$M^{-1}\ s^{-1}$) comparable to that of dried LiBr.

The labeling results, however, indicate that at least 65% of the LiBr/PhCF/MeCN reaction follows eq 1. The remaining 35% of product **3** could arise both by adventitious water protonation of carbenoid **2** and by direct protonation of PhCF, followed by anion capture of $PhCHF^+$. The dominant (if not exclusive) involvement of carbenoids in the reactions of PhCF and LiX (or QX) thus seems established. We are continuing our studies of carbene–MX reactions.

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A Reinvestigation of the Molecular Structures of *cis-mer*-$MoOCl_2(PR_3)_3$: Do Bond-Stretch Isomers Really Exist?

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Compositionally and geometrically identical molecules that differ only by the length of one or more bonds have recently been termed "bond-stretch isomers" by Hoffmann and co-workers.[1] The suggestion that such isomers may exist is not only of great interest from a structural point of view, but also has important implications with respect to chemical reactivity. For example, an understanding of the factors that may influence the facile lengthening of a bond is extremely important for modifying chemical behavior. The original report of the phenomenon of bond-stretch isomerism was by Chatt, Manojlovic-Muir, and Muir in 1971, in which the term "distortional isomerism" was used to describe the relationship between the blue and green forms of the octahedral complexes *cis-mer*-$MoOCl_2(PR_3)_3$ (Figure 1).[2] X-ray diffraction studies revealed that the blue form of *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ possesses a normal Mo=O bond length of 1.676 (7) Å,[3] whereas the green form of the related complex *cis-mer*-$MoOCl_2(PEt_2Ph)_3$ is characterized by an abnormally long Mo=O bond length of 1.803 (11) Å. The green form of *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ was structurally characterized later and was also found to possess a long Mo=O bond length of 1.80 (2) Å.[4] Since these initial reports, a number of other oxo complexes have been characterized as distortional or bond-stretch isomers.[5]

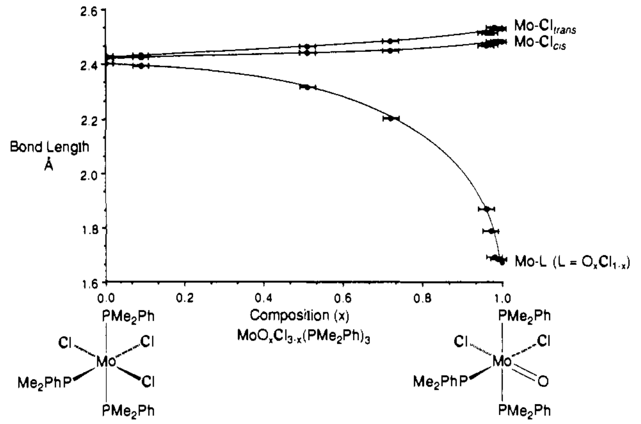

Figure 1. Apparent bond lengths as a function of composition.

Here we report our investigations of the molecular structure of *cis-mer*-$MoOCl_2(PMe_3)_3$,[6] and also a reinvestigation of the blue and green forms of *cis-mer*-$MoOCl_2(PMe_2Ph)_3$. These results suggest that, contrary to the original report, there is no evidence for the occurrence of bond-stretch or distortional isomerism for the *cis-mer*-$MoOCl_2(PR_3)_3$ system, and that the apparent lengthening of the Mo=O bond lengths is due to compositional disorder with the isostructural *mer*-$MoCl_3(PR_3)_3$.

Cotton has recently reported that the green complex *cis-mer*-$MoOCl_2(PMePh_2)_3$, for which the blue form is not known, possesses a normal Mo=O bond length of 1.667 (4) Å,[7] in contrast to the long bond lengths observed for the green complexes described above. Furthermore, Carmona and Wilkinson have reported both blue and green forms of the trimethylphosphine derivative *cis-mer*-$MoOCl_2(PMe_3)_3$,[6] of which the green form is the most stable. In view of Cotton's results, we were intrigued as to whether green *cis-mer*-$MoOCl_2(PMe_3)_3$ would show a normal or long Mo=O bond length. Thus, we determined the molecular structure of *cis-mer*-$MoOCl_2(PMe_3)_3$ by X-ray diffraction methods. Interestingly, two molecules of *cis-mer*-$MoOCl_2(PMe_3)_3$ are present in the asymmetric unit, which differ significantly only in the lengths of the Mo=O bonds. One of the molecules possesses a normal Mo=O bond length of 1.698 (8) Å, whereas the other molecule possesses an abnormally long Mo=O bond length of 1.866 (7) Å. Other bond distances are not significantly different between the two molecules. It therefore appeared that both bond-stretch isomers of *cis-mer*-$MoOCl_2(PMe_3)_3$ were present in the same crystal. Such an observation would provide a unique opportunity to study the phenomenon of bond-stretch isomerism. In particular, we expected to observe two absorptions in the IR spectrum corresponding to ν(Mo=O) of the long and short isomers. However, we found only one absorption in the Nujol mull IR spectrum at 950 cm^{-1} for *cis-mer*-$MoOCl_2(PMe_3)_3$.[8] In order to verify the results of our original X-ray diffraction study, a second crystal of *cis-mer*-$MoOCl_2(PMe_3)_3$, obtained from a different batch, was examined. Surprisingly, the results of this investigation showed two new Mo=O bond lengths of 1.772 (12) and 2.154 (8) Å. The discrepancy between the two structure determinations, which generated *four* unique Mo=O bond lengths, strongly suggested that these differences were not a manifestation of bond-stretch isomerism. Examination of the difference electron density plots revealed a large excess of electron density close to the oxo position of the molecules with long Mo=O bonds. The discrepancy was assigned to compositional disorder arising as a result of cocrystallization of *cis-mer*-$MoOCl_2(PMe_3)_3$ with small quantities of the isostructural trichloride complex *mer*-$MoCl_3$-

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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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^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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