2.8–3.1 Å)[6,14] cannot be discerned on the basis of the X-ray data. That the description of this disorder is inadequate presumably leads to the somewhat high *R* index.

It is possible to resolve the problem of oxidation states by other means. The Raman spectra of $Ni(dpg)_2I$ and $Pd(dpg)_2I$ (observed spinning with both Ar^+ and Kr^+ excitation) exhibit intense emissions at 160(vs) and 107(m) cm^{-1}. The bands are characteristic of ν_3 and ν_1 for $\mathbf{I_3}^-$ compounds,[15,16] and are not observed in the unoxidized complexes. There is no indication of $\mathbf{I_2}$ ($\nu_{I-I} \approx$ 200–212 cm^{-1}).[5,17] Furthermore, ^{129}I Mössbauer spectra of $Ni(dpg)_2\ ^{129}I$, to be discussed in detail elsewhere,[18] exhibit isomer shift and quadrupole splitting parameters which are in agreement with those of known I_3^- compounds,[19] and are incompatible with I^- or I_2.[19,20]

These results demonstrate that *all* members of the Ni, Pd, Pt group can form mixed valence compounds with the partial formal oxidation state of +2.3, that this can occur without metal–metal contacts as close as in the Krogmann salt, and that this can, in some cases, occur with ligands which are readily functionalized. Though the importance of the iodine chains for electron transport is not clear at present, the possibility that polyiodide chains themselves may represent a rational approach to the construction of electrically, magnetically, and optically one-dimensional materials merits further investigation.

Acknowledgments. We thank the Northwestern Materials Research Center (NSF-GH-33575) for support of this work and Drs. B. M. Hoffman, R. B. Petersen (Northwestern University), S. L. Ruby, B. Zabransky (Argonne National Laboratory), R. H. Soderberg (Dartmouth University), and J. S. Miller (Xerox) for helpful discussions.

Supplementary Material Available. A table of positional and thermal parameters will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number JACS-75-3545.

References and Notes

(1) (a) K. Krogmann, *Angew. Chem., Int. Ed. Engl.*, **8,** 35 (1969); (b) E. B. Yagubskii and K. L. Khidekel, *Russ. Chem. Rev.*, **41,** 1011 (1972); (c) T. W. Thomas and A. E. Underhill, *Chem. Soc. Rev.*, **1,** 99 (1972); (d) H. R. Zeller, *Adv. Solid State Phys.*, **13,** 31 (1973); (e) L. V. Interrante, Ed., "Extended Interactions between Metal Ions in Transition Metal Complexes", Vol. 5, ACS Symposium Series, 1974; (f) J. S. Miller and A. J. Epstein, *Prog. Inorg. Chem.*, in press.

(2) J. M. Williams, J. L. Petersen, H. M. Gerdes, and S. W. Petersen, *Phys. Rev. Lett.*, **33,** 107 (1974), and references therein.

(3) (a) L. E. Edelman, *J. Am. Chem. Soc.*, **72,** 5765 (1950); (b) M. Simek, *Collect. Czech. Chem. Commun.*, **27,** 337 (1962).

(4) A. E. Underhill, D. M. Watkins, and R. Pethig, *Inorg. Nucl. Chem. Lett.*, 9, 1269 (1973).

(5) (a) R. Foster, "Organic Charge-Transfer Complexes", Academic Press, New York, N.Y., 1969; (b) R. S. Mulliken and W. B. Person, "Molecular Complexes", Wiley-Interscience, New York, N.Y., 1969.

(6) (a) A. I. Popov in "Halogen Chemistry", Vol. 1, V. Gutmann, Ed., Academic Press, New York, N.Y., 1967, p 225; (b) J. M. Reddy, K. Knox, and M. B. Robin, *J. Chem. Phys.*, **40,** 1082 (1964).

(7) (a) A. S. Foust and R. H. Soderberg, *J. Am. Chem. Soc.*, **89,** 5507 (1967); (b) H. J. Keller and K. Seibold, *ibid.*, **93,** 1309 (1971).

(8) L. F. Mehne and B. B. Wayland, *Inorg. Chem.*, **14,** 881 (1975).

(9) These data are in agreement with those of Foust and Soderberg;[7a] we also find $Pd(dpg)_2I$ to be isostructural. Attempts to prepare the platinum analog have yielded $Pt(dpg)_2I_2$.

(10) C. V. Banks and D. W. Barnum, *J. Am. Chem. Soc.*, **80,** 4767 (1958).

