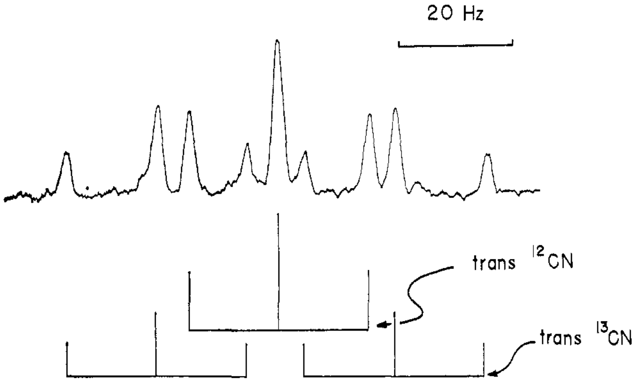

Figure 2. The ^{1}H nmr spectrum of the hydride absorption of ~55% ^{13}CN-enriched *trans*-[HPtCN(P(C$_2$H$_5$)$_3$)$_2$] in chloroform solution at 100 MHz and 30°. The spacing in the triplets shown in the figure corresponds to the phosphorus–hydrogen coupling constant.

time-averaged proton spectrum of saturated aqueous solutions of unenriched material, and confirmed by the spectrum of material prepared from 50 to 60% enriched potassium cyanide (Figure 1). The observation of discrete *cis* and *trans* ^{1}H–^{13}C coupling constants for **2** resolves unambiguously the uncertainty concerning the composition of this material. Wilkinson and coworkers had reported that reaction of potassium cyanide and tetracarbonyl-μ-dichloro-dirhodium(I) in aqueous methanol yielded a compound formulated as dipotassium tetracyanohydroaquorhodium(III), and suggested C_{4v} symmetry for the presumed $[HRh(CN)_4(H_2O)]^{2-}$ ion on the basis of ir evidence.[11] These workers suggested that the *trans*-cyano group of **2** appeared to be very labile toward replacement by water, presumably due to the *trans* effect of the hydride ion. More recently Krogmann and Binder reported the preparation of a compound formulated as **2** from the same reagents in absolute methanol solution.[12] The hydride chemical shift and H–^{103}Rh coupling constants characterizing the materials obtained by Wilkinson's and Krogmann's procedures are identical within experimental error. Moreover, the question of the exact composition of the rhodium cyano hydride could not be resolved by elemental analysis, since the compound is extremely hygroscopic. The observed spectrum of ^{13}C-enriched **2**, prepared by a modification of Krogmann's method, establishes the presence of two distinct types of cyanide groups in the ion in relative abundance 1:4, and is entirely consistent with the formulation $[HRh(CN)_5]^{3-}$. Although this spectrum does not exclude the existence of an ion $[HRh(CN)_4(OH_2)]^{2-}$ under different circumstances, the observed stability of **2** in aqueous solution does indicate that the *trans* cyano group in this compound is not labile toward water under the conditions obtaining in the solutions examined by nmr.

Attempts to observe ^{1}H–^{13}C spin–spin couplings in aqueous solutions of $K_3[HCo(CN)]_5$ (**3**) were unsuccessful. Using either unenriched or enriched (Figure 1) material, only a single broad line was observed for the hydride resonance. Although it is conceivable that the ^{1}H–^{13}C coupling constants in this compound are too small to be detected under the conditions of the experiment, the large coupling constants characterizing the spectra of **1** and **2** indicate that rapid intermolecular hydrogen or cyanide exchange would provide a more probable explanation for the absence of detectable coupling.[13] The observation that both the hydride and water resonances in aqueous solutions of **3** are broad suggests that the width of the line due to **3** reflects the presence of paramagnetic components in solution rather than exchange broadening. Attempts to slow the exchange reactions presumed to be responsible for the averaging of ^{1}H–^{13}C couplings by taking spectra at low tempertures in mixtures of water and dimethyl sulfoxide resulted in decomposition of **3**.

trans-**[HPtCN(P(C$_2$H$_5$)$_3$)$_2$]**.[14] A single-crystal X-ray study has established that *trans*-[HPtBr(P(C$_2$H$_5$)$_3$)$_2$] is square planar;[15] it seems reasonable to assume a similar geometry for *trans*-[HPtCN(P(C$_2$H$_5$)$_3$)$_2$] (**4**). The nmr spectrum of 50–60% ^{13}CN-enriched **4** in the region of hydride absorption consists of three multiplets. The outer two of these groups of lines, arising from molecules of **4** containing ^{195}Pt, are separated by $J(\text{H,Pt}) = 798$ Hz; the central multiplet is due to molecules of **4** containing platinum isotopes having zero nuclear spin. Straightforward examination of the central multiplet (Figure 2) gives the coupling parameters listed in Table I. The observation that the two phosphorus nuclei are equally coupled to the hydride confirms the *trans* H–Pt–CN geometry for the complex.

