Notes

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Organometallic Nitrosyl Chemistry. 9.[1] $(\eta^5\text{-}C_5H_5)W(NO)(\eta^3\text{-}C_3H_5)I$, a Chiral Organometallic Complex Containing a Very Asymmetric Allyl Ligand

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In the explanation of the remarkable stereoselectivity observed during reactions of $CpMo(CO)(NO)(\eta^3\text{-allyl})^+$ [Cp = $\eta^5\text{-}C_5H_5$] cations with nucleophiles, it has been suggested that electronic asymmetry of the metal atom in the cation probably distorts the allyl ligand so as to localize the π-electron density between the carbon atoms trans to NO.[2] We now wish to report that just such a distortion occurs to a marked degree in the related chiral complex $CpW(NO)(\eta^3\text{-}C_3H_5)I$, a feature which permits the straightforward assignment of its ^1H and ^{13}C NMR spectra.

Experimental Section

All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions, and all reactants were of reagent grade purity.

Preparation of $CpW(NO)(\eta^3\text{-}C_3H_5)I$. To a stirred solution of $[CpW(NO)I_2]_2$[3] (1.07 g, 1.0 mmol) in tetrahydrofuran (30 mL) at room temperature was added neat $Sn(C_3H_5)_4$ (0.25 mL, 1.0 mmol). The original green solution gradually acquired a red coloration while being stirred for 12 h. The final reaction mixture was taken to dryness in vacuo, the residue was dissolved in CH_2Cl_2 (20 mL), and the resulting solution was filtered through a short (3 × 5 cm) Florisil column. An equal volume of hexanes was added to the filtrate, and the mixture was slowly concentrated under reduced pressure to induce the crystallization of orange-brown $CpW(NO)(\eta^3\text{-}C_3H_5)I$ (0.62 g, 70% yield).

Anal. Calcd for $C_8H_{10}WNOI$: C, 21.50; H, 2.26; N, 3.13. Found:[4] C, 21.46; H, 2.21; N, 3.11. IR[5] (CH_2Cl_2): ν(NO) 1636 cm^{-1}. Melting point[6] 165 °C dec.

X-ray Diffraction Study of $CpW(NO)(\eta^3\text{-}C_3H_5)I$. Crystals suitable for X-ray analysis were grown by slow evaporation of a CH_2Cl_2–hexanes solution of the complex. A well-formed crystal of dimensions ca. 0.1 × 0.3 × 0.3 mm was mounted, and a series of precession photographs provided a preliminary unit cell, the Laue symmetry $2/m$, and the space group $P2_1/n$. The crystal was transferred to an Enraf-Nonius CAD4 diffractometer where automatic location and centering of 25 reflections ($20° < \theta < 25°$, graphite-monochromated Mo Kα radiation) were carried out. A least-squares analysis of the setting angles of these reflections confirmed the initial choice of unit cell and provided the orientation matrix for data collection. Peak profile analysis suggested an ω–2θ scan with $\Delta\omega = (1 + 0.35 \tan \theta)°$, and collection of intensities was performed in this mode to $2\theta = 55°$. The scan rate, based on a fast prescan at 10.06°/min, was computed to give ca. 1.5×10^3 counts, if possible, in a maximum time of 75 s. The minimum scan rate thus obtained was 1.26°/min. The counter aperture was 4 mm high and $(1.75 + \tan \theta)$ mm wide, the crystal to counter distance being 173 mm. The intensities of three check reflections measured periodically showed no systematic variation during the 30 h X-ray exposure. A total of 2359 observations included 1888 with $I/\sigma(I) > 3$, with $\sigma^2(I) = S + B + (0.04S)^2$ where S = scan count and B = the time-averaged background taken at a 25% extension of either end of the scan.

