A mixture of **10a** (0.050 g, 0.089 mmol) and $NEt_4Cl{\cdot}H_2O$ (0.15 g, 0.90 mmol) was dissolved in THF (10 mL) and stirred for 5 days. Workup as described above yielded yellow microcrystals of **9a** (0.045 g, 90% yield).

Reverse Isomerization Reactions. A CH_2Cl_2 (20 mL) solution of **9c** (0.20 g, 0.20 mmol) was treated with CO gas, as described for the synthesis of compounds **10** above. Once the solution was saturated with the gas, a single portion of $AgBF_4$ (0.10 g, 0.50 mmol) was added and a slow stream of CO maintained for 30 min until the reaction was complete (IR). Solvent was removed in vacuo and Et_2O (2 mL) added to the residue for transfer to the top of a Florisil-packed chromatography column (2 × 18 cm). Elution at −40 °C with Et_2O separated two yellow fractions. Solvent was removed from each, and both products were recrystallized from Et_2O (2 mL) by cooling to −78 °C. Thus, two microcrystalline yellow samples were obtained and identified in the usual manner, as compounds **10a** (0.050 g, 45% yield) and **4a** (0.047 g, 42% yield), respectively.

X-ray Crystal Structure Determinations. The crystal data and other experimental details for compounds **9a**, **11b**, and **12b** are summarized in Table VI. Crystals of **9a** were grown by the slow diffusion of Et_2O into a THF solution of the complex at 0 °C, those of **11b** from *n*-hexane (−20 °C), and those of **12b** by the slow diffusion of petroleum ether into a CH_2Cl_2 solution of the complex at ambient temperatures. For compound **9a** the asymmetric unit contains half a molecule of THF, which is disordered about the inversion center (0, 0.5, 0.5). The presence of THF was confirmed by recording a ^1H NMR spectrum of the same batch of crystals.

All data were corrected for Lorentz, polarization, and X-ray absorption effects, the latter by an empirical method based on azimuthal scan data.[19] The structures were solved by Patterson and difference Fourier methods, by which all non-hydrogen atoms were located and refined with anisotropic thermal parameters. The carborane cage hydrogen atoms of **11b** were directly located and refined without positional constraints but with fixed isotropic thermal parameters (U_{iso} = 0.08 Å^2). All other hydrogen atoms were included at calculated positions (C–H, 0.96; B–H, 1.1 Å[20]) with fixed isotropic thermal parameters ($1.2U_{equiv}$ of the parent carbon or boron atom).

Calculations were performed on a Digital micro-vax II computer with the SHELXTL PLUS suite of programs.[19] Atomic scattering factors with corrections for anomalous dispersion are inlaid in the programs.

Acknowledgment. We thank the SERC for research studentships (to S.A.B and M.U.P) and the Robert A. Welch foundation for support (S.A.B, N.C, F.G.A.S).

Supplementary Material Available: Microanalytical data for all new compounds and complete crystallographic structure determination descriptions for **9a**, **11b**, and **12b** and tables of atomic coordinates, complete lists of bond lengths and angles, and anisotropic displacement coefficients for compounds **9a**, **11b**, and **12b** (32 pages); listings of observed and calculated structure factors (67 pages). Ordering information is given on any current masthead page.

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(19) Sheldrick, G. M. SHELXTL PLUS programs for use with the Siemens R3m/V X-ray system.

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Bond-Stretch Isomerism in the Complexes *cis-mer*-$MoOCl_2(PR_3)_3$: A Reinvestigation

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Abstract: The molecular structures of a series of complexes *cis-mer*-$MoOCl_2(PR_3)_3$ (PR_3 = PMe_3, PMe_2Ph) have been investigated by X-ray diffraction methods. The data indicate a large range of apparent Mo═O bond lengths. The apparent lengthening of the Mo═O bond in these complexes is rationalized in terms of compositional disorder with the isostructural trichloride derivative *mer*-$MoCl_3(PR_3)_3$. These results suggest that, contrary to the original suggestion (Chatt, J.; Manojlovic-Muir, L.; Muir, K. W. *Chem. Commun.* **1971**, 655–656), there is no evidence for bond-stretch or distortional isomerism for the *cis-mer*-$MoOCl_2(PR_3)_3$ system.

Introduction

More than 20 years ago, Butcher and Chatt reported a series of octahedral molybdenum oxo complexes with a meridonal arrangement of phosphine ligands, *mer*-$MoOX_2(PR_3)_3$ (X = Cl, Br, I, NCO, NCS; PR_3 = PMe_2Ph, PEt_2Ph, $PPr^n{}_2Ph$, $PBu^n{}_2Ph$, $PMePh_2$, $PEtPh_2$, PPr^nPh_2, $MeC[CH_2PPh_2]_3$).[1] The complexes *mer*-$MoOX_2(PR_3)_3$ were either blue or green, depending upon the nature of both X and PR_3. However, one of these complexes, *mer*-$MoOCl_2(PMe_2Ph)_3$, could be isolated in *both* blue and green isomeric forms. The blue and green isomers had very similar melting points (blue, 155–157 °C; green 153–156 °C) but different ν(Mo═O) stretching frequencies (blue, 954 cm^{-1}; green, 943 cm^{-1}) and were originally proposed to be *geometric* isomers, namely *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ and *trans-mer*-$MoOCl_2(PMe_2Ph)_3$, differing only in whether the two chloride ligands were cis or trans. Single-crystal X-ray diffraction established a cis configuration of chloride ligands for the blue isomer, i.e., *cis-mer*-$MoOCl_2(PMe_2Ph)_3$, from which it was concluded that the green isomer (and, hence, *all* the green complexes) possessed a trans configuration, as illustrated in Figure 1. However, following the original report,[1] Chatt, Manojlovic-Muir, and Muir determined the molecular structure of the green complex *mer*-$MoOCl_2(PEt_2Ph)_3$ and found, to their surprise, that the chloride ligands were cis and *not* trans.[2] Although the alkyl substituents on the phosphine ligands adopted different orientations in blue *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ and green *cis-mer*-$MoOCl_2(PEt_2Ph)_3$, the coordination environments around the molybdenum centers were similar for both molecules, with the exception that the Mo═O bond length in green *cis-mer*-$MoOCl_2(PEt_2Ph)_3$ (1.803 (11) Å) was *significantly* longer than that observed in blue *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ (1.676 (7)

[†] Columbia University.

[‡] University of Delaware.

(1) Butcher, A. V.; Chatt, J. *J. Chem. Soc. A* **1970**, 2652–2656.

(2) (a) Chatt, J.; Manojlovic-Muir, L.; Muir, K. W. *Chem. Comm.* **1971**, 655–656. (b) Manojlovic-Muir, L. *J. Chem. Soc. A* **1971**, 2796–2800. (c) Manojlovic-Muir, L.; Muir, K. W. *J. Chem. Soc., Dalton Trans.* **1972**, 686–690.

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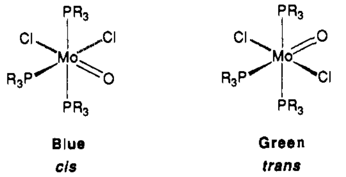

Figure 1. Original (incorrect) proposal for the structures of blue and green *mer*-MoOCl$_2$(PR$_3$)$_3$ complexes.[1]

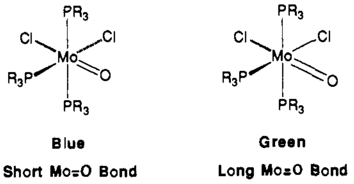

Figure 2. Proposed distortional isomerism for blue and green *mer*-MoOCl$_2$(PR$_3$)$_3$ complexes.[2]

Å). This result prompted the suggestion that the green isomer of *mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ also possessed an identical coordination environment to blue *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$, with the exception that the Mo=O bond lengths in the two isomers were different. The blue and green *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ complexes were thus termed "*distortional isomers*".[2a] The green isomer of *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ was structurally characterized at a later date and, consistent with the above proposal, also found to possess a long Mo=O bond length of 1.80 (2) Å.[3] A statistical survey by Mayer indicates that terminal Mo=O bond lengths for monooxomolybdenum complexes are normally in the range ca. 1.65–1.70 Å, and indeed, the narrowness of this range has been commented upon.[4] Thus, it is apparent that, of the pair of distortional isomers, it is the structure of the green isomer, with a particularly long Mo=O bond length, that is unprecedented.

