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Understanding Re−NO Bond Distances: An Analysis of Disorder in [(η^5-$C_5H_4SiMe_3$)Re$(CO)_2$NO]$^+$, [(η^5-C_5H_4Me)Re$(CO)_2$(NO)]$^+$, and Related Compounds

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Summary: Apparently elongated Re−NO and shortened Re−CO bonds in the new complexes [(η^5-C_5H_4R)Re$(CO)_2$-NO]BF_4 (R = $SiMe_3$, Me) can be understood in terms of random positional disorder in the unit cell. We report a thorough crystallographic analysis of similar compounds in the literature and find many instances with erroneous Re−NO and Re−CO bond lengths due to unrecognized or unreported disorder. Positional disorder is noted for achiral substituted cyclopentadienyl complexes of rhenium, whereas crystallographic packing disorder is noted for the chiral complexes.

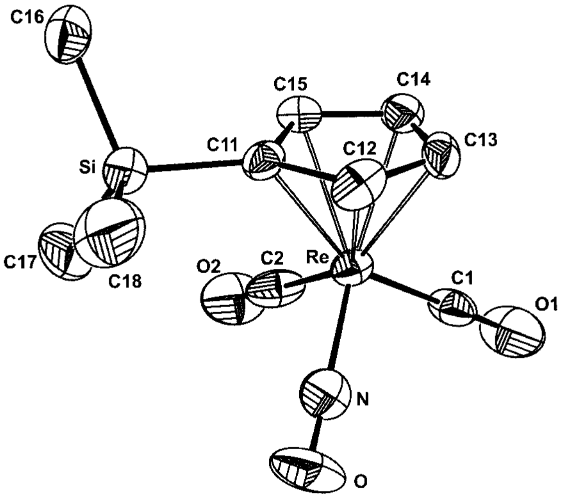

Figure 1. Structural diagram of [(η^5-$C_5H_4SiMe_3$)Re$(CO)_2$-(NO)]$^+$ (**I**) with ellipsoids at the 30% probability level. Selected distances (Å): Re−C(1), 1.88(1); Re−C(2), 1.90(1); Re−N, 1.87(1); $Cp_{centroid}$−Re, 1.93(1); C(1)−O(1), 1.14(1); C(2)−O(2), 1.13(2); N−O, 1.15(2); C(11)−Si, 1.87(1).

Random positional disorder of isoelectronic ligands in organometallic complexes is a well-recognized phenomenon in the crystallographic literature.[1−9] Of particular interest to our research group are complexes of the type [(η^5-$C_5H_{5-x}R_x$)Re$(CO)_y$(NO)L_z], which have the potential for stereospecifically binding prochiral unsaturated species.[10−16] In the literature, many structures with NO and CO ligands bound to Re, and possibly other transition metals, exhibit crystallographic disorder, which is either unreported or unrecognized. Our previously unreported complexes, [(η^5-$C_5H_4SiMe_3$)Re$(CO)_2$(NO)]$^+$$BF_4$ (**I**) and [(η^5-C_5H_4Me)Re$(CO)_2$(NO)]BF_4 (**II**),[17] exhibit unambiguous random positional disorder of the ligand set, which has enabled us to more thoroughly understand the disorder in analogous crystal structures reported in the literature.

We found **I** crystallizes from CH_2Cl_2/hexanes (50:50) as yellow, platelike prisms (orthorhombic, $P2_12_12_1$, $a/b/c$ = 7.9610(2)/12.8280(3)/15.7090(4) Å; $Z = 4$; $R/R_w = 3.6/3.6\%$; mp (DSC) = 141−143 °C), and **II** crystallizes from CH_2Cl_2/hexanes (50:50) as yellow platelike prisms (monoclinic, $P2_1/n$, $a/b/c$ = 7.8992(3)/11.4059(3)/13.3298(6) Å, $\beta = 96.961(2)°$; $Z = 4$; $R/R_w = 5.3/5.7\%$; mp (DSC) = 34−36 °C). ORTEP plots of **I** and **II** are shown in Figures 1 and 2, respectively.

In the crystal structures of **I** and **II** we noted that the observed bond distances for Re−CO (1.884 and 1.896 Å; 1.922 and 1.900 Å) and Re−NO (1.874 and 1.882 Å) were unexpectedly outside previously crystallographically reported ranges (literature: Re−CO = 1.898−1.978 Å; Re−NO = 1.734−1.766 Å).[18] We also noted that

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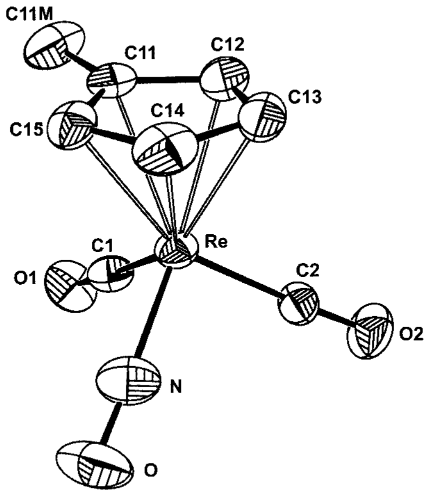