The H–^{13}C coupling constant in **4** is of approximately the same size as the corresponding *trans* coupling constants in **1** and **2**. This observation indicates that two-bond ^{1}H–^{13}C coupling constants of this magnitude are not restricted to one particular structural type and suggests that they may prove useful in the identification of *trans* H–M–CN geometries. However, a more interesting feature of the spectrum of **4** is an unexpected large isotope effect on the hydride chemical shift: the chemical shift of the hydride *trans* to ^{13}CN falls ~0.006 ppm downfield from that of the hydride *trans* to ^{12}CN. This chemical shift difference is apparent in the experimental spectrum: the triplet due to proton–phosphorus coupling in **4**-^{12}CN is centered at a slightly higher frequency than the six-line pattern due to proton–phosphorus and proton–carbon coupling in **4**-^{13}CN. This frequency difference, although small, is reproducible and independent both of the direction of sweep and the solvent.

Appreciable chemical shift differences have been observed between *fluorine* atoms bonded directly to ^{12}C and ^{13}C,[16] and to ^{32}S and ^{34}S,[17] in otherwise identical molecules. These isotope effects, and similar effects resulting from substitution of deuterium for hydrogen,[18] have been attributed to the influence of the difference in

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[11] D. N. Lawson, M. J. Mays, and G. Wilkinson, *J. Chem. Soc., A*, 52, (1966); see also H. L. Roberts and W. R. Symes, *ibid.*, 1450 (1968).

[12] K. Krogmann and W. Binder, *J. Organometal. Chem.*, **11**, P27 (1968).

[13] See J. M. Pratt and R. J. P. Williams, *J. Chem. Soc., A*, 1291 (1967), and R. G. S. Banks and J. M. Pratt, *ibid.*, 854 (1968), and references in each for a discussion of evidence pertinent to exchange reactions of 3.

[14] J. Chatt and B. L. Shaw, *ibid.*, 5075 (1962).

[15] P. G. Owston, J. M. Partridge, and J. M. Rowe, *Acta Cryst.*, **13**, 246 (1960).

[16] For examples, see N. Muller and D. T. Carr, *J. Phys. Chem.*, **67**, 112 (1963); G. V. D. Tiers and P. C. Lauterbur, *J. Chem. Phys.*, **36**, 1110 (1962).

[17] R. J. Gillespie and J. W. Quail, *ibid.*, **39**, 2555 (1963); R. A. Stewart, S. Fujiwara, and F. Aubke, *ibid.*, **49**, 965 (1968).

[18] D. D. Traficante and G. E. Maciel, *J. Amer. Chem. Soc.*, **87**, 4917 (1965); G. E. Maciel, P. D. Ellis, and D. C. Hofer, *J. Phys. Chem.*, 71, 2160 (1967); E. B. Whipple, W. E. Stewart, G. S. Reddy, and J. A. Goldstein, *J. Chem. Phys.*, **34**, 2136 (1961), and references in each.

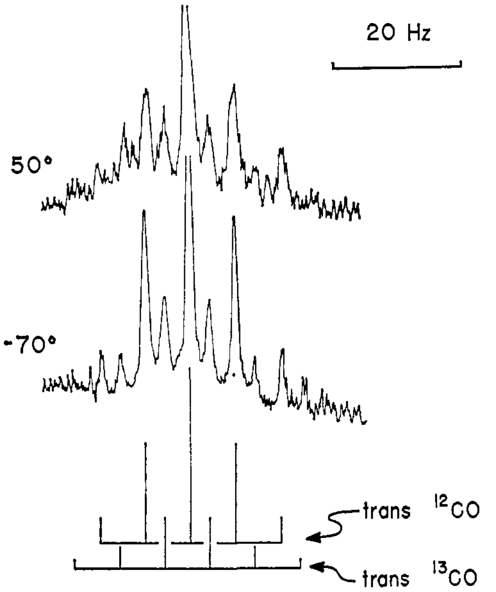


Figure 3. Observed and calculated ^{1}H nmr spectrum of ^{13}CO-enriched $HMn(CO)_5$ in diethyl ether solution at 100 MHz. The calculated line intensities are based on the assumption of approximately 20% isotopic enrichment.

mass of the isotopes involved on the amplitude of the zero-point vibrational motion of the bond to the magnetic nucleus being observed, and to the attendant changes in its average screening.[19] Although the magnitude of the isotope effect observed in **4** is surprisingly large, the motional coupling of M—H and C≡N (or C≡O) stretching vibrations *trans* to one another[20] should be sufficiently strong to make compounds such as **4** particularly susceptible to a chemical shift isotope effect resulting from vibronic interaction.