(11) (a) D. E. Williams, G. Wohlauer, and R. E. Rundle, *J. Am. Chem. Soc.*, **81,** 755 (1959); (b) dmg = dimethylglyoximate.

(12) "Handbook of Chemistry and Physics", 54th ed, Chemical Rubber Publishing Co., Clevland, Ohio, 1973–1974, p F-127.

(13) (a) F. H. Herbstein and M. Kapon, *Nature (London), Phys. Sci.*, **239,** 153 (1972), and references therein; (b) F. van Bolhuis, P. B. Koster, and T. Migchelsen, *Acta, Crystallogr.*, **23,** 90 (1967).

(14) J. Runsink, S. Swen-Walstra, and T. Migchelsen, *Acta. Crystallogr., Sect. B*, **28,** 1331 (1972).

(15) (a) A. G. Maki and R. Foneris, *Spectrochim. Acta, Part A*, **23,** 867 (1967); (b) G. C. Haywood and P. J. Hendra, *ibid.*, **23,** 2309 (1967); (c) S. G. W. Ginn and J. L. Wood, *Chem. Commun.*, 262 (1965).

(16) (a) F. Inagaki, I. Harada, T. Shimanouchi, and M. Tasumi, *Bull. Chem. Soc. Jpn.*, **45,** 3384 (1972); (b) M. Tasumi, *Chem. Lett.*, 75 (1972).

(17) (a) W. Kiefer and H. J. Bernstein, *J. Raman Spectrosc.*, **1,** 417 (1973); (b) H. Ratajczak and W. J. Orville-Thomas, *J. Mol. Struct.*, **14,** 155 (1972); (c) Reference 5, Chapter 4; (d) both I_2 and I_3^- can be readily detected in Raman spectra of $(phenacetin)_2H^+I_3^- \cdot I_2$[13a] (T. J. Marks, to be submitted for publication).

(18) (a) S. L. Ruby, B. Zabransky, and T. J. Marks, unpublished results at Argonne National Laboratory; (b) I. S. (mm/sec) ($e^2q^{129}Q$, MHz) ≈ 1.20 (1725) and 0.45–0.0(1060–900) vs. ZnTe; data refinement is still in progress.

(19) (a) M. J. Potasek, P. G. Debrunner, W. H. Morrison, Jr., and D. N. Hendrickson, *J. Chem. Phys.*, **60,** 2203 (1974); (b) B. S. Ehrlich and M. Kaplan, *ibid.*, **51,** 603 (1969).

(20) (a) G. M. Bancroft and R. H. Platt, *Adv. Inorg. Chem. Radiochem.*, **15,** 187 (1972); (b) S. Ichiba, H. Sakai, H. Negita, and Y. Maeda, *J. Chem. Phys.*, **54,** 1627 (1971); (c) S. Bukshpan, C. Goldstein, F. Sonnino, L. May, and M. Pasternak, *ibid.*, **62,** 2606 (1975); (d) S. Bukshpan, M. Pasternak, and T. Sonnino, *ibid.*, **62,** 2916 (1975).

(21) N.A.T.O. Postdoctoral Fellow, on leave from Laboratoire de Chimie de Coordination, Université P. Sabatier, Toulouse, France.

(22) Fellow of the Alfred P. Sloan Foundation.

Alain Gleizes,[21] Tobin J. Marks,*[22] James A. Ibers*
Department of Chemistry and the Materials Research Center
Northwestern University
Evanston, Illinois 60201

Received March 7, 1975

Reaction of a Diphenylacetylene Complex of Cobalt with Isocyanide. A Novel Metalloring Formation

Sir:

Recently, metallocycles are drawing much attention for their important role both in catalytic and stoichiometric reactions.[1]

In this communication, we wish to report the synthesis of a series of cobalt metallocycles, which closely relates to the formation of diiminocyclobutenes and triiminocyclopentenes from isocyanide complexes of Ni and Co.[2]

One millimole of π-cyclopentadienyl-π-diphenylacetylenetriphenylphosphinecobalt[3] (**1**) reacted smoothly at 25° with 2 mmol of phenylisocyanide to give an air-stable orange crystalline compound with empirical formula $C_5H_5Co(PhC_2Ph)(PhNC)_2$ (**2a**). Similar compounds were obtained with 4-methylphenyl-, 2,6-dimethylphenyl-, and *tert*-butylisocyanide. The ir spectra of all of these compounds exhibit strong absorptions near 1700 cm^{-1} indicating the presence of exo-C=N double bonds in a strained ring.[4] From ir and NMR spectra, and the formalism of the inert gas rule, a structure has been suggested. A diiminocobaltacyclopentene ring with the C=C double bond coordinated to the central cobalt atom is proposed. The suggested structure was confirmed by X-ray crystallography.