The phenomenon of distortional isomerism not only is of great interest from a structural point of view but also has important implications with respect to chemical reactivity. An understanding of the factors that may influence the facile lengthening of a bond is extremely important for modifying chemical behavior. In a theoretical analysis of this phenomenon, Jean, Lledos, Burdett, and Hoffmann introduced the term "bond-stretch isomerism", since it more precisely describes the type of distortion that is observed.[5]

Since the original report of distortional isomerism, a number of other complexes have been proposed to exhibit this phenomenon.[6] Some specific examples include blue (d(W=O) 1.72 (2) Å) and green (d(W=O) 1.89 (2) Å) [(Me$_3$N$_3$C$_6$H$_{12}$)W(O)Cl$_2$]$^+$,[6a] blue (d(Mo=O) 1.60 (2) Å) and green (d(Mo=O) 1.72 (2) Å) [Mo(CN)$_4$(O)(OH$_2$)]$^{2-}$,[6b] and yellow (d(Nb=O) 1.781 (6) Å) and green (d(Nb=O) 1.929 (6) Å) Nb(O)Cl$_3$(PMe$_3$)$_3$.[6g] In fact, on the basis of the *color change* that is commonly associated with this phenomenon, examples of bond-stretch or distortional isomerism have even been postulated for complexes *without* the aid of structure determination by X-ray diffraction![7]

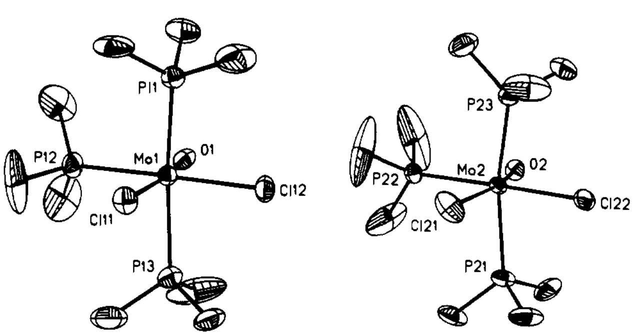

Figure 3. ORTEP drawings for the two crystallographically independent molecules of *cis-mer*-MoOCl$_2$(PMe$_3$)$_3$ (both molecules are drawn with similar orientations).

Table I. Bond Lengths (Å) around Mo in *cis-mer*-MoOCl$_2$(PMe$_3$)$_3$ (Crystal No. 1)

	molecule 1	molecule 2
Mo–O	1.698 (8)	1.866 (7)
Mo–Cl(1)	2.509 (4)	2.513 (2)
Mo–Cl(2)	2.469 (2)	2.470 (3)
Mo–P(1)	2.538 (3)	2.524 (3)
Mo–P(2)	2.497 (2)	2.497 (3)
Mo–P(3)	2.520 (3)	2.567 (4)

In this paper we report our investigations of the molecular structure of *cis-mer*-MoOCl$_2$(PMe$_3$)$_3$[8] and also a reinvestigation of the structures of the blue and green forms of *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$. These results demonstrate that, contrary to the original suggestion there is *no evidence* for bond-stretch or distortional isomerism for *cis-mer*-MoOCl$_2$(PR$_3$)$_3$ complexes, the first system that was proposed to exhibit the phenomenon.[9]

Results and Discussion

Carmona and Wilkinson have reported both blue and green isomers of the trimethylphosphine derivative *cis-mer*-MoOCl$_2$(PMe$_3$)$_3$,[8] analogous to the Chatt isomers *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$. However, unlike the dimethylphenylphosphine *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ system, where the green isomer (long Mo=O bond length) irreversibly converts to the blue isomer (short Mo=O bond length), the trimethylphosphine analogues appear to exhibit the opposite behavior, and the green isomer seems to be the more stable of the two forms. If the color of the isomer is an indication of the Mo=O bond length (i.e., blue—short and green—long), then the above observation is surprising since it indicates that the variation of alkyl groups on a tertiary phosphine ligand may have a pronounced effect on the strength of a Mo=O interaction. However, Cotton has recently reported a *normal* (i.e., short) Mo=O bond length of 1.667 (4) Å for the green complex *cis-mer*-MoOCl$_2$(PMePh$_2$)$_3$, for which the blue form is not known.[10] In view of Cotton's results, which show that a green complex may also have a normal (i.e., short) Mo=O bond length, in contrast to the long bond lengths observed previously, we were intrigued as to whether green *cis-mer*-MoOCl$_2$(PMe$_3$)$_3$ would possess a normal (i.e., short) or a long Mo=O bond length. Thus, we determined the molecular structure of *cis-mer*-MoOCl$_2$(PMe$_3$)$_3$ by X-ray diffraction methods. The asymmetric unit contains *two* crystallographically independent molecules of *cis-mer*-MoOCl$_2$(PMe$_3$)$_3$, as shown in Figure 3 (both molecules are drawn with similar orientations). Although the two molecules have similar

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(3) Haymore, B. L.; Goddard, W. A., III; Allison, J. N. *Proc. Int. Conf. Coord. Chem., 23rd* **1984**, 535.

(4) (a) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; Wiley: New York, 1988. (b) Mayer, J. M. *Inorg. Chem.* **1988**, *27*, 3899–3903.

(5) (a) Jean, Y.; Lledos, A.; Burdett, J. K.; Hoffmann, R. *J. Am. Chem. Soc.* **1988**, *110*, 4506–4516. (b) Jean, Y.; Lledos, A.; Burdett, J. K.; Hoffmann, R. *J. Chem. Soc., Chem. Commun.* **1988**, 140–142.

(6) (a) Wieghardt, K.; Backes-Dahmann, G.; Nuber, B.; Weiss, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 777–778. (b) Wieghardt, K.; Backes-Dahmann, G.; Holzbach, W.; Swiridoff, W. J.; Weiss, J. Z. *Anorg. Allg. Chem.* **1983**, *499*, 44–58. (c) Lincoln, S.; Koch, S. A. *Inorg. Chem.* **1986**, *25*, 1594–1602. (d) Gibson, V. C.; Kee, T. P.; Shaw, A.; Williams, D. N. 199th National Meeting of the American Chemical Society, Boston, MA, April 22–27, 1990; American Chemical Society: Washington, DC, 1990; INOR 134. (e) Bashall, A.; McPartlin, M. *Acta Crystallogr.* **1990**, *A46* (*Supp.*), C-221–C-222; IUC 15th International Conference of Crystallography, Bordeaux, France. (f) Lu, J.; Clarke, M. J. 199th National Meeting of the American Chemical Society, Boston, MA, April 22–27, 1990; American Chemical Society: Washington, DC, 1990; INOR 583. (g) Bashall, A.; Gibson, V. C.; Kee, T. P.; McPartlin, M.; Robinson, O. B.; Shaw, A. *Angew. Chem.* **1991**, *103*, 1021–1023; *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 980–982. (h) Also see ref 4a, p 153.

(7) For example, blue and green {η^3-HB(pz)$_3$}ReOCl$_2$,[7a] blue and green [(Me$_3$N$_3$C$_6$H$_{12}$)Mo(NO)Cl(OEt)]$^+$,[7b] and blue and green [(Me$_3$N$_3$C$_6$H$_{12}$)W(NO)Br(OEt)]$^+$.[7b] (a) Degnan, I. A.; Behm, J.; Cook, M. R.; Herrmann, W. A. *Inorg. Chem.* **1991**, *30*, 2165–2170. (b) Backes-Dahmann, G.; Wieghardt, K. *Inorg. Chem.* **1985**, *24*, 4044–4049.

(8) Carmona, E.; Galindo, A.; Sanchez, L.; Nielson, A. J.; Wilkinson, G. *Polyhedron* **1984**, *3*, 347–352.

(9) Portions of this work have been communicated. Yoon, K.; Parkin, G.; Rheingold, A. L. *J. Am. Chem. Soc.* **1991**, *113*, 1437–1438.

(10) Cotton, F. A.; Diebold, M. P.; Roth, W. J. *Inorg. Chem.* **1987**, *26*, 2848–2852.