$HMn(CO)_5$ (5) and *cis*-$HMn(CO)_4P(C_6H_5)_3$ (6). Single-crystal X-ray,[21] ir,[22] electron diffraction,[23] and broad-line nmr[24] studies have established C_{4v} symmetry for $HMn(CO)_5$ with the hydrogen atom occupying a octahedral coordination site. The ambient temperature high-resolution nmr spectrum of unenriched **5** in several solvents consists of a relatively broad central peak, flanked by two ^{13}C satellites separated by 14.0 Hz. Repeated attempts to detect a second ^{1}H–^{13}C coupling comparable to the larger coupling observed with **1**, **2**, and **4** by time averaging were unsuccessful. However, examination of the spectrum of $HMn(CO)_5$ enriched to approximately 20% in ^{13}CO by exchange with 50%-enriched carbon monoxide[22,25] indicated that a second coupling was in fact present (Figure 3): surprisingly, this coupling, identified as a *trans* H–^{13}C coupling on the basis of relative intensities of the lines in the multiplet of the observed spectrum, is *smaller* than the *cis* coupling in this compound. It is noteworthy that substitution of ^{13}CO for ^{12}CO in this molecule produces an isotope effect on the chemical shift of the *trans*-hydride very similar to that observed for **4**: the chemical shift of the hydride *trans* to ^{13}CO in **5** falls ~0.005 ppm downfield from that *trans* to ^{12}CO, while the chemical shift of hydride *cis* to ^{13}CO is apparently unaffected.

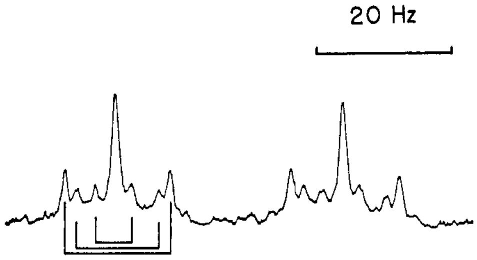
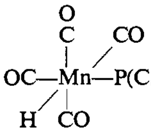


Figure 4. The ^{1}H nmr spectrum of the hydride absorption of ^{13}CO-enriched *cis*-$HMn(CO)_4P(C_6H_5)_3$ in diethyl ether at 100 MHz. The extent of enrichment is approximately 20%.

The same relative magnitudes of the *cis* and *trans* ^{1}H–^{13}C coupling constants were observed for *cis*-$HMn(CO)_4P(C_6H_5)_3$ (**6**).[26] The spectrum of the hydride of ~20% ^{13}CO-enriched **6**, shown in Figure 4, is composed to a first approximation of two multiplets separated by the ^{1}H–^{31}P coupling constant. Each of these multiplets consists of a central peak, arising primarily from molecules of **6** containing only ^{12}CO, flanked by three principal sets of satellites having relative intensities ~2:1:1. The C_s octrahedral structure postulated[2a] for **6** on the basis of ir evidence[26] should give rise to three types of ^{1}H–^{13}C coupling constants: two *cis* couplings, having relative intensity 2:1, between the hydride and the carbon monoxides which are respectively *cis* and *trans* to the triphenylphosphine moiety, and one *trans* coupling, having relative intensity 1, with the remaining carbon monoxide. The nmr spectrum is thus in full accord with the postulated structure.



6

We have assigned the three observed ^{1}H–^{13}C coupling constants in **6** as indicated in Table I using the following arguments. The doublet having the largest separation, 15.7 Hz, corresponds to the satellite pair of relative intensity 2, and can be assigned on the basis of this intensity to the coupling between hydrogen and the two geometrically equivalent carbon monoxides *cis* to both hydrogen and phosphorus. The doublet of relative intensity 1 having the smaller separation, 5.2 Hz, is assigned to coupling between hydrogen and the *trans* carbon monoxide for two reasons: first, the magnitude of this coupling is close to that of the similar *cis* coupling in **5**; and second, the center of this doublet displays the small downfield shift relative to the absorption frequency of unenriched **6** which was attributed to a ^{13}C chemical shift isotope effect in **4** and **5**. By default, the remaining doublet, with separation 12.1 Hz, is assigned to cou-

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[19] T. W. Marshall, *Mol. Phys.*, **4**, 61 (1961); H. S. Gutowsky, *J. Chem. Phys.*, **31**, 1683 (1959); N. F. Ramsey, *Phys. Rev.*, **87**, 1075 (1952).

[20] L. Vaska, *J. Amer. Chem. Soc.*, **88**, 4100 (1966), and references therein.

