Table I. Apparent Bond Lengths as a Function of Composition

composition[a]	color	d(Mo-L),[b] Å	d(Mo-Cl_{trans}), Å	d(Mo-Cl_{cis}), Å
$Mo(PMe_2Ph)_3OCl_2$	blue	1.675 (3)	2.528 (1)	2.481 (1)
$Mo(PMe_2Ph)_3O_{0.99}Cl_{2.01}$	blue	1.683 (3)	2.528 (1)	2.479 (1)
$Mo(PMe_2Ph)_3O_{0.98}Cl_{2.02}$	green-blue	1.694 (5)	2.529 (2)	2.481 (2)
$Mo(PMe_2Ph)_3O_{0.97}Cl_{2.03}$	green	1.789 (3)	2.510 (1)	2.471 (2)
$Mo(PMe_2Ph)_3O_{0.96}Cl_{2.04}$	green	1.871 (3)	2.510 (1)	2.465 (2)
$Mo(PMe_2Ph)_3O_{0.72}Cl_{2.28}$	green	2.205 (2)	2.481 (1)	2.447 (2)
$Mo(PMe_2Ph)_3O_{0.51}Cl_{2.49}$	green	2.316 (2)	2.460 (1)	2.437 (2)
$Mo(PMe_2Ph)_3O_{0.09}Cl_{2.91}$	yellow-green	2.391 (1)	2.430 (1)	2.422 (2)
$Mo(PMe_2Ph)_3Cl_3$	yellow	2.400 (1)	2.427 (1)	2.420 (1)

[a] The compositions indicated are only approximate and were determined by analysis of the ^1H NMR spectra of the bulk sample. The compositions were also calculated by using a model in which O and Cl (with fixed isotropic thermal parameter, U = 0.05 Å^2) were placed at fixed distances of 1.675 and 2.400 Å, respectively, from Mo, and allowing the site occupancies of the disordered atoms to refine. Although this procedure does not give the same compositions as determined by ^1H NMR spectroscopy, the observed trend is unaffected. [b] The Mo-L ($L = O_xCl_{1-x}$) bond lengths listed are those obtained from a model in which the coordinates of a single composite atom (L) are refined at the disordered site.

$(PMe_3)_3$.[9,10] The incorporation of chloride into the oxo site would be expected to result in an artificial increase of the "Mo=O" bond length.[11] Evidence for cocrystallization of *cis-mer*-$MoOCl_2(PMe_3)_3$ and *mer*-$MoCl_3(PMe_3)_3$ was readily provided by examination of the ^1H NMR spectra. Although *mer*-$MoCl_3(PMe_3)_3$ is paramagnetic, and escapes detection in the normal range, it is readily observed as two broad resonances at δ -16 and -33 ppm.

In view of the above evidence for compositional disorder within crystals of *cis-mer*-$MoOCl_2(PMe_3)_3$, we were prompted to reinvestigate the molecular structures of *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ and *cis-mer*-$MoOCl_2(PEt_2Ph)_3$, the original complexes for which distortional isomerism was first proposed. Thus, we have isolated and structurally characterized crystals of "*cis-mer*-$MoOCl_2(PMe_2Ph)_3$", which vary in color from blue, through green-blue, to emerald green. Examination of the ^1H NMR spectra over the range δ -30 to +10 ppm indicates that this color change is associated with increased contamination with paramagnetic *mer*-$MoCl_3(PMe_2Ph)_3$,[10,12] a yellow complex. The results of the X-ray diffraction studies are summarized in Table I and Figure 1, illustrating how the apparent "Mo=O" bond length varies as a function of the composition. The blue "isomer" of *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ is pure and shows the shortest Mo=O bond length. However, the green "isomer" is a mixture of blue *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ and yellow *mer*-$MoCl_3(PMe_2Ph)_3$. Indeed, we have independently obtained emerald green crystals of "*cis-mer*-$MoOCl_2(PMe_2Ph)_3$" from a solution containing a ca. 10:1 molar mixture of blue *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ and yellow *mer*-$MoCl_3(PMe_2Ph)_3$, which give rise to an apparent "Mo=O" bond length of 1.789 (3) Å. Such a process would clearly allow for the tailoring of a series of apparent "Mo=O" bond lengths. Thus, Table I and Figure 1 illustrate the continuum of apparent Mo-L (L = O, Cl) bond lengths that may be obtained going from pure *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ to pure *mer*-$MoCl_3(PMe_2Ph)_3$.