Table II. Bond Lengths (Å) around Mo in *cis-mer*-$MoOCl_2(PMe_3)_3$ (Crystal No. 2)

	molecule 1	molecule 2
Mo–O	1.772 (12)	2.154 (8)
Mo–Cl(1)	2.496 (7)	2.476 (4)
Mo–Cl(2)	2.462 (4)	2.448 (4)
Mo–P(1)	2.540 (5)	2.530 (6)
Mo–P(2)	2.493 (5)	2.512 (5)
Mo–P(3)	2.510 (5)	2.560 (6)

coordination geometries about the molybdenum centers, as illustrated by the selected bond lengths in Table I, the two molecules differ significantly 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. The observation of pairs of crystallographically inequivalent, but chemically equivalent, molecules in a crystal is not uncommon; however, chemically equivalent bond lengths are expected to differ only slightly (<0.05 Å) between the molecules due to crystal packing forces.[11] 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 solid-state IR spectrum corresponding to ν(Mo=O) of the long and short isomers. The region commonly associated with Mo=O stretching frequencies (ca. 900–1000 cm^{-1}) possesses a strong absorption at 950 cm^{-1}. Unfortunately, this is also a region where absorptions due to coordinated PMe_3 occur, so that the assignment of this band to ν(Mo=O) cannot be made with certainty. However, the use of ^{17}O and ^{18}O isotopic substitution reveals that the molybdenum–oxo and trimethylphosphine absorptions are coincident (Figure 4). Significantly, the data indicate that there is *only one absorption* assignable to ν(Mo=^{16}O) at 950 cm^{-1} in the solid-state IR spectrum of *cis-mer*-$MoOCl_2(PMe_3)_3$.[12] Moreover, only one resonance was detected in the solution ^{17}O NMR spectrum of *cis-mer*-$MoOCl_2(PMe_3)_3$ at δ 884 ppm. The observation of only one molybdenum–oxo stretching frequency in the solid-state IR spectrum of *cis-mer*-$MoOCl_2(PMe_3)_3$ is not consistent with the presence of two molecules which differ substantially in their Mo=O bond lengths.[13] Thus, 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, as shown in Table II, the results of this investigation showed *two new* Mo=O bond lengths of 1.772 (12) and 2.154 (8) Å, with other Mo—Cl and Mo—P bond lengths being similar to the first structure determination. The discrepancy between the two structure determinations, which thus generated *four* unique Mo=O bond lengths of 1.698 (8), 1.772 (12), 1.866 (7), and 2.154 (8) Å, strongly suggested that these differences were not a manifestation of the phenomenon of bond-stretch isomerism. Indeed, the extremely long Mo=O bond length of 2.154 (8) Å is completely unprecedented.[4] The important question to be answered is, therefore, what is causing these apparent changes in bond lengths.

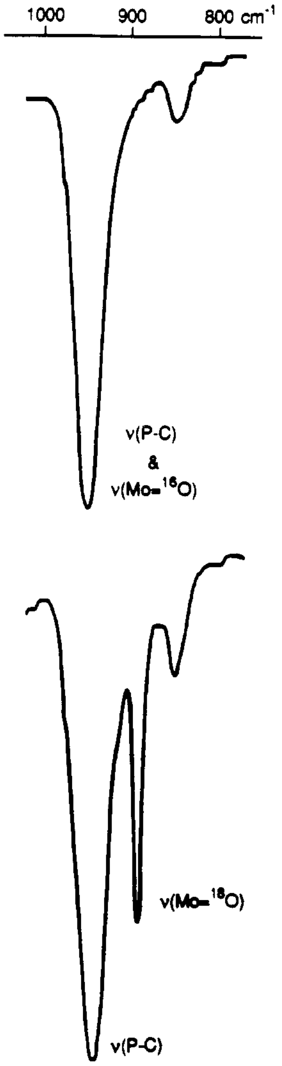

Figure 4. IR spectrum of ^{16}O and ^{18}O-labeled *cis-mer*-$MoOCl_2(PMe_3)_3$.

Examination of difference electron density plots revealed an excess of electron density close to the oxo position of the molecules with long Mo=O bonds. We considered that the excess of electron density at the oxo site may be due to partial occupancy by chlorine. Partial occupancy by chlorine may be achieved by several possible mechanisms, namely (i) disorder between the oxo ligand and the *trans*-chloride ligand due to packing identical molecules in different orientations at the same crystallographic site, (ii) disorder between the oxo ligand and the *cis*-chloride ligand due to cocrystallization with the isostructural geometric isomer *trans-mer*-$MoOCl_2(PMe_3)_3$, and (iii) disorder between the oxo ligand and a chloride ligand due to cocrystallization with the isostructural trichloride complex *mer*-$MoCl_3(PMe_3)_3$.[14] Incorporation of chloride into the oxo site by any one of the above mechanisms would be expected to result in an artificial increase of the "Mo=O" bond length, since the chloride ligand would be located at a much greater distance from the molybdenum (ca. 2.45 Å for Mo—Cl vs ca. 1.68 Å for Mo=O). For example, disorder between O and Cl in the complex $\{\eta^3\text{-HB(pz)}_3\}MoOCl_2$ has been shown to result in the observation of three composite bond lengths (2.072 (5), 2.203 (4), 2.294 (3) Å) as a result of packing identical molecules in different orientations about the pseudo-3-fold molecular axis. These bond lengths are intermediate between *d*(Mo=O) and *d*(Mo—Cl) and do not correspond to either the true Mo=O or Mo—Cl bond lengths.[6c]

The observation of different *pairs* of Mo=O bond lengths for two different crystals of *cis-mer*-$MoOCl_2(PMe_3)_3$ suggested that disorder between the oxo ligand and the *trans*-chloride was not responsible for the apparent bond length differences. Evidence for the nature of the disorder in crystals of *cis-mer*-$MoOCl_2(PMe_3)_3$ was provided by examination of the ^1H NMR spectra. Figure 5 shows the ^1H NMR spectrum of *cis-mer*-$MoOCl_2(PMe_3)_3$ in the normal range δ 0–10 ppm, consisting of a virtually coupled triplet due to the two *trans*-PMe_3 ligands and a doublet

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(11) Indeed, the similarity of such bond lengths often provides a good indication of the accuracy of the structure determination. Rheingold, A. L.; Harper, J. R. *J. Organomet. Chem.* **1991**, *403*, 335–344.

(12) For *cis-mer*-$MoOCl_2(PMe_3)_3$: ν(Mo=^{16}O) 950 cm^{-1}; ν(Mo=^{17}O) 920 cm^{-1}; ν(Mo=^{18}O) 900 cm^{-1}.

(13) (a) Cotton, F. A.; Wing, R. M. *Inorg. Chem.* **1965**, *4*, 867–873. (b) Hardcastle, F. D.; Wachs, I. E. *J. Raman Spectrosc.* **1990**, *21*, 683–691.

(14) The complex *mer*-$MoCl_3(PMe_3)_3$ has been previously reported. See: Reference 8. Atwood, J. L.; Hunter, W. E.; Carmona-Guzman, E.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1980**, 467–470.

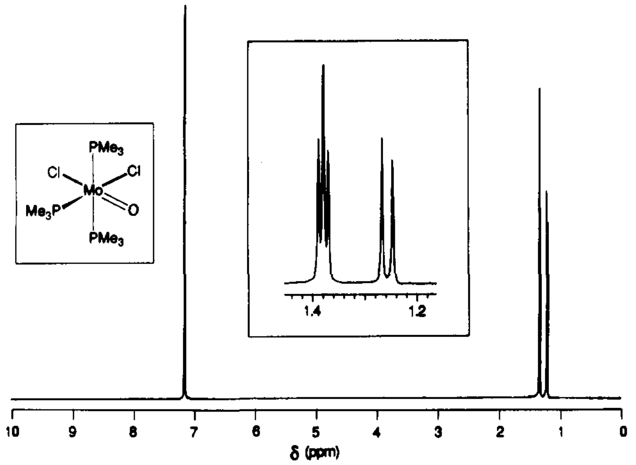

Figure 5. ^{1}H NMR spectrum of "*cis-mer*-MoOCl$_2$(PMe$_3$)$_3$" in C$_6$D$_6$ (δ 7.15 ppm) over the range δ 0–10 ppm.

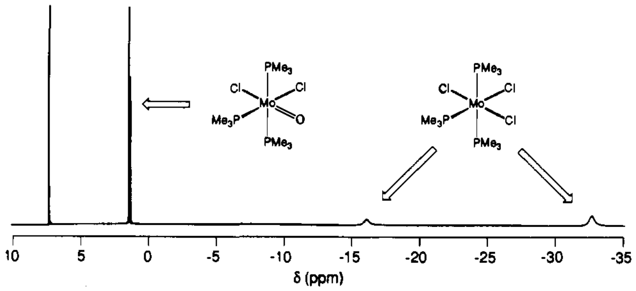

Figure 6. ^{1}H NMR spectrum of "*cis-mer*-MoOCl$_2$(PMe$_3$)$_3$" in C$_6$D$_6$ (δ 7.15 ppm) over the range δ −35 to +10 ppm.

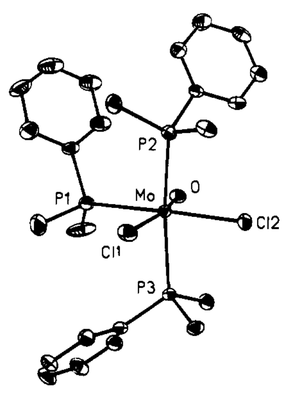

Figure 7. ORTEP drawing of *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$.