[21] S. J. LaPlaca, J. A. Ibers, and W. C. Hamilton, *Inorg. Chem.*, **3**, 1491 (1964); *J. Amer. Chem. Soc.*, **86**, 2288 (1964).

[22] P. S. Braterman, R. W. Harrill, and H. D. Kaesz, *ibid.*, **89**, 2851 (1967); W. F. Edgell, J. W. Fisher, G. Asato, and W. M. Risen, Jr., *Inorg. Chem.*, **8**, 1103 (1969).

[23] A. G. Robiette, H. M. Sheldrick, and R. N. F. Simpson, *Chem. Commun.*, 506 (1968).

[24] G. M. Sheldrick, *ibid.*, 751 (1967); T. C. Farrar, S. W. Ryan, A. Davison, and J. W. Fuller, *J. Amer. Chem. Soc.*, **88**, 184 (1966); D. L. VanderHart, H. S. Gutowsky, and T. C. Farrar, *ibid.*, **89**, 5056 (1967).

[25] F. Basolo, A. T. Brault, and A. J. Pöe, *J. Chem. Soc.*, 676 (1964).

[26] W. Hüber, E. Winter, and E. Shubert, *Chem. Ber.*, **95**, 3070 (1962); W. Hieber, G. Faulhaber, and F. Theubert, *Z. Anorg. Allgem. Chem.*, **314**, 125 (1962).

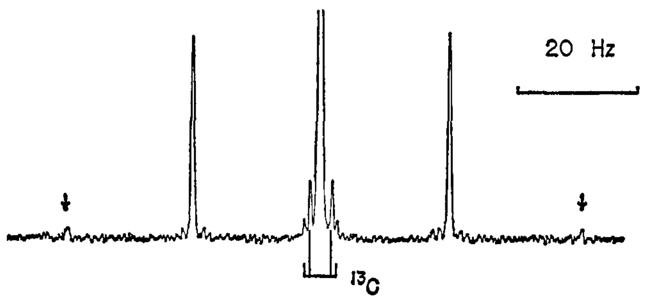

Figure 5. The ^1H nmr spectrum of $[HW_2(CO)_{10}]^-$ in tetrahydrofuran solution at 100 MHz. The positions of the satellites due to coupling with naturally abundant ^{12}C are indicated by the lines under the spectral trace; peaks due to $[H^{183}W_2(CO)_{10}]^-$ are indicated by arrows above the trace.

pling between hydrogen and the carbon monoxide *trans* to triphenylphosphine.

The observation of distinct *cis* and *trans* $^1H-^{13}C$ couplings in **5** and **6** is pertinent to attempts to resolve a current problem concerning the structural rigidity of manganese carbonyl hydrides. This problem is based on two types of observations. First, the structurally distinct radial and axial carbonyl groups of **5** have been shown to exchange with labeled carbon monoxide at equal rates.[22,25] Second, infrared studies of a variety of phosphorus trifluoride derivatives of **5** have indicated that certain of these compounds (*e.g.*, $HMn(CO)_3(PF_3)_2$) exist as equilibrium mixtures of geometrical isomers; however, attempts to separate these isomers using a variety of techniques, including high-efficiency vapor phase chromatography, have been unsuccessful. On the basis of these and related experiments, it has been suggested that the axial and radial carbonyl groups of **5** interchange rapidly in solution, either by one of several types of intramolecular hydride migration in **5** itself, or by dissociation of a proton from **5** followed by pseudorotation of the resulting manganese pentacarbonyl anion.[27,28]

Unambiguous elaboration of an *intra*molecular mechanism for fast interchange of ligands in **5** would constitute an important contribution toward understanding the rearrangements of octahedral complexes. Since the $^1H-^{13}C$ couplings in **5** provide an attractive probe with which to examine any interchange of axial and radial carbonyl groups, we have examined the temperature dependence of the nmr spectrum of enriched **5** (Figure 3). Unfortunately, there is no indication of any averaging of $^1H-^{13}C$ couplings in this compound in diethyl ether solution over the temperature range -70 to $+50°$. The individual spectral lines do broaden slowly on increasing the temperature. However, since qualitatively similar line broadening is observed in cyclohexane solution over a much narrower temperature range (~ -10 to $+30°$), we believe that the line widths in these spectra probably reflect the viscosity dependence of quadrupole-broadened $^1H-^{55}Mn$ spin-spin coupling,[29,30] rather than the onset of a spectroscopically detectable exchange process involving hydride or carbon monoxide ligands on **5**. Thus, the observation of distinguishable *cis* and *trans* $^1H-^{13}C$ coupling constants in **5** and **6** demonstrates that any rearrangement in these compounds, whether intra- or intermolecular, must be slow on the nmr time scale (here $k \lesssim 0.2$ sec^{-1}).