Compound **2a** crystallized in space group *Cc* with unit cell dimensions $a = 19.756$ Å, $b = 10.904$ Å, $c = 12.986$ Å, and $\beta = 114.43°$; there are four molecules per unit cell. Intensity data were collected using monochromatic Mo $K\alpha$ radiation on a Rigaku four-circle automatic diffractometer operating in the ω–2θ scan mode up to $2\theta \leq 60°$. Using 2741 independent reflections ($>3\sigma$), the structure was solved by the Patterson and Fourier methods and refined by block-matrix least-squares calculations to a discrepancy index of $R = 0.058$. The locations of all 25 hydrogen atoms were determined. As shown in Figure 1, the cobaltacyclopentene ring is highly bent to enable coordination of the double bond. The relevent bond lengths and angles are: Co–

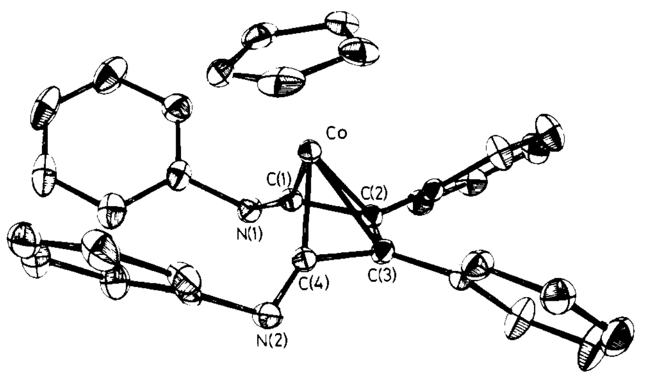
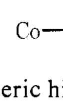


Figure 1. The molecular geometry of $C_5H_5Co[(PhC_2Ph)(PhNC)_2]$ (**2a**).

C(1), 1.853 (8); Co-C(2), 2.020 (8); Co-C(3), 2.019 (7); Co-C(4), 1.837 (6); C(1)-C(2), 1.441 (10); C(2)-C(3) 1.419 (10); C(3)-C(4) 1.437 (9); C(1)-N(1), 1.250 (11); C(4)-N(2), 1.254 (7) Å; Co-C(1)-C(2), 74.50 (41); Co-C(4)-C(3), 75.04(42)°.

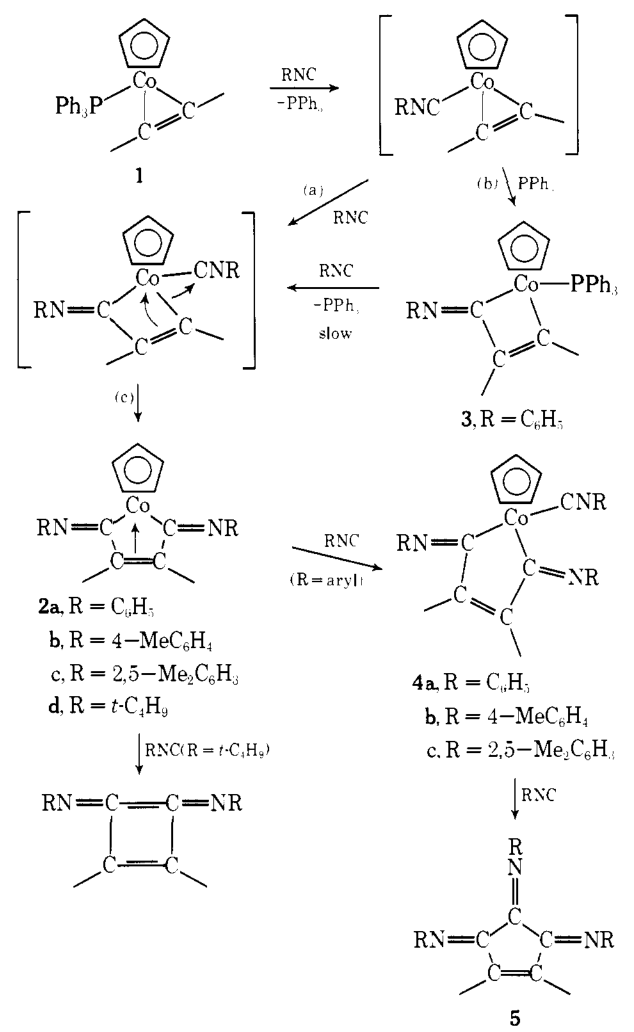
When the molar ratio of phenylisocyanide to π-cyclopentadienyl-π-diphenylacetylenetriphenylphosphinecobalt (**1**) is less than two, the products include **2a** plus an air-stable red-brown crystalline compound with empirical formula $C_5H_5Co(PPh_3)(PhC_2Ph)(PhNC)$ (**3**). Addition of excess triphenylphosphine to the initial reaction mixture gives a higher yield of **3**. Since the ir spectrum of **3** did not show the characteristic absorptions of coordinated diphenylacetylene (~1818 cm^{-1}) and coordinated isocyanide (~2100 cm^{-1}), the structure, π-cyclopentadienyltriphenylphosphine(2-phenylimino-3,4-diphenylcobaltacyclobutene) was assigned to **3**. Compound **3** reacted with phenylisocyanide very slowly at room temperature suggesting that the formation of **3** is not a direct pathway to **2a**.