Table III. Selected Bond Lengths (Å) for *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$

Mo–P(1)	2.489 (1)	Mo–P(2)	2.533 (1)
Mo–P(3)	2.529 (1)	Mo–Cl(1)	2.528 (1)
Mo–Cl(2)	2.481 (1)	Mo–O	1.675 (3)

Table IV. Selected Bond Angles (deg) for *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$

P(1)–Mo–P(2)	95.8 (1)	P(1)–Mo–P(3)	95.4 (1)
P(2)–Mo–P(3)	160.5 (1)	P(1)–Mo–Cl(1)	85.8 (1)
P(2)–Mo–Cl(1)	80.0 (1)	P(3)–Mo–Cl(1)	85.0 (1)
P(1)–Mo–Cl(2)	177.6 (1)	P(2)–Mo–Cl(2)	85.1 (1)
P(3)–Mo–Cl(2)	83.1 (1)	Cl(1)–Mo–Cl(2)	92.1 (1)
P(1)–Mo–O	84.1 (1)	P(2)–Mo–O	99.7 (1)
P(3)–Mo–O	97.2 (1)	Cl(1)–Mo–O	169.8 (1)
Cl(2)–Mo–O	98.0 (1)		

Table V. Selected Bond Lengths (Å) for *mer*-MoCl$_3$(PMe$_2$Ph)$_3$

Mo–P(1)	2.572 (1)	Mo–P(2)	2.610 (1)
Mo–P(3)	2.567 (1)	Mo–Cl(1)	2.427 (1)
Mo–Cl(2)	2.420 (1)	Mo–Cl(3)	2.400 (1)

due to the single *cis*-PMe$_3$ ligand, as originally reported.[8] As such, the spectrum shown in Figure 5 offers little information as to the nature of the disorder in crystals of *cis-mer*-MoOCl$_2$(PMe$_3$)$_3$. However, as shown by the ^{1}H NMR spectrum of the same sample in the range δ −35 to +10 ppm (Figure 6), two broad resonances are also observed at δ −16 and −33 ppm in the ratio 1:2. These broad resonances correspond to those of *mer*-MoCl$_3$(PMe$_3$)$_3$, with one *cis*-PMe$_3$ ligand and two *trans*-PMe$_3$ ligands, and was confirmed by comparison with that of an authentic sample.[15] This result provides conclusive evidence that the bulk sample of *cis-mer*-MoOCl$_2$(PMe$_3$)$_3$ is contaminated with the trichloride impurity *mer*-MoCl$_3$(PMe$_3$)$_3$.[16] In view of the isostructural relationship between *cis-mer*-MoOCl$_2$(PMe$_3$)$_3$ and *mer*-MoCl$_3$(PMe$_3$)$_3$, cocrystallization resulting in compositional disorder may be expected. Indeed, such a method of doping paramagnetic complexes into crystals of isostructural diamagnetic complexes is used extensively in single-crystal EPR studies.[17] Thus, the observation of four apparently unique Mo═O bond lengths in *cis-mer*-MoOCl$_2$(PMe$_3$)$_3$, and yet only one ν(Mo═O) absorption, may be readily explained as a result of compositional disorder with isostructural *mer*-MoCl$_3$(PMe$_3$)$_3$.

In view of the above evidence for compositional disorder within crystals of *cis-mer*-MoOCl$_2$(PMe$_3$)$_3$ resulting in the observation of anomalous bond lengths, we were prompted to reinvestigate the original complexes for which distortional isomerism was first proposed, namely blue and green *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$. We have isolated crystals of *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ which vary in color from blue, through green-blue, to emerald green. Examination of the ^{1}H NMR spectra of these crystals indicates that the color change is associated with increased contamination with paramagnetic *mer*-MoCl$_3$(PMe$_2$Ph)$_3$,[18] a yellow complex. This observation leads to the conclusion that the *bulk sample* of the *green "isomer"* of *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ is a mixture of *blue cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ and *yellow mer*-MoCl$_3$(PMe$_2$Ph)$_3$! It is possible that the difficulty of observing small amounts of paramagnetic *mer*-MoCl$_3$(PMe$_2$Ph)$_3$ under normal ^{1}H NMR conditions prevented earlier workers from reaching this conclusion. However, the same conclusion has been obtained independently by Enemark and co-workers who have used an extensive series of spectroscopic techniques to analyze the problem.[19] Importantly, Enemark demonstrated that the observation of two different ν(Mo═O) stretching frequencies (blue, 954 cm^{-1}; green, 943 cm^{-1}), which was originally cited as supporting evidence for distortional isomerism, was not reproduced. Solid-state Raman studies showed that the correct ν(Mo═O) stretching frequency for blue *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ is 943 cm^{-1},[19] identical to that of the green "isomer". We have also confirmed that this absorption in the blue complex is correctly assigned to ν(Mo═O) by the observation of the isotopic shift for the ^{18}O-labeled derivative *cis-mer*-Mo(^{18}O)Cl$_2$(PMe$_2$Ph)$_3$ (ν(Mo═^{18}O) 897 cm^{-1}), which is similar in magnitude to that for the trimethylphosphine derivative *cis-mer*-MoOCl$_2$(PMe$_3$)$_3$.[12]

The observations that (i) green *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ is contaminated with *mer*-MoCl$_3$(PMe$_2$Ph)$_3$ and (ii) both blue and

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(15) Although the ^{1}H NMR spectrum of *mer*-MoCl$_3$(PMe$_3$)$_3$ was not given in the original report, identification of the impurity was based upon comparison of the ^{1}H NMR spectrum with that of an authentic sample of *mer*-MoCl$_3$(PMe$_3$)$_3$ prepared by the literature method. Complexes of the class *mer*-MoCl$_3$(PR$_3$)$_3$ have also recently been spectroscopically investigated: Poli, R.; Mui, H. D. *Inorg. Chem.* **1991**, *30*, 65–77.

(16) The origin of the trichloride impurity *mer*-MoCl$_3$(PR$_3$)$_3$ is not known with certainty but is most likely due to either disproportionation or reduction by PR$_3$.

(17) (a) Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6416–6422. (b) Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6422–6433.

(18) Anker, M. W.; Chatt, J.; Leigh, G. J.; Wedd, A. G. *J. Chem. Soc., Dalton Trans.* **1975**, 2639–2645.

(19) Desrochers, P. J.; Nebesny, K. W.; LaBarre, M. J.; Lincoln, S. E.; Loehr, T. M.; Enemark, J. H. *J. Am. Chem. Soc.* **1991**, *113*, 9193–9200.

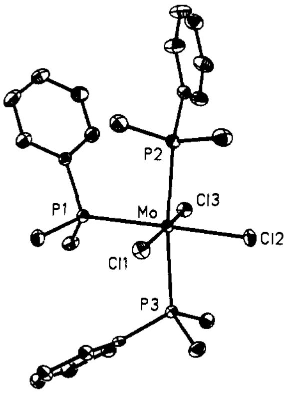

Figure 8. ORTEP drawing of *mer*-$MoCl_3(PMe_2Ph)_3$.

Table VI. Selected Bond Angles (deg) for *mer*-$MoCl_3(PMe_2Ph)_3$

P(1)-Mo-P(2)	92.7 (1)	P(1)-Mo-P(3)	96.1 (1)
P(2)-Mo-P(3)	167.2 (1)	P(1)-Mo-Cl(1)	89.4 (1)
P(2)-Mo-Cl(1)	83.5 (1)	P(3)-Mo-Cl(1)	87.4 (1)
P(1)-Mo-Cl(2)	177.4 (1)	P(2)-Mo-Cl(2)	89.2 (1)
P(3)-Mo-Cl(2)	82.3 (1)	Cl(1)-Mo-Cl(2)	92.7 (1)
P(1)-Mo-Cl(3)	86.7 (1)	P(2)-Mo-Cl(3)	100.2 (1)
P(3)-Mo-Cl(3)	89.6 (1)	Cl(1)-Mo-Cl(3)	174.8 (1)
Cl(2)-Mo-Cl(3)	91.1 (1)		

green isomers possess the same ν(Mo=O) stretching frequency provide a good indication that the apparently long Mo=O bond length may be a result of compositional disorder. However, in order to verify this proposal, it is critical to prove that the mixture is *homogeneous* in the solid state (i.e., a solid solution), so that *single crystals* composed of both *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ and *mer*-$MoCl_3(PMe_2Ph)_3$ may be obtained, and that these crystals give rise to long Mo=O bond lengths. Indeed, we have found that mixtures of *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ and *mer*-$MoCl_3(PMe_2Ph)_3$ do form single crystals over a wide range of compositions, the results of which are described below.