Attempts to obtain coupling constants on unenriched $HMn(CO)_3[P(OC_6H_5)_3]_2$[31] and $HMn(CO)_3[P(C_6H_5)_3]$[31] were unsuccessful due to a combination of solubility and line-width problems.

$Na[HW_2(CO)_{10}]$[7] and $Na[HMo_2(CO)_{10}]$.[7] The $[HW_2(CO)_{10}]^-$ ion (**7**) and the $[HMo_2(CO)_{10}]^-$ ion (**8**) are assumed to be isostructural with the $[HCr_2(CO)_{10}]^-$ ion (**9**).[32] Although the hydrogen atom was not located in the single-crystal X-ray study of this last compound, its Cr–Cr distance of 3.74 Å and apparent D_{4h} symmetry strongly suggested that the hydrogen is situated as a linear symmetrical bridge between two $Cr(CO)_5$ moieties. This structure places eight magnetically equivalent carbons *cis* to the hydride, and two *trans.*[33] Thus, coupling of the hydride ion with naturally abundant ^{13}C in **7** and **8** would be expected to give rise to two sets of satellite doublets having relative intensity 4:1.

The original observation of the ^{13}C satellites in the $[HW_2(CO)_{10}]^-$ ion by Hayter[7] clearly resolved only the *cis* coupling. The spectra used in this work were obtained at higher instrument sensitivity, and establish the presence of satellites due both to the *cis* coupling (3.5 Hz) and to the slightly larger *trans* coupling (4.3 Hz) (Figure 5). Spectra taken of the $[HMo_2(CO)_{10}]^-$ ion under similar conditions showed only one flanking doublet due to $^1H-^{13}C$ coupling ($J(H,^{13}C) = 4.3$ Hz). Comparison of the combined intensity of the components of this doublet with that of the center peak established that the doublet is due to coupling of the hydride with the naturally abundant ^{13}C in eight to ten carbon monoxide molecules. Thus, the 4.3-Hz coupling in **8** must correspond to a *cis* coupling. Unfortunately, the intensity data are not sufficiently accurate to establish if the *trans* coupling in **8** is coincidentally indistinguishable from the *cis* coupling, or if it is so small that it is obscured by the center band.

The signal-to-noise ratio in the spectrum of **7** is sufficiently high that the weak peaks due to $[H^{183}W_2(CO)_{10}]^-$ are easily observable (Figure 5). The experimentally determined peak heights for the hydride resonances of the $[H^{183}W_2(CO)_{10}]^-$, $[H^{183}WW(CO)_{10}]^-$, and $[HW_2(CO)_{10}]^-$ ions are in the ratio 0.47:10:61:10:0.47; the corresponding theoretical ratios based on a structure analogous to that of **9** are 0.42:10.0:60.8:10.0:0.42. Note, however, that although this agreement between theoretical and observed spectra is entirely compatible with a formulation for **7** analogous to that of **9**, it does not

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(27) W. J. Miles, Jr., and R. J. Clark, *Inorg. Chem.*, 7, 1801 (1968).

(28) For reviews of evidence pertinent to intramolecular rearrangements in six-coordinate compounds, see E. L. Muetterties, *J. Amer. Chem. Soc.*, **90**, 5097 (1968); T. L. Brown, *Inorg. Chem.*, **7**, 2673 (1968).

(29) For references, see G. M. Whitesides and H. L. Mitchell, *J. Amer. Chem. Soc.*, **91**, 2245 (1969).

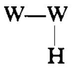
(30) This conclusion receives further support from the observation that the line width of pure unenriched **5** is anomalously large ($\sim$1.5 Hz at peak half-height). Moreover, the width of the ^{13}C resonances of **5** in cyclohexane (peaks with relative intensity $\sim$1:4 at $+0.1$ and -17.7 ppm, respectively, with respect to $^{13}CS_2$) is approximately 75 Hz. The temperature independence of the $^1H-^{13}C$ couplings in enriched **5** demonstrate that these anomalously broad lines are not due to ligand interchange reactions. Hence, extensively relaxed spin-spin coupling to manganese seem the most reasonable explanation for the ^{13}C line widths. The ^{13}C spectrum of **5** was obtained by Dr. F. Weigert and Professor J. D. Roberts at the California Institute of Technology.

(31) R. Ugo and F. Bonati, *J. Organometal. Chem.*, **8**, 189 (1967).

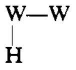
(32) L. B. Handy, P. M. Treichel, L. F. Dahl, and R. G. Hayter, *J. Amer. Chem. Soc.*, **88**, 366 (1966).

(33) This statement carries with it no implication that the hydrogen occupies a single symmetrical potential well between the metal atoms, but only that if the potential is actually a double well, oscillation of the hydride between the two equivalent minima must be rapid on the nmr time scale.