Compound **2c** reacted with an excess of 2,6-dimethylphenylisocyanide at room temperature to give an air stable orange crystalline compound with empirical formula $C_5H_5Co(PhC_2Ph)(2,6\text{-}Me_2C_6H_3NC)_3$ (**4c**). The ir spectrum of **4c** does not show C=N stretching absorptions near 1700 cm^{-1}, but did show these absorptions at 1605 and 1582 cm^{-1}. These facts indicate a release of the strain in the cobaltacyclopentene ring which existed in **2c**. An absorption at 2125 cm^{-1} showed the presence of coordinated isocyanide. Therefore, **4c** was identified as π-cyclopentadienyl-2,6-dimethylphenylisocyanide [2,5-bis(2,6-dimethylphenylimino)3,4-diphenylcobaltacyclopentene]. Compound **4c** reacts further with 2,6-dimethylphenylisocyanide or carbon monoxide at 130° to give tris(2,6-dimethylphenylimino)diphenylcyclopentene (**5**). The reactions to form analogous compounds (**4a** and **4b**) from **2a** and **2b** are markedly slower than the formation of **4c**. This difference may be explained by weaker coordination of the double bond to the cobalt in **2c**, as compared to **2a** and **2b**. Differences in the strength of the


$$Co-\overset{C}{\underset{C}{\|}}$$

bond may be due to the steric hindrance of the ortho-methyl groups of the 2,6-dimethylphenylimino moieties. The formation of the *tert*-butylisocyanide analog of **4** could not be detected. The electronic effect of the *tert*-butyl groups may be responsible for this. In this regard it is of interest that **2b** reacted with carbon monoxide under pressure to give π-cyclopentadienylcarbonyl[2,5-bis(4-methylphenylimino)-3,4-diphenylcobaltacyclopentene] at 80° and 2,5-bis(4-methylphenylmino)-3,4-diphenylcyclopentenone at 140°, whereas **2d** reacted with carbon monoxide or *tert*-butylisocyanide to give only bis(*tert*-butylimino)diphenylcyclobutene (isolated as diphenylcyclobutenedione).

Scheme I



In an attempt to prepare **5** catalytically, a benzene solution of diphenylacetylene and 2,5-dimethylphenylisocyanide was heated at 140° in the presence of **1**. The yield of **5** was only slightly better than that expected from stoichiometry (103% based on **1**).

Scheme I summarizes all of these results together with some speculations on the mechanism. The first step may involve replacement of triphenylphosphine with isocyanide, followed by competitive attack of isocyanide and triphenylphosphine (steps a and b). The main route to **2** is attack by isocyanide (step a) because firstly **3** was obtained in only a low yield in the reaction of **1** with isocyanide and, secondly, the reaction **3** → **2** was much slower than **1** → **2**. The driving force of the next step (reaction c) may be the intramolecular coordination of the C=C double bond to the cobalt.