In conclusion, this investigation has demonstrated that the observation of short and long Mo=O bond lengths in the initial report describing distortional isomerism is a consequence of compositional disorder of *cis-mer*-$MoOCl_2(PR_3)_3$ with *mer*-$MoCl_3(PR_3)_3$. It is most likely that this explanation was not discovered in the initial report of distortional isomerism due to the difficulty of observing small amounts of paramagnetic *mer*-$MoCl_3(PR_3)_3$ under normal ^1H NMR conditions. Therefore, our results strongly suggest that at present there is no evidence for bond-stretch isomerism for the *cis-mer*-$MoOCl_2(PR_3)_3$ system and, more generally, that the observation of long metal-oxo bond lengths should be interpreted with caution.

Note Added in Proof: Spectroscopic and chromatographic evidence that the green "isomer" of *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ is a mixture of *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ and *mer*-$MoCl_3(PMe_2Ph)_3$ has been obtained independently (Desrochers, P. J.; Enemark, J. H., personal communication).

Supplementary Material Available: Tables of crystal and intensity collection data, atomic coordinates, bond distances and angles, anisotropic displacement parameters, and ORTEP drawings for all structures (79 pages). Ordering information is given on any current masthead page.

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(11) *Intramolecular* disorder between O and Cl is well-known to give bond lengths intermediate between that expected for M=O and M-Cl. Although under favorable circumstances it is possible to refine disordered O and Cl ligands (for example, see Lam, C. T.; Lewis, D. L.; Lippard, S. J. *Inorg. Chem.* **1976**, *15*, 989-991), this procedure is frequently unsuccessful since the partial atoms tend to converge to the same position (for example, see ref 5c). Thus, the model that we have adopted here is to refine both oxygen and chlorine at the same site, but with variable occupancy such that their total is unity. It should be noted, however, that surprisingly successful refinement may be achieved for many of the structures by refining the atom as oxygen only.

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^1H 3D NOESY-TOCSY Nuclear Magnetic Resonance Spectrum of an Oligonucleotide Dodecamer Duplex Containing a GG Mismatch

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The dodecamer $d(CGGGAATTCGCG)_2$ containing a GG mismatch has been studied in our laboratory;[1,2] however, some of the cross peaks in the 2D NOESY spectrum are masked by the presence of additional overlapping cross peaks. We show in this paper how the use of 3D NOESY-TOCSY NMR can resolve in the third dimension those cross peaks that overlap in the 2D spectra. This 3D experiment includes the results that can be obtained from a selective 2D TOCSY-NOESY experiment recently published.[3] In addition, a single 3D spectrum provides the information for assigning all of the nonexchangeable protons including strongly overlapping peaks such as the H5′ and H5″ protons. It provides a much more reliable and simplified sequence-specific assignment methodology than 2D NMR.

For larger systems, peak overlap and increased spectral line widths present significant barriers to the required nearly complete signal assignments of the larger biomolecules.[4] Recently a number of laboratories have demonstrated that the addition of a third