Figure 2. Structural diagram of [(η^5-C$_5$H$_4$Me)Re(CO)$_2$(NO)]$^+$ (**II**) with ellipsoids at the 30% probability level. Selected distances (Å): Re−C(1), 1.92(1); Re−C(2), 1.90(1); Re−N, 1.88(1); Cp$_{\text{centroid}}$−Re, 1.94(1); C(1)−O(1), 1.15(1); C(2)−O(2), 1.14(1); N−O, 1.15(1); C(11)−C(11M); 1.48(2).

the observed Re−CO and Re−NO bond distances were very similar in length. Since the CO ligand is a weaker π-acceptor than NO, the Re−NO bond length is expected to be shorter than the Re−CO bond, which is reflected in the literature values.[18] Discrepancies in bond distances are usually an indication of unusual behavior, which may be attributed to factors such as steric hindrance, *trans*- or *cis*-bonding effects, π-back-bonding, or crystallographic packing disorder. Our observed Re−NO bond lengths of 1.87 and 1.88 Å in **I** and **II** would make these two of the longest Re−NO bond lengths for cyclopentadienyl complexes of rhenium reported (Table 1). Lengthening of the Re−NO bond in **I** and **II** to this extent is unlikely to arise from either steric or bonding effects. (The cone angle of η^5-C$_5$H$_4$Me is 141°, whereas the cone angle of η^5-C$_5$H$_4$SiMe$_3$ is 158°.[19] However, the Re−NO bond lengths for **I** and **II** differ by 0.01 Å (Table 1), indicating that the Re−NO bond length is largely independent of the steric size of the cyclopentadienyl ligand.) Review of the crystallographic structural data for **I** and **II** indicates that positional disorder is responsible for the apparent elongation of the Re−NO bond. In **I**, the Re−NO and both Re−CO distances are nearly equivalent at an average of 1.88 Å, which is equivalent to the arithmetic mean of the average bond length of the reported literature values of two rhenium carbonyls (1.94 Å) and one Re−NO (1.75 Å). Attempts at refinement of the nitrogen atom showed no distinct thermal positional preference at each of the three positions. Therefore, the nitrogen position was arbitrarily chosen as the atom closest to the metal to be consistent with the expected relative π-acceptor abilities of NO and CO. The disorder in the crystal structures of **I** and **II** indicate that during crystal packing there is no positional preference for the nitrosyl ligand, due to the isostructural and isoelectronic nature of the NO and CO ligands; thus the nitrosyl randomly packs in any of the three possible configurations.

We have found 22 structures in the Cambridge Crystallographic Data Center that contain cyclopentadienyl rhenium structures with both Re−NO and Re−CO ligands (Table 1).[20−36] We found an additional 40 structures that contain both Re−NO and Re−CO ligands, but without the cyclopentadienyl ligand (see Supporting Information). In this communication, we analyze all 62

Table 1. Reported Re−NO (Å) and Re−CO (Å) Bond Lengths for All Complexes Comparable to I and II in the Cambridge Crystallographic Database