Repeated centering of the 25 setting reflections was followed by a least-squares analysis of the 2θ values with α and γ constrained at 90°; the resulting cell parameters were a = 11.1137 (7) Å, b = 12.4168 (6) Å, c = 7.5056 (7) Å, and β = 95.078 (3)°. There are four formula units in the unit cell, and D_c = 2.6843 (3) g cm^{-3}. The crystal was found to be bounded by the (010), (110), $(\bar{1}10)$, (101), and $(10\bar{1})$ planes and their inverses, the crystal being mounted approximately parallel to [001]. Application of Lorentz and polarization corrections was followed by an absorption correction (μ(Mo Kα) = 135.6 cm^{-1}) using a Gaussian integration method and the program BICABS,[7] which gave transmission factors for $|F|^2$ ranging between 0.1612 and 0.2449. Correct application of the absorption correction was confirmed by a series of ψ scans for selected reflections.

The structure was solved and refined in the following manner. The positions of the tungsten and iodine atoms were determined from a Patterson synthesis; refinement and a subsequent Fourier synthesis revealed the remaining nonhydrogen atoms. Full anisotropic refinement minimizing $\sum w(|F_o| - |F_c|)^2$ with weights $w = 1/\sigma^2(F)$ gave R = 0.025 and R_w = 0.039 for the observed reflections. A difference Fourier synthesis contained peaks at the expected positions for the allyl hydrogen atoms and severals peaks in the region of the W and I atoms. Although the temperature factors for the cyclopentadienyl ligand suggested disorder of this ring, difference syntheses (even with isotropic carbons in the ring) did not provide an acceptable alternative configuration, and the one-ring anisotropic approximation was retained. Idealized positions for the $(\eta^5\text{-}C_5H_5)$ H atoms were calculated (C–H = 0.95 Å), and all hydrogens were included in the model. The final full-matrix, least-squares refinements were carried out with anisotropic W, I, N, O, and C atoms, positionally refined allyl H atoms, fixed $(\eta^5\text{-}C_5H_5)$ H atoms, and an isotropic extinction parameter g[8] and anomalous dispersion corrections for W and I.[9] The refinement converged to R = 0.021 and R_w = 0.029 for the observed reflections and R = 0.036 and R_w = 0.031 for all reflections. The error in an observation of unit weight was 0.98 and the value of g was 7.88×10^3. The average shift/error on the last cycle was 0.18 with an outstandingly bad value of 6.4 for the y parameter of the ill-defined H(11). Scattering factors were taken from ref 10 and 11 (H atoms).

A final difference Fourier synthesis contained peaks up to 0.8 e/Å^3, mainly in the region of the heavy atoms, to which no chemical significance could be attached. Although other peaks in the region of the allyl ligand, particularly a peak of 0.5 e/Å^3 at 0.68, 0.19, 0.39 approximately midway between C(1) and C(3), suggest the possibility of a small amount of disorder of this ligand, the peaks are not sufficiently above the general background to be regarded as significant. Final atomic positional and thermal parameters are presented in Tables I and II. Values of $|F_o|$ vs. $|F_c|$ for the 2359 reflections are given in Table III.[12]

Results and Discussion

The new organometallic complex $CpW(NO)(\eta^3\text{-}C_3H_5)I$ can be conveniently prepared in 70% yield by the treatment of $[CpW(NO)I_2]_2$ with an equimolar amount of $Sn(C_3H_5)_4$ in tetrahydrofuran at ambient temperature, i.e.

$$[CpW(NO)I_2]_2 \xrightarrow[\text{THF}]{Sn(C_3H_5)_4} 2CpW(NO)(\eta^3\text{-}C_3H_5)I \quad (1)$$

The compound is an orange-brown, diamagnetic solid which dissolves in polar organic solvents to give reasonably air-stable solutions. Its IR spectrum (in CH_2Cl_2) exhibits a strong absorption at 1636 cm^{-1} attributable to a terminal nitrosyl ligand, and its low-resolution mass spectrum[13] displays a parent-ion peak and a fragmentation pattern corresponding to the sequential loss of ligands from the metal center.