X-ray diffraction studies have been performed on a series of crystals of composition *mer*-$MoO_xCl_{3-x}(PMe_2Ph)_3$ ($0 \leqslant x \leqslant 1$). ORTEP drawings for the two extremes of this series, i.e., *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ and *mer*-$MoCl_3(PMe_2Ph)_3$, are shown in Figures 7 and 8, respectively. Selected bond lengths and angles for *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ and *mer*-$MoCl_3(PMe_2Ph)_3$ are presented in Tables III–VI. Interestingly, the blue crystal of *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ which we examined was not isomorphous to that used for the previously reported structure,[2b] even though both crystals were orthorhombic *Pbca*. In particular, the volumes of the two cells were significantly different (5630 vs 5429 Å^3),[20] and this is reflected by the different orientations adopted by the phosphine substituents. The conformation of the molecule reported previously is much more symmetric (with pseudomirror symmetry through the plane defined by the Mo, O, and Cl atoms) than the conformation reported here. In fact, the orientation of the phosphine substituents in *cis-mer*-$MoOCl_2(PMe_2Ph)_3$, shown in Figure 7, much more closely resembles that reported for the green "isomer" of *cis-mer*-$MoOCl_2(PEt_2Ph)_3$. Nevertheless, despite these differences in orientation of the phosphine ligands, the coordination environments about molybdenum for both structures of *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ are very similar. In particular, the Mo=O bond length of the molecule shown in Figure 7 (1.675 (3) Å) is identical, within experimental error, with that previously reported for the other conformer (1.676 (7) Å).[2b] The close similarity of these bond lengths is gratifying, since it serves to reemphasize the notion that crystal packing forces may have only small effects upon bond lengths.

Neither of the above orthorhombic forms of the blue oxo complex *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ are isomorphous with the monoclinic trichloride *mer*-$MoCl_3(PMe_2Ph)_3$, as reflected by a slightly different orientations of the phosphine substituents, especially at P(2) (compare Figures 7 and 8). Nevertheless, molecules of *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ and *mer*-$MoCl_3(PMe_2Ph)_3$ cocrystallize readily, giving both orthorhombic and monoclinic modifications, depending upon composition. Representative ORTEP drawings for two molecules of the *mer*-$MoO_xCl_{3-x}(PMe_2Ph)_3$ series are shown in Figure 9. The structure on the left was obtained from an oxo-rich orthorhombic crystal, while the structure on the right was obtained from a monoclinic crystal.

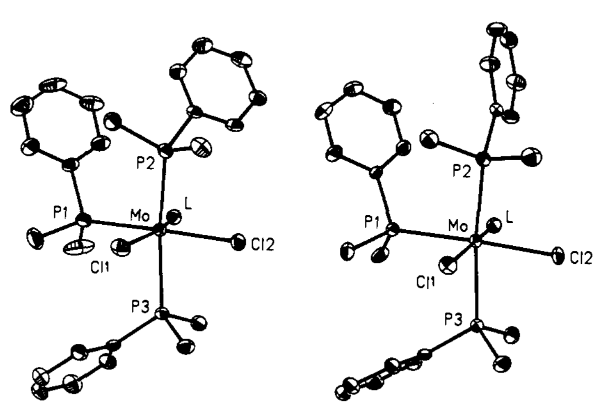

Figure 9. ORTEP drawings of *cis-mer*-$Mo(L)Cl_2(PMe_2Ph)_3$ ($L = O_xCl_{1-x}$). The structure on the left is for an oxo-rich orthorhombic crystal, while the structure on the right is for a monoclinic crystal.

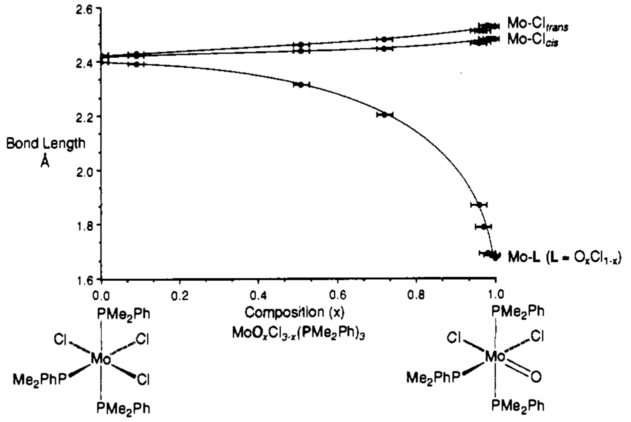

Figure 10. Apparent bond lengths as a function of composition.

The key results of the X-ray diffraction study of the *mer*-$MoO_xCl_{3-x}(PMe_2Ph)_3$ series are summarized in Table VII and Figure 10. The data clearly illustrate how the apparent "Mo=O" bond length varies as a function of the composition, thus resulting in a potential continuum of bond lengths. 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 variable mixture of blue *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ and yellow *mer*-$MoCl_3(PMe_2Ph)_3$, thus resulting in long Mo=O bond lengths. These results clearly demonstrate that there is no evidence for bond-stretch isomerism for the *cis-mer*-$MoOCl_2(PR_3)_3$ system. Indeed, recent ab initio calculations by Song and Hall support this conclusion, in that the two stable bond length minima obtained by extended Hückel calculations could not be reproduced at a higher level of calculation.[21] The caution in the communication of the original theoretical study that "...the metrical details of this type of isomerism are not fully revealed and that these systems deserve extremely careful crystallographic examination"[5b] thus appears to be well-founded.

The pronounced increase in Mo=O bond length as a function of composition is also accompanied by a slight, but definite, ap-

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[20] The previously reported *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ crystal has the following unit cell: orthorhombic, *Pbca*, *a* = 17.009 (6) Å, *b* = 16.528 (5) Å, *c* = 19.311 (8) Å, *V* = 5429 Å^3, *Z* = 8.[2b]

[21] Song, J.; Hall, M. B. *Inorg. Chem.* **1991**, *30*, 4433–4437.

Table VII. Apparent Bond Lengths in *mer*-MoO$_x$Cl$_{3-x}$(PMe$_3$)$_3$ as a Function of Composition

composition	color	*d*(Mo–L), Å	*d*(Mo–Cl$_{trans}$), Å	*d*(Mo–Cl$_{cis}$), Å
Mo(PMe$_2$Ph)$_3$OCl$_2$	blue	1.675 (3)	2.528 (1)	2.481 (1)
Mo(PMe$_2$Ph)$_3$O$_{0.99}$Cl$_{2.01}$	blue	1.683 (3)	2.528 (1)	2.479 (1)
Mo(PMe$_2$Ph)$_3$O$_{0.98}$Cl$_{2.02}$	green-blue	1.694 (5)	2.529 (1)	2.481 (2)
Mo(PMe$_2$Ph)$_3$O$_{0.97}$Cl$_{2.03}$	green	1.789 (3)	2.510 (1)	2.471 (2)
Mo(PMe$_2$Ph)$_3$O$_{0.96}$Cl$_{2.04}$	green	1.871 (3)	2.510 (1)	2.465 (2)
Mo(PMe$_2$Ph)$_3$O$_{0.72}$Cl$_{2.28}$	green	2.205 (2)	2.481 (1)	2.447 (2)
Mo(PMe$_2$Ph)$_3$O$_{0.51}$Cl$_{2.49}$	green	2.316 (2)	2.460 (1)	2.437 (2)
Mo(PMe$_2$Ph)$_3$O$_{0.09}$Cl$_{2.91}$	yellow-green	2.391 (1)	2.430 (1)	2.422 (2)
Mo(PMe$_2$Ph)$_3$Cl$_3$	yellow	2.400 (1)	2.427 (1)	2.420 (1)

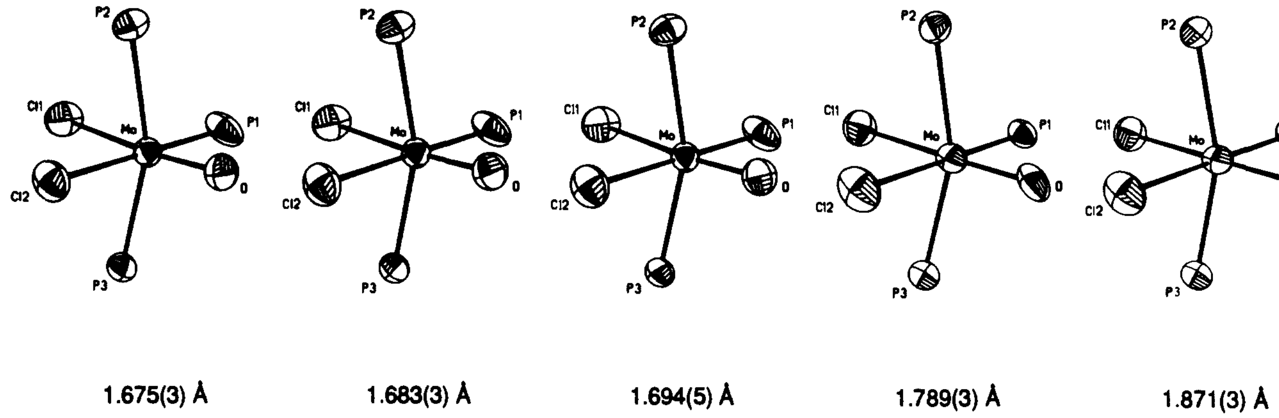

Figure 11. Variation of thermal parameters at the disordered site as a function of composition.