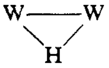
by itself provide very compelling evidence for this structure, since *identical* intensity ratios would be observed for at least four distinct structures: (a) a slowly (on the nmr time scale) equilibrating mixture of unsymmetrical ions represented schematically by **10a** and **10b**, each having the hydride ion specifically bonded to one tungsten atom, *provided* that the tungsten in the naturally abundant $[H^{189}W_2(CO)_{10}]^-$ that is not directly bonded to the hydride is strongly virtually coupled to it;[34] (b) a rapidly equilibrating mixture of unsymmetrical ions **10a** $\rightleftharpoons$ **10b**,[35] (c) a bent hydrogen-bridged species **11**; (d) a linear species **12**, analogous to **9**, with the bridging hydrogen either symmetrically disposed or rapidly oscillating between the tungsten atoms.



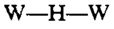
10a



10b



11



12

Discussion

No satisfactory theoretical treatment of long-range ^1H–^{13}C coupling constants capable of dealing with the ^1H–M–^{13}C couplings reported in this paper has been developed. Even for the simpler and considerably more thoroughly studied class of molecules containing the ^1H–C–^{13}C fragment, understanding of the factors influencing the magnitudes of two-bond proton–carbon coupling constants is incomplete: the available data in this latter group of compound indicate clearly only that terms other than the Fermi contact interaction contribute to the coupling.[6,37] Since the magnitude of the two-bond spin–spin couplings in the transition metal hydrides studied here is probably determined by a balancing of contributions even more complicated than that involved in the ^1H–C–^{13}C fragment, speculation concerning details of these couplings should sensibly be deferred until more experimental data are available. Nonetheless, from a practical point of view, two features of the data in Table I deserve brief comment.

First, the *trans* ^1H–^{13}C coupling constants in compounds **1**, **2**, and **4** are anomalously large by comparison with couplings derived from organic molecules; in fact, the *trans* ^1H–Rh^{13}CN coupling in **2** (56.2 Hz) is by a small margin the largest known two-bond ^1H–^{13}C coupling.[38] The magnitude of these coupling constants is particularly striking by comparison with the much smaller ^1H–M–^{13}CO coupling constants. Moreover, the relative magnitudes of these couplings are in an order opposite to that which would be expected on the intuitive grounds that a σ bond connecting a metal atom and cyanide group should contain less "s character" in the carbon bonding orbital than a metal–carbonyl σ bond, since the electronegativity of oxygen is greater than that of nitrogen.[39,40] Although this observation suggests that terms other than the Fermi contact interaction are important in determining the magnitude of ^1H–M–^{13}C couplings, the data of Table I are too sparse to identify the major coupling mechanism.

Second, the similarity in the size of the *cis* and *trans* ^1H–M–^{13}CO coupling constants reported in Table I is interesting, particularly by contrast with the appreciable difference in sizes characteristically associated with the corresponding ^1H–^{31}P and ^{31}P–^{31}P coupling constants.[41] Whatever the differences in the mechanism of coupling in these spin systems, it does not appear to be practical to use the absolute magnitude of ^1H–M–^{13}C couplings constants to assign stereochemistry in complex metal carbonyl hydrides. Thus, examination of ^1H–M–^{13}CO coupling constants appears to have the greatest promise as a stereochemical probe when applied to problems which simply require differentiation between structures differing in the number of distinct types of carbonyl groups.

Experimental Section

General. Nmr spectra were recorded on either a Varian HA-60 or HA-100 spectrometer equipped with a V-6040 variable-temperature probe and controller. Calibration of the temperature control unit was accomplished by measuring peak separations in methanol or ethylene glycol samples. All spectra were taken in frequency-sweep mode, using TMS or prominent solvent peaks as lock signals. Appropriate factors were used to convert frequency separations from the lock signal to chemical shifts in ppm from TMS. For hydride resonances occurring more than 1.0 kHz from the lock signal, the internal 2.5 kHz spectrometer audiomodulation frequency was replaced by a suitable frequency derived from a Krohn-Hite Model 450 oscillator. Time averaging was accomplished using a Varian C-1024 CAT. Ir spectra were taken on a Perkin-Elmer 237 B grating spectrometer.

Ether solvents were distilled under nitrogen from lithium aluminum hydride immediately before use; all solvents for nmr samples were degassed by several freeze–thaw cycles (liquid nitrogen) before use. Metal carbonyls and carbonyl halides were obtained from Alfa Inorganics Inc., or Strem Chemicals. Potassium cyanide and carbon monoxide (50–60% ^{13}C) were obtained from Isomet Corp. and Mallinckrodt Nuclear, respectively.