The crystal structure of the complex consists of a well-spaced array of molecular units, the intermolecular contacts corresponding to normal van der Waals distances. In the solid state, $CpW(NO)(\eta^3\text{-}C_3H_5)I$ exists as both the R and S enantiomers of the endo conformer. The molecular structure of the R form[14] is shown in Figure 1, and bond distances and bond angles are summarized in Table IV. The most chemically interesting feature of the structure is the marked asymmetry

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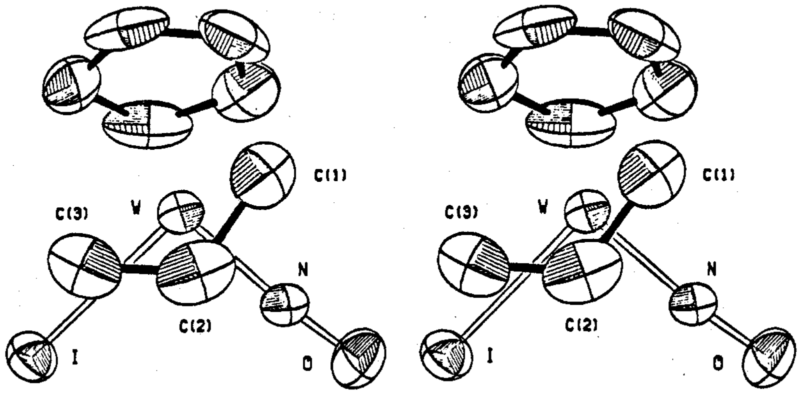


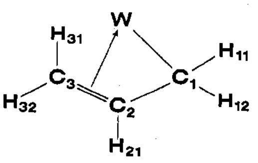
Figure 1. ORTEP stereoview (50% probability ellipsoids) of the molecular structure of CpW(NO)(η^3-C_3H_5)I. The hydrogen atoms have been omitted for clarity.

Table I. Final Positional Parameters (Fractional Parameters $\times 10^4$, W and I Parameters $\times 10^5$, H Parameters $\times 10^3$)[a]

atom	*x*	*y*	*z*
W	82061 (2)	11935 (2)	21556 (3)
I	69937 (4)	852 (4)	−7207 (6)
N	8724 (5)	−48 (4)	3094 (7)
O	9207 (5)	−861 (4)	3711 (8)
C(1)	7759 (8)	1756 (7)	4861 (10)
C(2)	6722 (9)	1164 (7)	4170 (12)
C(3)	6117 (7)	1489 (8)	2648 (13)
C(11)	8737 (9)	3005 (6)	1586 (16)
C(12)	9630 (9)	2551 (8)	2713 (13)
C(13)	10172 (7)	1763 (8)	1838 (17)
C(14)	9572 (9)	1657 (7)	134 (14)
C(15)	8688 (9)	2457 (8)	−69 (13)
H(11)	779 (8)	229 (8)	499 (14)
H(12)	818 (9)	143 (9)	558 (14)
H(21)	657 (8)	42 (8)	462 (12)
H(31)	609 (9)	225 (8)	231 (13)
H(32)	545 (9)	114 (7)	216 (14)
H(1)	824 (0)	360 (0)	184 (0)
H(2)	984 (0)	277 (0)	394 (0)
H(3)	1085 (0)	133 (0)	229 (0)
H(4)	972 (0)	112 (0)	−71 (0)
H(5)	815 (0)	261 (0)	−112 (0)

[a] Estimated standard deviations are in parentheses.

of the allyl ligand. The C(1)–C(2) length of 1.43 (1) Å is indicative of principally a single bond between the two atoms whereas the C(2)–C(3) distance of 1.34 (1) Å suggests the presence of a double bond.[16] Furthermore, the W–C(1) bond distance of 2.244 (7) Å falls in the range expected for single W–C σ bonds[17] whereas the W–C(2) and W–C(3) bond lengths are somewhat longer. The geometries of the cyclopentadienyl and nitrosyl ligands are completely consistent with their functioning as five- and three-electron donors, respectively, to the metal center. Consequently, to account for the diamagnetism of the complex and to provide the metal atom with the favored 18-electron configuration, we represent the tungsten–allyl linkage as



As anticipated, the C–C bond of the allyl ligand which has more double bond character (i.e., C(2)–C(3)) is situated trans to the NO group which is acknowledged to be the better π-acceptor ligand.