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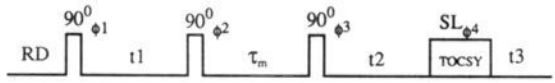
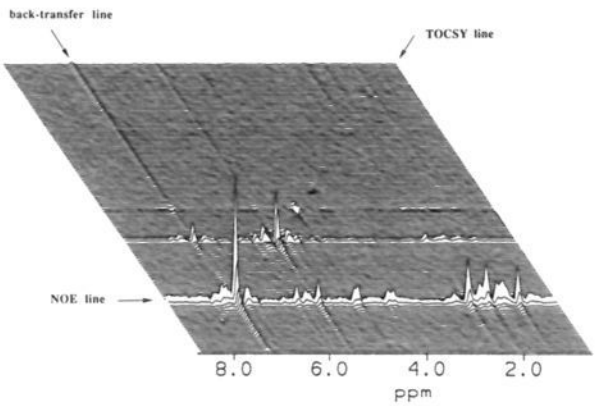


Figure 1. Pulse sequence for the 3D NOESY–TOCSY experiment. The relaxation delay (RD) and mixing time (τ_m) periods are indicated. The phase cycling used is as follows: $\phi_1 = x, -x, x, -x, x, -x, x, -x$; $\phi_2 = x, x, x, x, x, x, x, x$; $\phi_3 = x, -x, y, -y, -x, x, -y, y$; $\phi_4 = -y, y, x, -x, y, -y, -x, x$; $\phi_{acq} = x, x, y, y, -x, -x, -y, -y$.



	ω1		ω2		ω3	type
A:	C9H6	→	C9H6	→	C9H6	body diagonal
B:	C9H5	→	C9H5	→	C9H6	TOCSY
C:	C9H6	→	C9H5	→	C9H6	back transfer
D:	C9H5	→	C9H6	→	C9H6	NOESY

Figure 2. Cross-sectional plane perpendicular to $\omega_3 = 7.32$ ppm in the 3D pure absorption phase NOESY–TOCSY spectrum of the duplex dodecamer at 600 MHz, showing the base H8/H6 and deoxyribose region. 2D stacked plot representation through C9 H6/T8 H6 (ω_3). The body diagonal for C9 H6 as well as the NOE, TOCSY, and back-transfer peaks are shown. The magnetization transfer pathways for the peaks indicated are given in the plot above.

homonuclear[5-10] or heteronuclear[11,12] frequency dimension to the NMR spectra largely resolves these difficulties. Thus a ^{1}H homonuclear 3D NOESY–TOCSY and the reverse TOCSY–NOESY spectrum,[7,13,14] (a variation of a 2D version[15]) can considerably simplify the assignment of protein signals. In this paper we demonstrate the utility of the 3D NOESY–TOCSY experiment applied to an oligonucleotide.

While a number of base-pair mismatch duplexes have been studied by NMR as well as by X-ray crystallography,[16-20] there have surprisingly been no detailed NMR studies on the GG mismatch. While this mismatch has a low frequency of occurrence in biological systems, the repair efficiency for the GG mismatch is also very poor.

Synthesis and purification of the dodecamer[1] followed a manual modification[21] of the solid phase support methodology. The amount of oligonucleotide for the NMR sample was ca. 35 mg/0.55 mL of D_2O, containing 0.1 M NaCl, 0.1 M phosphate buffer, pH 7.0 (uncorrected meter reading).

The pulse sequence and the phase cycling of the 3D NOESY–TOCSY experiment are shown in Figure 1. The TOCSY and NOE mixing times were respectively 30 and 300 ms. The States[22] hypercomplex method was applied in both the t1 and t2 dimensions. The 3D spectrum was acquired as sets of pseudo TOCSY planes by varying t2 and keeping t1 constant. The phase of the first pulse in the t2 domain was incremented by 90° for each t2 increment to obtain sign discrimination in t2. Two pseudo TOCSY planes were acquired for each t1 increment with the phase of the first 90° pulse in the t1 dimension shifted by 90°. Sixty-four complex points were acquired in the t2 dimension, and 90 complex points were acquired in the t1 dimension. The relaxation delay was 0.7 s, and the total experiment time was 60 h. The data were acquired on a Varian VXR 600 600-MHz NMR spectrometer, and eight scans were acquired for each FID. The TOCSY mixing pulse was obtained with a $(MLEV16)_n$ pulse sequence[23,24] preceded by a trim pulse of 2 ms. The processing was done by using the FTNMR program of D. Hare locally modified to handle 3D data sets. Sine bell windows shifted by 90° were applied in the three dimensions, and no base-line correction was used. The resulting fully transformed spectrum contained 512 × 512 × 512 real points.