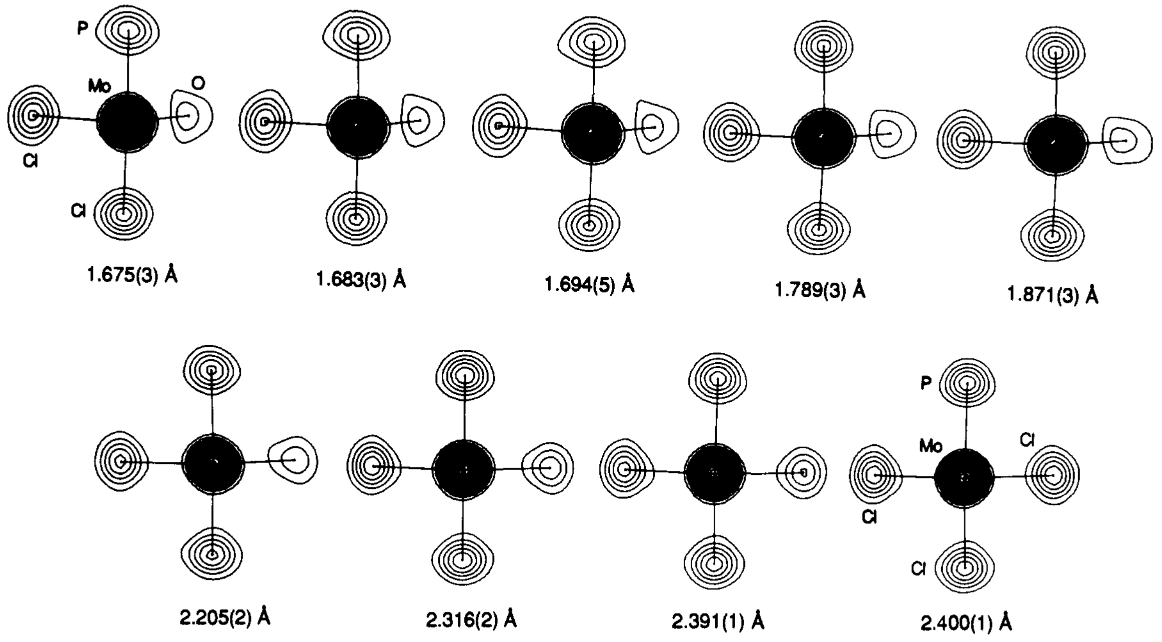

Figure 12. Variation of electron density at the disordered site as a function of composition.

parent *decrease* of the Mo–Cl$_{trans}$ bond length, while the Mo–Cl$_{cis}$ bond length is not significantly affected by the compositional changes. These apparent changes of the Mo–Cl$_{trans}$ bond length are a consequence of the weaker trans influence of the chloro vs the oxo ligand, as evidenced by comparison of the structures of the pure complexes *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ and *mer*-MoCl$_3$(PMe$_2$Ph)$_3$. Thus, as the chloride content of the crystal increases, the long Mo–Cl$_{trans}$ bond length of the oxo complex (2.528 (1) Å) approaches that of the trichloride complex (2.427 (1) Å). It is interesting that such secondary perturbations were also used in the argument for the rationalization of bond-stretch isomerism.[5]

The question of why this explanation for the phenomenon of bond-stretch isomerism had previously escaped crystallographic detection must be answered, especially since it may be expected that disorder between oxygen and chlorine would be readily revealed by the presence of abnormal temperature factors.[22] However, the original report of the structure of the green "isomer" *cis-mer*-MoOCl$_2$(PEt$_2$Ph)$_3$ cites that "...the amplitudes of vibration of the molybdenum, chlorine, phosphorus and oxygen atoms are normal".[2c] For the purposes of our study, with the exception of the pure complexes *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ and *mer*-MoCl$_3$(PMe$_2$Ph)$_3$, the atom at the disordered site of *mer*-MoO$_x$Cl$_{3-x}$(PMe$_2$Ph)$_3$ was refined as a composite of O and Cl (variable occupancy) with a fixed isotropic thermal parameter. However, for many of the structures, surprisingly successful refinement could be obtained by refining the disordered site as only oxygen, as illustrated by the partial structures shown in Figure

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[22] For example, under favorable circumstances, disorder between oxygen and chlorine may be succesfully refined. Lam, C. T.; Lewis, D. L.; Lippard, S. J. *Inorg. Chem.* **1976**, *15*, 989–991.

11.[23] Although examination of the thermal ellipsoid of the oxygen for the molecule with a Mo=O bond length of 1.871 (3) Å may strongly suggest a disordered site, even a brief examination of the recent chemical literature will reveal thermal parameters that are significantly worse than those observed in Figure 11 and yet have been accepted as publishable (good?) structures.

It is also illuminating to examine electron density plots for the series *mer*-MoO$_x$Cl$_{3-x}$(PMe$_2$Ph)$_3$. Figure 12 illustrates the variation in electron density at the disordered site as the chloride occupancy increases. All the plots are drawn with the same contour spacing, and on this scale oxygen and chlorine atoms are characterized by two- and five-electron density contours, respectively. It can be seen that only a *single* electron density maximum is observed at the disordered site, which moves dramatically away from the molybdenum center as the chloride occupancy increases. Although the electron density distribution associated with the Mo=O bond is observed to distort upon increasing the chloride occupancy, the expected increase in electron density at the disordered site is *not readily* apparent. Even at a distance of 2.205 (2) Å, the disordered site is still characterized by two contours of electron density, i.e., that of oxygen. These experimental observations are supported well by model crystallographic calculations by Enemark and Desrochers.[24] It should be noted that the disordered chlorine and oxygen atoms are *not* located along a single vector from molybdenum. Comparison of the structures of the pure complexes *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ and *mer*-MoCl$_3$(PMe$_2$Ph)$_3$ reveal that there is a difference in the Mo–O and Mo–Cl bond vectors in the planes shown in Figure 12. Lack of axial colocation of the disordered oxygen and chlorine atoms would be expected to affect the shapes of the thermal ellipsoids for the disordered structures, such that they would be less elongated than expected along the averaged vector.

Our results indicate that the most sensitive probe for the presence of a chloride impurity at the disordered site is neither (i) the observation of abnormal temperature parameters nor (ii) the presence of excess electron density at the disordered site, but rather the apparent bond length itself. The reason for this extreme sensitivity of the apparent bond length is due to two factors; (i) the much longer bond length of Mo—Cl (ca. 2.45 Å) vs Mo=O (ca. 1.68 Å) and (ii) the much greater scattering power of Cl vs O.

The sensitivity of the apparent bond length to the composition of the disordered site may thus result in the incorrect determination of bond lengths, even when there is no *obvious* crystallographic anomaly. It is very likely that many other structures, not just those proposing bond-stretch isomerism, may suffer from these problems, and we have recently documented the deliberate manipulation of apparent bond lengths in a series of [tris(pyrazolyl)hydroborato]zinc complexes.[25] A likely example of compositional disorder that is related to the *cis-mer*-MoOCl$_2$(PR$_3$)$_3$/*mer*-MoCl$_3$(PR$_3$)$_3$ system described here is concerned with the molecular structure of the tungsten complex *cis-mer*-WOCl$_2$(PMe$_3$)$_3$, reported by Wilkinson, Hursthouse, and co-workers.[26] *cis-mer*-WOCl$_2$(PMe$_3$)$_3$ is isomorphous with the molybdenum analogue, and as expected, the asymmetric unit of *cis-mer*-WOCl$_2$(PMe$_3$)$_3$ possesses two crystallographically independent molecules in which bond lengths to chlorine and phosphorus were similar for both molecules. However, a W=O bond length (1.67 (1) Å) was only reported for *one* of the two molecules. Retrieval of the atomic coordinates from the Cambridge Crystallographic Data Base revealed that the other molecule is characterized by a *long* W=O bond length (1.77 Å)! The presence of the trichloride *mer*-WCl$_3$(PMe$_3$)$_3$ contaminant is clearly suggested.