The asymmetry of the tungsten–allyl linkage persists in solution, as evidenced by the ^1H and ^{13}C NMR spectra of the complex (Table V).[18] The ^{13}C spectrum exhibits resonances due to the three inequivalent allyl carbon atoms which can be assigned on the basis of their chemical shifts. The resonance attributable to C(1) has a chemical shift which resembles those characteristic of ~sp^3-hybridized carbon atoms in transition-metal alkyls, while the C(2) and C(3) resonances occur at lower field in the region expected for ~sp^2 carbon atoms bonded to transition metals.[19] Consistent with the tungsten–allyl bonding depicted above, the ^1H NMR spectrum (Figure 2) confirms that the hydrogen atoms bonded to C(1) and C(3) are in different environments, the chemical shifts of the latter reflecting their predominantly vinylic nature. The observed

Table II. Final Thermal Parameters and Their Estimated Standard Deviations

(a) Anisotropic Thermal Parameters ($U_{ij} \times 10^3$, W and I $\times 10^4$ Å^2)[a]

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W	318 (2)	292 (2)	317 (2)	8 (1)	61 (1)	−10 (1)
I	484 (3)	469 (3)	402 (2)	−59 (2)	−8 (2)	−36 (2)
N	41 (3)	29 (2)	44 (3)	−3 (2)	−1 (2)	0 (2)
O	71 (4)	43 (3)	69 (4)	13 (3)	−9 (3)	7 (3)
C(1)	83 (6)	57 (4)	33 (4)	6 (4)	16 (3)	−8 (3)
C(2)	75 (6)	56 (5)	56 (5)	1 (4)	40 (4)	−3 (4)
C(3)	39 (4)	64 (5)	70 (5)	2 (4)	22 (4)	−20 (4)
C(11)	71 (5)	27 (3)	117 (8)	−9 (3)	39 (5)	5 (4)
C(12)	75 (6)	74 (6)	66 (5)	−38 (5)	0 (4)	−12 (5)
C(13)	30 (4)	68 (6)	120 (9)	−3 (4)	10 (4)	24 (6)
C(14)	81 (6)	56 (5)	87 (7)	−27 (5)	58 (5)	−21 (5)
C(15)	69 (5)	71 (6)	66 (5)	−24 (5)	1 (4)	35 (5)

(b) Assigned Isotropic Thermal Parameters ($U \times 10^3$)

atom	*U*, Å^2	atom	*U*, Å^2
H(11)	76	H(1)	76
H(12)	76	H(2)	79
H(21)	76	H(3)	77
H(31)	76	H(4)	77
H(32)	76	H(5)	76

[a] The anisotropic thermal parameters employed in the refinement are U_{ij} in the expression $f = f^0 \exp(-2\pi^2 \Sigma_{i=1,j=1}{}^3 U_{ij} h_i h_j a_i{}^* a_j{}^*)$ and for isotropic atoms the expression is $f = f^0 \exp(-8\pi^2 U \cdot (\sin^2 \theta)/\lambda^2)$.

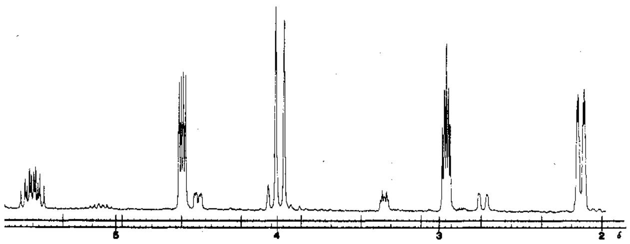


Figure 2. The 270-MHz ^1H FT NMR spectrum in the allyl region of CpW(NO)(η^3-C_3H_5)I in $CDCl_3$.

Table IV. Bond Distances and Bond Angles for $CpW(NO)(\eta^3\text{-}C_3H_5)I^a$

Bond Distances (Å)

W-I	2.8026 (5)	C(1)-C(2)	1.43 (1)
W-N	1.770 (5)	C(2)-C(3)	1.34 (1)
W-C(1)	2.244 (7)	N-O	1.216 (7)
W-C(2)	2.329 (8)	C(11)-C(12)	1.37 (1)
W-C(3)	2.411 (7)	C(12)-C(13)	1.35 (1)
W-C(11)	2.374 (7)	C(13)-C(14)	1.40 (1)
W-C(12)	2.324 (8)	C(14)-C(15)	1.40 (1)
W-C(13)	2.329 (8)	C(15)-C(11)	1.41 (1)
W-C(14)	2.313 (7)	C(1)-H(11)	0.7 (1)
W-C(15)	2.386 (8)	C(1)-H(12)	0.8 (1)
W-CP	2.029	C(2)-H(21)	1.0 (1)
		C(3)-H(31)	1.0 (1)
		C(3)-H(32)	0.9 (1)