$HMn(CO)_5$ was prepared following the procedure of Edgell,[42] dried over Linde 4A molecular sieves, and purified by bulb-to-bulb distillation. This hydride was enriched in ^{13}CO by stirring 0.06 g (0.31 mmol) of pure material in ~0.3 ml of ether with ~1.53 mmol (50–60% ^{13}CO) of carbon monoxide for 100 hr at room temperature. *trans*-[HPt(^{13}CN)(P(C$_2$H$_5$)$_3$)$_2$] was prepared by reaction of ^{13}C-enriched potassium cyanide with *trans*-[HPtCl(P(C$_2$H$_5$)$_3$)$_2$] in methanol and recrystallized from light petroleum.[14] Enriched K$_3$-[HIr(CN)$_5$] was prepared from K^{13}CN and chlorobis(1,3-cyclo-

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[34] F. A. L. Anet, *Can. J. Chem.*, **39**, 2262 (1961); J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1962); R. K. Harris, *Can. J. Chem.*, **42**, 2275 (1964).

[35] Previous considerations of this problem[7,36] have calculated the intensity of the outer peaks due to the H^{189}W$_2$ fragment incorrectly: a rapidly equilibrating mixture (**10**) of ions containing this moiety will give rise to a 1:2:1 triplet, with spacing equal to the hydrogen–tungsten coupling constant, regardless of virtual coupling between the two tungsten atoms and the hydride.

[36] A. Davison, W. McFarlane, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3653 (1962).

[37] G. J. Karabatsos and C. E. Orzech, Jr., *J. Amer. Chem. Soc.*, **86**, 3574 (1964). It is significant that the most promising of the presently available theoretical approaches to the calculation of coupling constants has been notably less successful in estimating long-range ^1H–^{13}C coupling constants than long-range ^1H–^1H coupling constants: *cf.* J. A. Pople, J. W. McIver, Jr., and N. S. Ostlund, *J. Chem. Phys.*, **49**, 2960, 2965 (1968).

[38] The larger two-bond ^1H–^{13}C coupling in $H_3C^{13}\text{–}C{\equiv}C\text{–}H$ is 50.8 Hz: J. N. Shoolery, L. F. Johnson, and W. A. Anderson, *J. Mol. Spectrosc.*, **5**, 110 (1960).

[39] H. A. Bent, *Chem. Rev.*, **61**, 275 (1961). Note, however, that the ^{31}P nuclei in strong σ-donating phosphines and phosphites are less strongly coupled to ^{183}W in complexes of the type LW(CO)$_5$ than are the ^{31}P nuclei in weak σ donors; *cf.* S. O. Grim, P. R. McAllister, and R. M. Singer, *Chem. Commun.*, 38 (1969).

[40] For recent theoretical discussions of metal–carbonyl and –cyanide bonding, see K G. Caulton and R. F. Fenske, *Inorg. Chem.*, **7**, 1273 (1968); A. F. Schreiner and T. L. Brown, *J. Amer. Chem. Soc.*, **90**, 3366, 5947 (1968); J. J. Alexander and H. B. Gray, *ibid.*, **90**, 4260 (1968); N. A. Beach and H. B. Gray, *ibid.*, **90**, 5713 (1968).

[41] However, see P. K. Maples and C. S. Kraihanzel, *Chem Commun.*, 922 (1968); W. E. Stanclift and D. G. Hendricker, *Inorg. Chem.*, **7**, 1242 (1968).

[42] W. F. Edgell and W. M. Risen, Jr., *J. Amer. Chem. Soc.*, **88**, 5451 (1966).

hexadiene)iridium(I)[43] by Krogmann's procedure.[8] Hayter's procedure was used in the preparation of the $[HM_2(CO)_{10}]^-$ anions.[7] Aqueous solutions of $M_3[HCo(CN)_5]$ were prepared by reducing solutions of $[Co(CN)_5]^{3-}$ with hydrogen, sodium borohydride, or 1% sodium amalgam.[13]

$K_3[HRh(CN)_5]$. Solid bis(*cis,cis*-1,5-cyclooctadiene)-μ-dichlorodirhodium(I) (0.10 g, 0.4 mmol) was added to a boiling solution of potassium cyanide (0.26 g, 4.0 mmol) in 5 ml of degassed absolute methyl alcohol. The red-purple mixture was gently refluxed for 10 min and then cooled to room temperature. The resulting white crystalline precipitate was separated by filtration, washed with cold methyl alcohol, and dried under vacuum (0.126 g, 90% yield).

Anal. Calcd for $K_3[HRh(CN)_5]H_2O$: C, 16.26; H, 0.86; N, 18.97. Found: C, 16.12; H, 0.66; N, 18.71.