A related problem is associated with the molecular structure of the tungsten(III) complex *mer*-WCl$_3$(PMe$_2$Ph)$_3$ that was recently reported.[27] Notably, the two *chemically equivalent* W–Cl$_{trans}$ bonds possessed significantly different bond lengths of 2.437 (1) and 2.295 (2) Å. Crystal packing forces were offered as a possible explanation for the large difference in bond lengths. However, examination of Table VII and Figure 10 reveal that a more likely explanation for a *short* 2.295 (2) Å W–Cl bond length is due to cocrystallization with the *oxo* impurity *cis-mer*-WOCl$_2$(PMe$_2$Ph)$_3$, in an analogous fashion to the molybdenum system described in this paper. We have recently reinvestigated the molecular structure of *mer*-WCl$_3$(PMe$_2$Ph)$_3$ and have determined different W–Cl bond lengths to the original report. Furthermore, contamination of *mer*-WCl$_3$(PMe$_2$Ph)$_3$ by the tungsten–oxo complex *cis-mer*-WOCl$_2$(PMe$_2$Ph)$_3$ was also verified by ^{1}H and ^{31}P NMR spectroscopy.[28] The phenomenon has thus turned full circle; rather than having a chloride impurity resulting in an artificially long metal–oxo bond length, we now observe an oxo impurity resulting in an artificially short metal–chloride bond length.

In addition to affecting observed bond lengths, compositional disorder can also result in the incorrect formulation of a compound. Chatt and Rowe reported the synthesis of a violet complex, tentatively proposed to be the hydroxide complex *trans*-Re(OH)Cl$_3$(PEt$_2$Ph)$_2$ on the basis of a preliminary X-ray structure determination.[29] In a subsequent publication, Chatt and co-workers reformulated the "violet complex" as a 10–22% solid–solution of intensely violet *trans*-ReCl$_4$(PEt$_2$Ph)$_2$ in the green oxo complex *trans*-Re(O)Cl$_3$(PEt$_2$Ph)$_2$, and *not* the hydroxide derivative *trans*-Re(OH)Cl$_3$(PEt$_2$Ph)$_2$.[30] Recent work by Mayer and Conry using NMR, IR, and CV studies confirm Chatt's reformulation.[31] It is, therefore, intriguing that following Chatt's description that the "violet complex" was a mixture, other workers determined the structure by X-ray diffraction and concluded, on the basis of a long Re–O bond length (1.795 (4) Å), that the "violet complex" is, in fact, the hydroxide derivative *trans*-Re(OH)Cl$_3$(PEt$_2$Ph)$_2$![32] The possibility that the "violet complex" was a mixture was rejected on the grounds that "the anisotropic temperature factors of oxygen are quite normal".[32]

One of the main reasons for neglecting to consider compositional disorder when performing single-crystal X-ray structure determinations is undoubtably due to the common belief that single crystals are inherently pure compounds. It appears to be only when it becomes crystallographically *obvious* that a site is disordered that compositional disorder is considered. A good example of this statement is provided by the "violet complex" described above. Even though Chatt reported it as a solid solution, the possibility of compositional disorder was rejected on a crystallographic basis because the atom in question refined well as oxygen. Although in hindsight it may be all too easy to criticize the early work associated with distortional isomerism, we emphasize that the crystallographic results cited in this paper do not represent poor crystallography. Rather, these observations serve as a reminder of the complex manner in which chemistry may often conspire to fool us. The observation of low *R* values, low esd's, and well-behaved thermal parameters are not always sufficient indications of a *true* structure.

Conclusion

This investigation has demonstrated that the observation of long Mo=O bond lengths in *cis-mer*-MoOCl$_2$(PR$_3$)$_3$ is a consequence of compositional disorder with isostructural *mer*-MoCl$_3$(PR$_3$)$_3$. There is, therefore, no evidence for bond-stretch or distortional isomerism for *cis-mer*-MoOCl$_2$(PR$_3$)$_3$ complexes, the first system that was proposed to exhibit the phenomenon. By inference, all

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(23) For Mo=O bond lengths greater than 1.871 (3) Å, the oxygen atom refined nonpositive definite.

(24) Enemark, J. H.; Desrochers, P. J. Personal communication.

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(31) Conry, R. R.; Mayer, J. M. Personal communication.

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Table VIII. Crystal and Intensity Collection Data

	cis-mer-MoOCl$_2$(PMe$_3$)$_3$	*cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$	*mer*-MoCl$_3$(PMe$_2$Ph)$_3$
formula	$C_9H_{27}OP_3Cl_2Mo$	$C_{24}H_{33}OP_3Cl_2Mo$	$C_{24}H_{33}P_3Cl_3Mo$
formula weight	411.1	597.3	616.8
lattice	monoclinic	orthorhombic	monoclinic
cell constants			
a, Å	17.414 (2)	11.294 (1)	16.256 (2)
b, Å	12.819 (2)	17.627 (3)	10.329 (1)
c, Å	19.403 (3)	28.280 (5)	18.175 (3)
β, deg	116.16 (1)		113.56 (1)
V, Å^3	3887 (1)	5630 (1)	2797.4 (6)
Z	8	8	4
space group	$P2_1/c$ (No. 14)	*Pbca* (No. 61)	$P2_1/c$ (No. 14)
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
ρ(calcd), g cm^{-3}	1.40	1.41	1.46
goodness of fit	1.470	1.332	1.379
R	0.0488	0.0300	0.0246
R_w	0.0618	0.0327	0.0294

Table IX. Unit Cell Parameters for *mer*-MoO$_x$Cl$_{3-x}$(PMe$_2$Ph)$_3$

	x in *mer*-MoO$_x$Cl$_{3-x}$(PMe$_2$Ph)$_3$								
	0	0.09	0.51	0.72	0.96	0.97	0.98	0.99	1.0
a (Å)	16.256 (2)	16.263 (3)	16.182 (2)	16.121 (4)	16.075 (2)	16.090 (3)	11.315 (2)	11.314 (2)	11.294 (1)
b (Å)	10.329 (1)	10.341 (1)	10.361 (2)	10.375 (2)	10.418 (1)	10.434 (3)	17.621 (6)	17.637 (3)	17.627 (3)
c (Å)	18.175 (3)	18.167 (4)	18.124 (3)	18.081 (5)	18.000 (2)	17.986 (3)	28.310 (6)	28.255 (5)	28.280 (5)
β (deg)	113.56 (1)	113.55 (1)	113.57 (1)	113.75 (2)	114.16 (1)	114.32 (1)	90	90	90
U (Å^3)	2797 (1)	2801 (1)	2785 (1)	2768 (1)	2751 (1)	2752 (1)	5645 (2)	5638 (1)	5630 (1)

previous examples of bond-stretch isomerism may be suspect. It is most likely that the present explanation was not considered in the original proposal due to (i) the common belief that single crystals are invariably pure compounds and (ii) the observation that disordered sites may refine with *apparent* success. In view of this latter fact, unusual bond lengths should be treated with considerable caution.

Experimental Section

General Considerations. All manipulations were performed using a combination of glovebox, high-vacuum, or Schlenk techniques.[33] Solvents (except alcohols) were purified and degassed by standard procedures. NMR spectra were measured on Varian VXR 200, 300, and 400 spectrometers. IR spectra were recorded as Nujol mulls between KBr disks on a Perkin-Elmer 1420 spectrophotometer. MoCl$_3$(THF)$_3$ and MoCl$_4$(THF)$_2$ were prepared as previously reported.[34] The compositions of the *mer*-MoO$_x$Cl$_{3-x}$(PMe$_2$Ph)$_3$ solid–solutions were determined by ^{1}H NMR spectroscopy of the bulk sample.

Preparation of *cis-mer*-MoOCl$_2$(PMe$_3$)$_3$. *cis-mer*-MoOCl$_2$(PMe$_3$)$_3$ was prepared by a slight modification of the method of Carmona and Wilkinson.[8] A suspension of MoCl$_4$(THF)$_2$ (0.60 g, 1.6 mmol) in THF (20 mL) was treated with PMe$_3$ (0.81 mL, 9.1 mmol) and H$_2$O (280 μL, 1.6 mmol). The mixture was stirred at room temperature overnight over which period the dark orange mixture became green. The mixture was filtered, and the solvent was removed from the filtrate under reduced pressure, giving a green solid which was washed with pentane (0.42 g, 65%). Single crystals composed of a solid–solution of *cis-mer*-MoOCl$_2$(PMe$_3$)$_3$ and *mer*-MoCl$_3$(PMe$_3$)$_3$ were obtained from a solution of the green product in Et$_2$O at room temperature. The ^{18}O- and ^{17}O- (ca. 50% enriched) labeled derivatives were synthesized in an analogous manner.

Preparation of *mer*-MoCl$_3$(PMe$_3$)$_3$. *mer*-MoCl$_3$(PMe$_3$)$_3$ was prepared by a slight modification of the method of Carmona and Wilkinson.[8] A suspension of MoCl$_3$(THF)$_3$ (5.0 g, 12 mmol) in THF (100 mL) was treated with PMe$_3$ (6.4 mL, 72 mmol) at room temperature. The mixture was stirred at room temperature for 4 h over which period the orange-brown solution became yellow-brown. The mixture was filtered, concentrated to ca. 10 mL, and placed at −78 °C, depositing yellow crystals. Crystallization was completed by addition of Et$_2$O (30 mL). The crystals of *mer*-MoCl$_3$(PMe$_3$)$_3$ were isolated by filtration and dried in vacuo (2.7 g, 52%).