Bond Angles (deg)

N-W-CP	121.7	W-N-O	172.8 (5)
I-W-CP	110.1	C(1)-C(2)-C(3)	119.0 (8)
I-W-N	89.8 (2)	W-C(1)-C(2)	75.4 (4)
I-W-C(1)	136.0 (2)	W-C(2)-C(3)	76.8 (4)
I-W-C(2)	99.9 (3)	W-C(2)-C(1)	68.4 (4)
I-W-C(3)	77.8 (2)	W-C(3)-C(2)	70.5 (5)
N-W-C(1)	90.1 (3)	C(11)-C(12)-C(13)	109.2 (9)
N-W-C(2)	87.3 (3)	C(12)-C(13)-C(14)	108.5 (8)
N-W-C(3)	110.8 (3)	C(13)-C(14)-C(15)	107.8 (8)
CP-W-C(1)	107.2	C(14)-C(15)-C(11)	106.0 (8)
CP-W-C(2)	137.2	C(15)-C(11)-C(12)	108.3 (8)
CP-W-C(3)	126.6		

[a] CP is the unweighted centroid of the $(\eta^5\text{-}C_5H_5)$ ring.

Table V. ^1H and ^{13}C NMR Spectral Data for the Endo Isomer of $CpW(NO)(\eta^3\text{-}C_3H_5)I^a$

^1H NMR Data[b]

Cp	H(11)	H(12)	H(21)	H(31)	H(32)
5.96	2.08 $J_{11-21} = 10.1$ $J_{11-12} = 2.6$	2.90 $J_{12-21} = 6.6$ $J_{12-32} = 3.8$	5.44	3.92 $J_{31-21} = 14.3$ $J_{31-11} = 1.8$ $J_{31-32} = 1.0$	4.53 $J_{32-21} = 7.3$ $J_{32-11} = 1.0$

^{13}C NMR Data

Cp	C(1)	C(2)	C(3)
99.84	37.52	111.13	76.47

[a] The solvent was $CDCl_3$, and the chemical shifts (δ) are accurate to ±0.01 ppm. [b] Coupling constants are in Hz; those involving H_{21} are accurate to ±0.1 Hz, whereas the others have errors of ca. ±0.5 Hz.

AGMRX pattern for the allyl ligand contrasts with the A_2M_2X pattern displayed by the symmetric $\eta^3\text{-}C_3H_5$ group of $CpW(CO)_2(\eta^3\text{-}C_3H_5)$.[20] Assignments of resonances to individual protons have been made on the basis of coupling constants and on the assumption that the endo conformer is the principal species in solution. The indicated assignments and coupling constants (Table V) have been confirmed by a series of homonuclear decoupling experiments. The ^1H NMR spectrum also indicates the presence of another isomer of $CpW(NO)(\eta^3\text{-}C_3H_5)I$, presumably the exo conformer, but the resonances due to this isomer are not sufficiently resolved to permit detailed assignments. The observed ratio of endo:exo conformers is ca. 7:1.

The molybdenum congener, $CpMo(NO)(\eta^3\text{-}C_3H_5)I$, can be isolated in 88% yield from the reaction analogous to that represented by eq 1. Its ^{13}C and ^1H NMR spectra indicate that the allyl ligand in this complex also exhibits a significant σ–π distortion.[21] It thus appears that such distortions may well be a general feature of allyl ligands attached to metal centers having electronic asymmetry.[22]

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Registry No. $CpW(NO)(\eta^3\text{-}C_3H_5)I$, 71341-42-9; $[CpW(NO)I_2]_2$, 71341-43-0; $Sn(C_3H_5)_4$, 7393-43-3.