References and Notes

(1) (a) J. P. Collman, J. W. Kang, W. F. Little, and M. F. Sullivan, *Inorg. Chem.*, **7**, 1298 (1968); (b) R. H. Grubbs and T. K. Brunk, *J. Am. Chem. Soc.*, **94**, 2538 (1972); (c) A. R. Fraser, P. H. Bird, S. A. Bezman, J. R. Shapley, R. White, and J. A. Osborn, *ibid.*, **95**, 597 (1973); (d) J. X. McDermott and G. M. Whitesides, *ibid.*, **96**, 947 (1974); (e) K. P. C. Vollhardt and R. G. Bergman, *ibid.*, **96**, 4996 (1974); (f) Y. Wakatsuki, K. Aoki, and H. Yamazaki, *ibid.*, **96**, 5284 (1974); (g) Y. Wakatsuki and H. Yamazaki, *Tetrahedron Lett.*, 3383 (1973); (h) A. J. Chalk, *J. Am. Chem. Soc.*, **94**, 5928 (1972); (i) W. Hübel and E. H. Braye, U.S. Patent 3,280,017 (1966); *Chem. Absr.*, **66**, 2462 (1967); (j) E. Müller, C. Beissner, H. Jakle, E. Langer, H. Muhm, G. Odenigbo, M. Sauerbier, A. Segnitz, D. Streichfuss, and R. Thomgs, *Justus Liebigs Ann. Chem.*, **754**, 64 (1971); (k) R. Burt, M. Cooke, and M. Green, *J. Chem. Soc., A*, 2981 (1970); (l) Y. Wakatsuki and H. Yamazaki, *J. Chem. Soc., Chem. Commun.*, 280 (1973); (m) Y. Wakatsuki, T. Kura-

mitsu, and H. Yamazaki, *Tetrahedron Lett.*, 4549 (1974), and references therein.
(2) (a) Y. Suzuki and T. Takizawa, *J. Chem. Soc., Chem. Commun.*, 837 (1972); (b) Y. Suzuki, Ph.D. Thesis, Tokyo University, 1973.
(3) H. Yamazaki and N. Hagihara, *J. Organomet. Chem.*, **21**, 431 (1970).
(4) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules", Wiley, New York, N.Y., 1960, p 148.

Hiroshi Yamazaki,* Katsuyuki Aoki
Yasuhiro Yamamoto, Yasuo Wakatsuki
The Institute of Physical and Chemical Research
Wako-shi, Saitama 351, Japan
Received February 7, 1975

Spin Echo Double Resonance Detection of Deuterium Quadrupole Resonance Transitions in $DMn(CO)_5$[1]

Sir:

Hydride compounds of the transition metals form an important class of substances.[2] Aside from the intrinsic interest which attaches to an understanding of the nature of the metal–hydrogen bond, the fact that many transition metal hydrides are important in catalysis provides an additional incentive for their study. The number of physical studies which shed light on metal–hydrogen bonding is rather limited. Although bond distance data have become more abundant in recent years,[2-4] information on the electronic structural characteristics of the bond is not plentiful. We report here a direct determination of the quadrupole coupling constant at deuterium in solid $DMn(CO)_5$ by use of the nuclear spin echo double resonance (SEDOR) technique. The experiment provides not only the quadrupole coupling constant at deuterium but in addition gives a direct measure of the Mn–D bond distance with an accuracy comparable to that obtainable from a diffraction experiment.

The pure nuclear quadrupole resonance (NQR) transitions at 77°K for ^{55}Mn ($I = 5/2$) in $DMn(CO)_5$ occur at 13.683 MHz ($\pm 3/2 \rightarrow \pm 5/2$) and 6.890 MHz ($\pm 1/2 \rightarrow \pm 3/2$).[5] From these results we calculate a quadrupole coupling constant of 45.66 MHz, and asymmetry parameter η of 0.07. Employing a pulse spectrometer at zero magnetic field, nuclear spin echo signals resulting from these transitions are readily observable following a 90–180° pulse sequence. The deuterium pure quadrupole transitions are excited by application of a 180° pulse via a B channel, low frequency transmitter, using a second orthogonal coil. The double resonance experiment is carried out by monitoring the ^{55}Mn spin echo amplitude, while sweeping the B channel in frequency. When the B channel transmitter passes through the low frequency D quadrupole resonances, the altered dipolar coupling is observed as a change in ^{55}Mn spin echo amplitude. Figure 1 shows the double resonance spectra obtained from the change in spin echo amplitude for both (a) upper and (b) lower Mn transitions.