Preparation of *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$. *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ was prepared by an adaption of Carmona's method, since this procedure would more conveniently allow for the synthesis of isotopically labeled derivatives.[8,35] A suspension of MoCl$_4$(THF)$_2$ (5.0 g, 13 mmol) in THF (100 mL) was treated with PMe$_2$Ph (9.0 g, 65 mmol) upon which the dark orange mixture produced a green-red dichroic solution. H$_2$O (0.24 mL, 13 mmol) was added and the mixture stirred overnight at room temperature.[36] The mixture was filtered, and the solvent was removed under reduced pressure. The sticky residue that was obtained was washed with pentane, giving a green solid (4.94 g, 64%). The green solid was extracted into hot methanol and filtered. The green filtrate deposited deep blue crystals of pure *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ upon cooling to room temperature. Subsequent crops obtained from the mother liquor were green. Crystallization could also be effected from ethanol in a similar manner. However, the blue crystals obtained from ethanol were found to be contaminated with small quantities of the trichloride *mer*-MoCl$_3$(PMe$_2$Ph)$_3$. Green crystals were also obtained by crystallization of mixtures of blue *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ and yellow *mer*-MoCl$_3$(PMe$_2$Ph)$_3$ from ethanol.

Preparation of *mer*-MoCl$_3$(PMe$_2$Ph)$_3$. *mer*-MoCl$_3$(PMe$_2$Ph)$_3$ was prepared by a slight modification of Chatt's method.[18] A suspension of MoCl$_3$(THF)$_3$ (5.0 g, 12 mmol) in THF (100 mL) was treated with PMe$_2$Ph (7.74 g, 56 mmol) and zinc granules (3.0 g, 46 mmol) at room temperature. The mixture was stirred overnight at room temperature over which period the orange-brown solution became yellow-brown. The mixture was filtered and the solvent removed from the filtrate under reduced pressure, giving a brown solid which was washed with pentane giving *mer*-MoCl$_3$(PMe$_2$Ph)$_3$ as a yellow solid (3.72 g, 50%). Yellow crystals were obtained from a concentrated solution of *mer*-MoCl$_3$(PMe$_2$Ph)$_3$ in THF at room temperature, whereas yellow-green crystals contaminated with *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ were obtained from ethanol.

X-ray Structure Determination Procedures. Crystal data, data collection, and refinement parameters for "*cis-mer*-MoOCl$_2$(PMe$_3$)$_3$" and the pure complexes *cis-mer*-MoOCl$_2$(PMe$_2$Ph)$_3$ and *mer*-MoCl$_3$(PMe$_2$Ph)$_3$ are summarized in Table VIII. Complete tables of crystal data, data collection, and refinement parameters for all structures are given in the supplementary material of ref 9. Unit cell parameters for all structures of the *mer*-MoO$_x$Cl$_{3-x}$(PMe$_2$Ph)$_3$ series are given in Table IX. A typical procedure for the structure determination is as follows. A single crystal was mounted in a glass capillary and placed on a Nicolet R3m diffractometer. The unit cell was determined by the automatic indexing of 25 centered reflections and confirmed by examination of the axial photographs. Intensity data were collected using graphite-monochromated Mo Kα X-radiation (λ = 0.71073 Å) at room temperature. Check reflections were measured every 100 reflections, and the data were scaled accordingly and corrected for Lorentz, polarization, and absorption

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(36) If the reaction has not proceeded to completion at this stage, an extra 1 equiv of H$_2$O is added and the mixture stirred for a further 1 day.

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effects. The structure was solved using Patterson and standard difference map techniques on a Data General NOVA 4 computer using SHELXTL.[37] Space group assignments were determined uniquely by systematic absences. Hydrogen atoms were included in calculated positions (d(C–H) = 0.96 Å; $U_{iso}(H) = 1.2U_{iso}(C)$).

For the impure complex "*cis-mer*-$MoOCl_2(PMe_3)_3$", high thermal motion of the carbon atoms of the PMe_3 ligand was evident, most probably due to rotational disorder. However, the immediate coordination environment about the molybdenum in both structures was well-defined.

The composite "atom" at the disordered site of the *mer*-$MoO_xCl_{3-x}(PMe_2Ph)_3$ series was modeled by refining each atom of the composite pair with a fixed isotropic thermal parameter (U = 0.05 Å^2) and the constraint that their positional parameters maintain common values. The site occupancies were allowed to refine subject to the constraint that their sum was 1.0. Although the compositions determined using this model are not identical to those determined by ^{1}H NMR analysis, the observed trend is unaffected.[38] Attempts to refine partial oxygen and chlorine atoms at different distances from the molybdenum were unsuccessful, since the partial atoms converged to the same position (for other examples see ref 6c). Selected bond lengths and angles for the pure complexes *cis-mer*-$MoOCl_2(PMe_2Ph)_3$ and *mer*-$MoCl_3(PMe_2Ph)_3$ are given in Tables III–VI.

Complete tables of atomic coordinates, bond distances and angles, anisotropic displacement parameters, and ORTEP drawings for all structures are given in the supplementary material of ref 9.

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Registry No. *cis-mer*-$MoOCl_2(PMe_3)_3$, 90397-97-0; *mer*-$MoCl_3(PMe_3)_3$, 90761-72-1; *cis-mer*-$MoOCl_2(PMe_2Ph)_3$, 30134-06-6; *mer*-$MoCl_3(PMe_2Ph)_3$, 36926-67-7; $MoCl_4(THF)_2$, 16998-75-7; $MoCl_3(THF)_3$, 31355-55-2.

Supplementary Material Available: Tables of atomic coordinates for all structures (3 pages). Ordering information is given on any current masthead page.

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[38] The composition as determined by refining site occupancies typically indicated slightly higher oxo contents than determined by ^{1}H NMR analysis of the bulk sample. The small discrepancy may be due to the possibility that the composition of the crystal selected for X-ray analysis was not representative of the bulk sample. Alternatively, the difference in compositions may be an artifact due to the fact that disorder model in which oxygen and chlorine are refined at the *same* site does not model well the true system in which these atoms are at different sites.

The Dimolybdenum(V) Sulfur Bridge and Diazonium Ions: Formation of Dimolybdenum Diazosulfides

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Abstract: Arenediazonium ions, $ArNN^+$, bind to the sulfur bridge of the dimolybdenum anions $[Mo_2(NAr')_2(S_2P(OC_2H_5)_2)_2(\mu\text{-}S)_2(\mu\text{-}O_2CR)]^-$ to give dimolybdodiazosulfides $[Mo_2(NAr')_2(S_2P(OC_2H_5)_2)_2(\mu\text{-}S)(\mu\text{-}O_2CR)(\mu\text{-}SNNAr)]$ containing the $ArNNS^-$ bridge ligand. The diazosulfides were reasonably stable at low temperatures, decomposing slowly to products characteristic of aryl radical intermediates, including H abstraction of solvent. An imido exchange reaction was observed between the metal imido groups and the arenediazo portion. Back-bridge attack was identified as a radical mechanistic step available to the $Mo_2(\mu\text{-}S)_2$ core. Characterization methods included ^{15}N NMR spectroscopy, for which data for organic diazosulfides ArNNSR and imidomolybdenum dimers are reported.

Introduction

The reactions of arenediazonium ions with transition-metal systems have been of interest for some time in both organic and inorganic chemistry. Several well-developed organic synthetic schemes utilize the arenediazonium–transition-metal ion combination, although the exact intermediate involved is not necessarily understood.[1,2] Discrete metal–diazo complexes have been studied for some time as the products of reactions of transition-metal reagents with diazonium ions: common product types include metal–diazenido, M–NNAr, and metal–diazene, M–NHNAr, complexes.[3-5] Studies of these systems have been of particular interest as analogues of nitrosyl- and dinitrogen–metal systems, including possible applications to mechanisms of dinitrogen fixation.[3,5,6]

In the diazenido and diazene complexes, the diazonium coordinates via nitrogen to the metal. A very different type of product is available for reaction of diazonium ions with sulfidometal systems. This reactivity is based on the organic chemistry of thiolate–diazonium ion reactions,[7] which yield diazosulfides directly (eq 1) or which lead overall to thiodediazoniation (eq 2). The latter provides a synthetic route to aryl sulfides.[7] Diazosulfides themselves have been of interest in photographic applications,[8] as sources of aryldiazenyl radicals,[9] and in synthetic applications.[10]

$$ArNN^+ + RS^- \rightleftharpoons ArNNSR \qquad (1)$$

$$ArNN^+ + RS^- \longrightarrow ArSR + N_2 \qquad (2)$$

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