Supplementary Material Available: Table III, a listing of structure amplitudes (21 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Part 8: Legzdins, P.; Martin, D. T. *Inorg. Chem.* **1979**, *18*, 1250–4.

(2) Adams, R. D.; Chodosh, D. F.; Faller, J. W.; Rosan, A. M. *J. Am. Chem. Soc.* **1979**, *101*, 2570–8 and references therein.

(3) The synthesis and characterization of $[CpW(NO)I_2]_2$ will be described in a future publication.

(4) Elemental analyses were performed by Mr. P. Borda of this department.

(5) The IR spectrum was recorded on a Perkin-Elmer 457 spectrophotometer and was calibrated with the 1601-cm^{-1} band of polystyrene film.

(6) The melting point was taken in a capillary and is uncorrected.

(7) (a) Busing, W. R.; Levy, H. A. *Acta Crystallogr.* **1957**, *10*, 180–2. (b) Coppens, P.; Leiserowitz, L.; Rabinovich, D. *Ibid.* **1965**, *18*, 1035–8.

(8) (a) Becker, P. J.; Coppens, P. *Acta Crystallogr., Sect. A* **1974**, *30*, 129–47. (b) Becker, P. J.; Coppens, P. *Ibid.* **1975**, *31*, 417–25. (c) Coppens, P.; Hamilton, W. C. *Ibid.* **1970**, *26*, 71–83.

(9) Cromer, D. T.; Liberman, D. *J. Chem. Phys.* **1970**, *53*, 1891–8.

(10) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *24*, 321–4.

(11) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175–87.

(12) Supplementary material.

(13) Obtained at 70 eV on an Atlas CH4B spectrometer using the direct-insertion method with the assistance of Mr. J. W. Nip. The probe temperature was 140 °C.

(14) The priority sequence of the ligands is $I > \eta^5\text{-}C_5H_5 > \eta^3\text{-}C_3H_5 > NO$ if the organic groups are each considered as one ligand and if the extension of the *R,S* system to organometallic complexes with π-bonded ligands[15] is used.

(15) Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598–9 and references therein.

(16) Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, N.Y., 1960; pp 232–9.

(17) The estimated standard deviations for the H(11) and H(12) distances and angles are far too high for any conclusions to be drawn regarding their being positioned in a pseudotetrahedral fashion (bent back away from the W atom) around C(1).

(18) ^1H FT NMR spectra were recorded at 270 MHz and ambient temperature by Mrs. M. M. Tracey on a departmental spectrometer employing an Oxford Instruments superconducting magnet and Nicolet Instrument Corp. hardware. ^{13}C NMR spectra were recorded on a Varian Associates CFT20 spectrometer. The indicated chemical shifts are downfield from Me_4Si.

(19) Mann, B. E. *Adv. Organomet. Chem.* **1974**, *12*, 135–213.

(20) Faller, J. W.; Chen, C. C.; Mattina, M. J.; Jakubowski, A. *J. Organomet. Chem.* **1973**, *52*, 361–86.

(21) After completion of this work, we learned from Professor J. W. Faller that he and his co-workers have fully characterized the series of complexes $CpMo(NO)(\eta^3\text{-allyl})X$ (X = NCO, CN or I; allyl = C_3H_5 or C_4H_7), all of which contain a distorted η^3-allyl ligand.

(22) ^1H NMR spectra similar to, but less fully resolved than, that depicted in Figure 2 have recently been reported for the complexes $CpMo(\eta^3\text{-allyl ester})(CO)(PPh_3)$ (Collin, J.; Charrier, C.; Pouet, M. J.; Cadiot, P.; Roustan, J. L. *J. Organomet. Chem.* **1979**, *168*, 321–36).

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Determination of the Barrier to Rotation about the Iron–Ligand Bond in Cationic $(\eta^5\text{-}C_5H_5)Fe(CO)(L)$ (L = PPh_3, $P(OPh)_3$) π-Alkyne and π-Alkene Complexes

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In 1964 Cramer reported the first detailed dynamic NMR study of rotation of alkenes about the bond axis from a transition metal to the midpoint of the carbon–carbon double bond.[1] Since that time, many similar processes have been studied and the activation energies or the so-called barriers