This material gave the same nmr spectrum as that prepared using the procedure of Krogmann.[12]

***cis*-$HMn(CO)_4P(C_6H_5)_3$** was prepared by a modification of a literature procedure.[44] Manganese pentacarbonyl hydride (~0.20 g, 1 mmol) was distilled under vacuum into a liquid nitrogen cooled Schlenck tube containing a solution of triphenylphosphine (0.26 g, 1 mmol) in dry, degassed diethyl ether (3 ml). The mixture was warmed to room temperature and stirred until carbon monoxide evolution ceased (~5 hr). From time to time the evolved gas was pumped out of the tube. Evaporation of the resulting yellow solution under reduced pressure and recrystallization of the product from boiling toluene afforded 0.3 g of pale yellow crystals, mp 137° (under nitrogen) (lit.[45] mp 137.5°); ir (cyclohexane) 2060 (vs), 1985 (vs), 1970 (vs), 1960 (vs), 1940 (vw) cm^{-1}.

Anal. Calcd for $C_{22}H_{16}O_4MnP$: C, 61.21; H, 3.74. Found: C, 61.80; H, 4.01.

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(45) W. Hüber, E. Winter, and E. Schubert, *Chem. Ber.*, **95**, 3070 (1962).

Linear and Cyclic Permethylpolyarsines

Fritz Knoll,[1] Heinrich C. Marsmann,[2] and John R. Van Wazer[3]

Contribution from the Central Research Department, Monsanto Company,
St. Louis, Missouri 63166. Received September 20, 1968

Abstract: At room temperature, molecules in the family of fully methyl-substituted polyarsines undergo exchange reactions through the making and breaking of As–As bonds while the C–As bonds remain perfectly stable. As a result, mixtures of tetramethyldiarsine with arsenomethane react to form equilibrium mixtures of molecules in which the diarsine and cyclic pentameric arsenomethane predominate because of the relatively large value of the pertinent ring–chain equilibrium constants. This equilibrium has been studied by proton nuclear magnetic resonance (nmr) of the methyl groups bonded to the arsenic. In addition, nmr and mass spectrometric studies have been carried out on the neat, yellow, liquid form of pure arsenomethane. The data have been interpreted to mean that liquid arsenomethane consists primarily of a cyclic pentamer exhibiting a single detectable conformation.

In spite of the fact that cacodyl (tetramethyldiarsine) was the first organometallic compound[4] to be synthesized and that the earliest work in this area was published over 200 years ago,[5] the literature on the peralkyl- or perarylarsines is small. Although this may be due in some part to the toxicity of these compounds, the major reason for the paucity of literature has probably been the lack of appropriate experimental methods. Since nuclear magnetic resonance (nmr) appeared to be particularly suited for a study of the permethylpolyarsines, the work reported here was undertaken to shed more light on this ancient area of chemistry.

Experimental Section

Reagents. Arsenomethane, $(CH_3As)_n$, was prepared by treating sodium methylarsenate with hypophosphorous acid.[6] The oily product was washed with dilute NaOH and water and then distilled under high vacuum. It was found to persist as a clear yellow liquid[7] for several months at room temperature if air and light are excluded.

Tetramethyldiarsine, $(CH_3)_2AsAs(CH_3)_2$, was made in a similar manner by reducing cacodylic acid with an excess of hypophosphorous acid.[8] The reaction is exothermic; hence the solution of cacodylic acid in water had to be added slowly. The reaction was carried out under argon. The lower phase was dried with $CaSO_4$ and fractionated. The liquid going over at 158° was redistilled to give a product showing a single sharp nmr peak at −1.06 ppm (internally referenced to tetramethylsilane).

Most of the reactions studied herein were carried out in sealed-glass nmr tubes so that there was no gain or loss of material in the system.

Physical Measurements. The nmr measurements were made with a Varian A-60 spectrometer equipped with a V-604 variable-temperature controller. The reference standard was tetramethylsilane added to the samples, with downfield shifts being given a negative sign. The nmr peaks were determined by cutting and weighing, as well as with a Du Pont curve resolver. Viscosities were measured in a dry-nitrogen-filled drybox on a Haake Rotovisco instrument, using the plate-cone attachment and calibrating with Bureau of Standards oils. The mass spectra were obtained on a CEC 21-104 medium-resolution rapid-scan spectrometer, in some cases with the liquid sample being contained in a capillary tube inserted into the vacuum chamber close to the point of ionization. In other experiments, the sample was completely volatilized into a 3-l. glass-sampling system. Using a moderate value for the ac-

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(1) On leave of absence from the University of Bonn, 1966–1967.

(2) On leave of absence from Goettingen University, 1967–1969.

(3) To whom reprint requests should be sent at his new address: Chemistry Department, Vanderbilt University, Nashville, Tenn. 37203.

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