In a 3D NOESY–TOCSY NMR spectrum the peaks possessing the same frequency along the three axes ($\omega1 = \omega2 = \omega3$) are located along the body diagonal. The plane $\omega1 = \omega2$ (TOCSY plane) contains peaks representing magnetization transferred during the TOCSY mixing period only. The plane $\omega2 = \omega3$ (NOESY plane) contains peaks representing magnetization transferred during the NOE mixing period only. The third plane, $\omega1 = \omega3$ (back-transfer plane), is a plane representing magnetization being transferred twice during the two mixing times back to the original spin. Planes perpendicular to any of the three axes contain all of this information plus true 3D magnetization transfer cross peaks. Although the data may be analyzed in any of the planes, we chose to analyze the dodecamer using planes perpendicular to the ω3 axis (Figure 2). The sensitivity of the 3D NOESY–TOCSY experiment is quite good, as can be seen from the stacked plot of an ω3 plane taken at the C9 H6/T8 H6 frequency (Figure 2). The ω3 planes contain the history of all magnetization transfer pathways of a spin leading to the final ω3 frequency. Two interesting frequencies to detect in ω3 are the CH5 and the CH6 frequency.

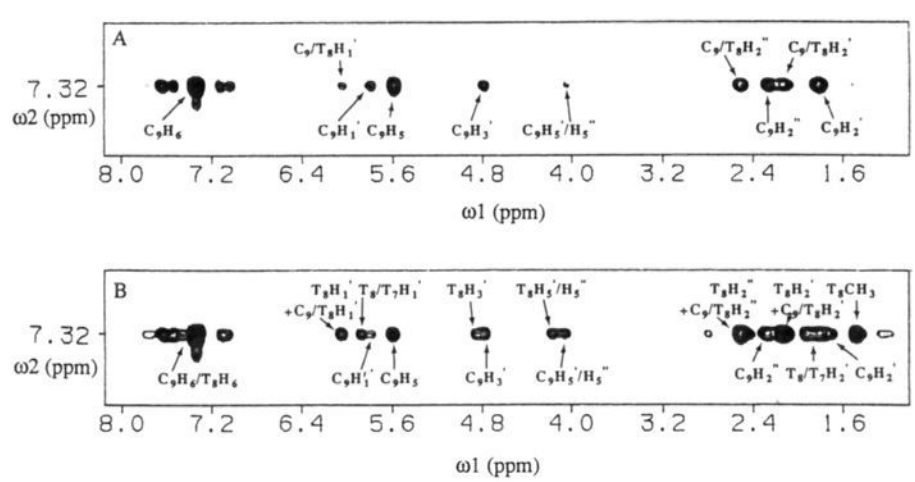


Figure 3. 2D contour plots (only the plane region at $\omega2 = 7.32$ ppm is shown) for cross-sectional ω_3 planes in the 3D NOESY–TOCSY NMR spectrum of the dodecamer: (A) ω_3 cut through C9 H5 and (B) ω_3 cut through C9 H6/T8 H6.

There is a fundamental difference between detecting a CH6 and a CH5 proton in the $\omega 3$ dimension. If one detects CH6, and if the frequency of CH6 overlaps with the resonance of another H6 proton, nothing is gained by using the 3D experiment relative to 2D NMR because the magnetization transfer pathway (sugar protons $\xrightarrow{J1}$ CH6 $\xrightarrow{J2}$ CH6) is the same as the original 2D NOESY transfer. Overlap of the H6/sugar proton NOESY cross peaks remains. In addition, the true 3D cross peaks which could possibly resolve the overlap (sugar protons $\xrightarrow{J1}$ CH5 $\xrightarrow{J2}$ CH6) have little or no intensity because the direct NOESY magnetization transfer between sugar protons and CH5 is very inefficient.