The centers of the doublet occur at 51.05 kHz in both transitions. The splitting observed is ascribable entirely to dipolar coupling, so there is a single deuterium transition; i.e., the asymmetry parameter η is approximately zero. The frequency of the observed transition corresponds to a quadrupole coupling constant of 68.07 kHz. This is by far the lowest deuterium quadrupole coupling constant ever observed in a direct, zero magnetic field experiment.[6]

The crystal structure of $HMn(CO)_5$ has been determined by both X-ray and neutron diffraction techniques.[3,4] The packing of molecules in the structure is such that the dipolar interaction between the Mn and D pair within a given molecule is much greater than that of either nucleus with any other nucleus on an adjacent molecule. It is thus permissible to treat the Mn–D spin systems as isolated pairs.

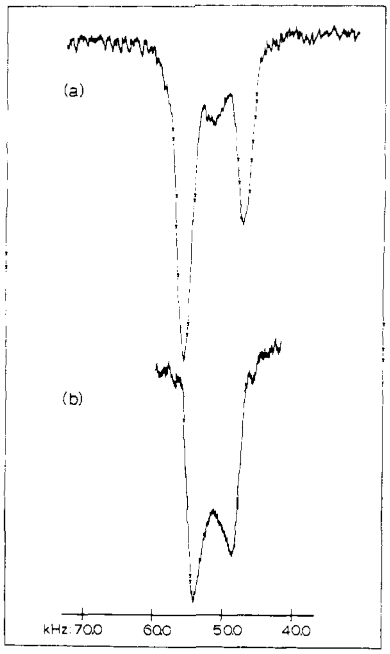


Figure 1. SEDOR spectrum of ^{2}D in $DMn(CO)_5$: (a) $\pm 3/2 \rightarrow \pm 5/2$ ^{55}Mn transition; (b) $\pm 1/2 \rightarrow \pm 3/2$ ^{55}Mn transition.

Application of the 90–180° pulse sequence at a radiofrequency corresponding to the higher ^{55}Mn quadrupole transition causes a mixing of the 5/2 and 3/2 spin states of the same sign. Since spin-lattice relaxation is slow ($T_1 \sim 0.3$ sec) on the time scale in which the spin echo is observed, the dipolar coupling between D and ^{55}Mn following the 90° pulse (the 180° pulse does not change the magnitudes of mixing coefficients, only their signs) corresponds to the average value of the ^{55}Mn–D couplings appropriate to Mn in the 5/2 and 3/2 spin states, i.e.

$$E_{\mathrm{dd}}{}^{\mathrm{mk}} = \langle \psi_{\mathrm{Mn}} \psi_{\mathrm{D}} | \mathcal{H}_{\mathrm{dd}} | \psi_{\mathrm{Mn}} \psi_{\mathrm{D}} \rangle$$

where

$$\begin{aligned} \psi_{\mathrm{Mn}} &= \frac{1}{\sqrt{2}} (\phi_{\pm m} + i\phi_{\pm(m-1)}),\ m = 5/2.\ 3/2 \\ \psi_{\mathrm{D}} &= \phi_k,\ k = \pm 1,\ 0 \\ \mathcal{H}_{\mathrm{dd}} &= \frac{-\gamma_{\mathrm{Mn}} \gamma_{\mathrm{D}} \hbar^2}{r^3} (3 \cos^2 \theta - 1) I_{z,\mathrm{Mn}} I_{z,\mathrm{D}} \end{aligned} \tag{1}$$

The label dd refers to the dipolar interaction, and *m* and *k* refer to the spin states of the Mn and D nuclei, respectively. The angle θ is that between the principal field gradient axes of Mn and D, and $\mathcal{H}_{\mathrm{dd}}$ is the portion of the complete dipolar coupling Hamiltonian appropriate for heteronuclear coupling.[10]

Application of the 90–180° pulse sequence at the frequency of the lower transition similarly mixes the 1/2 and 3/2 spin states of like sign. The dipolar splitting in the deuterium spectrum using the lower frequency Mn transition is calculated to be one-half that obtained using the higher frequency ^{55}Mn transition, in agreement with the results shown in Figure 1.

The only prior determinations of quadrupole coupling constants for deuterium bound to transition metals have been made by Wei and Fung,[11] who observed the broadline NMR spectrum of D in high field for $(C_5H_5)_2MoD_2$ and $(C_5H_5)_2WD_2$. From the line shape it is possible to deduce the quadrupole coupling contant, but the experiment is not very precise, especially if η is much different from 0. The