However, if the CH5 frequency in the $\omega 3$ dimension is detected, the CH6 of the same base via the TOCSY mixing process is detected (sugar protons $\xrightarrow{J1}$ CH6 $\xrightarrow{J2}$ CH5). In that case if CH6 overlaps with another H6 resonance then the CH6 will be *selectively detected.* Parts A and B of Figure 3 compare two $\omega 3$ planes ($\omega 2$ = 7.32 ppm region shown only) detected at the frequency of C9 H5 or C9 H6. In the regular 2D NOESY spectrum, T8 H6 resonates at the same frequency as C9 H6 and therefore the cross peaks C9 H6/T8 H1′, C9 H6/T8 H2′, and C9 H6/T8 H2″ are undetectable because they are hidden by the cross peaks T8 H6/T8 H1′, T8 H6/T8 H2′, and T8 H6/T8 H2″. By detecting the $\omega 3$ plane at the C9 H5 frequency, one clearly sees that the signals originating from T8 H6 have disappeared. One can now detect and unambiguously assign C9 H6/T8 H1′, C9 H6/T8 H2′, and C9 H6/T8 H2″.

This single 3D spectrum provides the information for assigning all of the nonexchangeable protons including even strongly overlapping peaks in crowded spectral regions such as the H5′ and H5″ protons in a much more reliable manner than 2D NMR and greatly simplifies the process for assignment of all the protons in the system. This experiment is particularly useful for C and T bases, where the scalar coupling between CH5 and CH6, and between TH6 and TCH3, allows one to take full advantage of the increased resolution provided by the TOCSY mixing process.[25]

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Novel Zirconocene-Promoted Carbon–Carbon Bond Formation via a 1,2-Migration Reaction of Alkynylzirconium Derivatives

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We report on a novel class of carbon–carbon bond forming reaction of alkynylzirconocene derivatives which, we believe, proceeds via 1,2-migration as in eqs 1 and 2 (Scheme I). One distinguishing feature of the reaction is that, unlike some other known 1,2-migration reactions such as those involving α,β-unsaturated organoborates,[2] *it proceeds without the assistance of an external electrophile.* In search for new migratory insertion reactions of organotransition metals,[3-5] we generated $Li[Cp_2Zr(C{\equiv}CPh)_3]$ (**1a**) by treating Cp_2ZrCl_2, where Cp = η^5-C_5H_5, with 3 equiv of LiC≡CPh in THF at −78 to 25 °C over a few hours. Treatment of **1a** with 3 N HCl indeed produced (*Z*)-1,4-diphenyl-1-buten-3-yne (**2a**) as a >96% isomerically pure compound in 61% GLC yield based on Zr (eq 1). Similarly, the reaction of Cp_2ZrCl_2 with 3 equiv of LiC≡CC(Me)=CH_2, followed by iodinolysis with 2 equiv of I_2, produced **3c** in almost quantitative GLC yield along with 4-iodo-2-methyl-1-buten-3-yne (100% based on Zr) (eq 1).

Zirconocene derivatives containing both alkynyl and aryl groups also undergo a similar reaction. Thus, treatment of preformed $Cp_2Zr(C{\equiv}CPh)_2$[6a] with 2 equiv of PhLi (−78 to 25 °C) provided, upon quenching with 3 N HCl, (*Z*)-stilbene (**5a**) in 85% GLC yield based on Zr along with only a 6% yield of **2a**, and the reaction of Cp_2ZrPh_2[6b] with 1 equiv of LiC≡CPh provided, after treatment with 3 N HCl, >98% isomerically pure **5a** in 81% GLC yield (eq 2). The amount of **2a** was trace, if any. The use of DCl in place of HCl gave (*Z*)-dideuteriostilbene with >95% deuterium in-

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