complex	Re−NO	Re−CO
[(η^5-C$_5$H$_4$SiMe$_3$)Re(CO)$_2$(NO)]BF$_4$ (**I**)	1.874	1.884
		1.896
[(η^5-C$_5$H$_4$Me)Re(CO)$_2$(NO)]BF$_4$ (**II**)	1.882	1.922
		1.900
[(1,4,7-triazacyclononane)Re(CO)(NO)(CH$_3$)]-[1*S*-C$_{10}$H$_{14}$BrO$_4$S]·H$_2$O[20]	1.828	1.819
[{(1,4,7-triazacyclononane)Re(CO)(NO)}$_2$-	1.770	1.834
(μ-CH$_2$OCH$_2$)]I$_2$[20]	1.706	1.844
[(η^5-C$_5$H$_5$)Re(CO)(NO)(PPh$_3$)]$_2$[W$_6$O$_{19}$][21]	1.819	1.865
[(η^5-C$_5$Me$_5$)Re(CO)$_2$(NO)]I$_2$[22]	1.900	1.890
[(η^5-C$_5$Me$_5$)Re(CO)$_2$(NO)]BF$_4$[22]	1.855	1.886
[(η^5-C$_5$Me$_5$)Re(CO)(NO)(I)][22]	1.847	1.918
[(η^5-C$_5$H$_5$)Re(CO)(NO)(SMe$_2$)]CF$_3$SO$_3$[23]	1.775	1.901
[η^5:η^1-C$_5$H$_4$(CH$_2$)$_2$NMe$_2$Re(CO)(NO)]BPh$_4$[24]	1.833	1.857
[(η^5-C$_5$Me$_5$)(CO)(NO)ReC(OSiMe$_3$)═P-*t*-Bu][25]	1.766	1.932
[(η^5-C$_5$H$_5$)(CO)(NO)ReC(OSiMe$_3$)═P-*t*-Bu][25]	1.752	1.908
[(1,4,7-triazacyclononane)Re(CO)(NO)(NH$_3$)]Br$_2$[26]	1.818	1.874
[(η^5-C$_5$Me$_5$)(CO)(NO)Re(μ_2-η^3-CO$_2$)-WCp$_2$]BF$_4$[27]	1.845	1.888
[(tmtaa)Ti(μ_2-η^3-O$_2$C)Re(CO)(NO)(η^5-C$_5$Me$_5$)]BF$_4$[28]	1.775	1.924
[(η^5-C$_5$Me$_5$)(CO)(NO)Re(CO$_2$)Rh(η^4-COD)]$_2$·	1.786	1.903
CH$_2$Cl$_2$·C$_5$H$_{12}$[29]	1.818	1.878
[(η^5-C$_5$Me$_5$)(CO)(NO)Re(CO$_2$)Sn(Cl)Me$_2$][30]	1.783	1.926
[(η^5-C$_5$Me$_5$)Re(CO)(NO)(CO$_2$)Sn(O$_2$C)(NO)-(CO)Re(η^5-C$_5$Me$_5$)Me$_2$][30]	1.776	1.909
[(η^5-C$_9$Me$_7$)Re(CO)$_2$(NO)]BF$_4$[31]	1.928	1.898
	1.900	
[(η^5-C$_5$Me$_5$)Re(CO)(NO)(CO$_2$)SnPh$_3$][32]	1.795	1.903
[(η^5-C$_5$Me$_5$)Re(CO)(NO)(CO$_2$)Re(CO)$_3$PPh$_3$][32]	1.766	1.896
[(η^5-C$_5$Me$_5$)Re(CO)(NO)(CO$_2$)SnMe$_3$][33]	1.780	1.902
[(η^5-C$_5$Me$_5$)Re(CO)(NO)(CO$_2$)Re(PPh$_3$)$_2$(CO)$_2$][34]	1.813	1.867
[(η^5-C$_5$Me$_5$)Re(CO)(NO)(CO$_2$)Mo(η^5-C$_5$H$_5$)][35]	1.855	1.798
[(η^5-C$_5$Me$_5$)Re(CO)(NO)(CO$_2$)Zr(Cl)(η^5-C$_5$H$_5$)$_2$][36]	1.769	1.915

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reported structures containing both Re−CO and Re−NO bonds. All the structures listed in Table 1 have Re−NO bond distances that either are at the upper limit or exceed the expected range of 1.734−1.766 Å.[18] Similarly, the Re−CO bond distances are either reported at the lower limit or less than the expected range of 1.898−1.978 Å.[18] The Re−NO and Re−CO bond distances for the majority of the complexes listed in Table 1 can be understood in terms of a crystallographic disorder argument. There are two variations of the disorder depending on the nature of the compound: random positional disorder in achiral complexes and packing disorder in chiral complexes. Random positional disorder occurs when there is no positional preference for a ligand relative to the other ligands during crystal packing. Packing disorder occurs when different stereoisomers pack in adjacent unit cells (see below).

In the literature of the selected complexes (Table 1), several workers have commented on the discrepancy of the Re−NO and Re−CO bond lengths. However, many workers have failed to explicitly recognize a disorder model and, consequently, report erroneous Re−NO and Re−CO bond distances. Furthermore, if the complex is chiral and the disorder is not properly recognized, then the incorrect absolute stereochemistry can be assigned. In the following section, we present illustrative examples of positional and packing disorder for complexes reported in the literature. In the case of the complexes discussed, the disorder was not recognized in the original papers. All other structures with anomalous Re−NO and Re−CO bond lengths presented in Table 1 can be understood by analogous disorder analyses.

Wieghardt has reported the structure of $[(1,4,7\text{-triazacyclononane})Re(NO)(CO)(CH_3)]^+$ as a pure enantiomer with an *S* configuration.[20] The Re−NO and Re−CO bond lengths in $[(1,4,7\text{-triazacyclononane})Re(NO)(CO)(CH_3)]^+$ were reported as 1.828 and 1.819 Å, respectively.[20] With the reported space group and our recognition of disorder, it is most likely that the reported structure is that of a mixture of stereoisomers.

Racemic $[(\eta^5\text{-}C_5H_5)Re(CO)(NO)(PPh_3)]_2[W_6O_{19}]$ reported by Gladysz exhibits a lengthened Re−NO bond (1.819 Å), which, at the time of publication, was the longest observed for this class of compounds.[21] Correspondingly, the Re−CO bond length was shorter than expected. On the basis of the crystallographic observations in the title compounds, the elongated Re−NO bond length in $[(\eta^5\text{-}C_5H_5)Re(CO)(NO)(PPh_3)]_2[W_6O_{19}]$ can also be understood using a crystallographic packing disorder model. In solution, $[(\eta^5\text{-}C_5H_5)Re(CO)(NO)(PPh_3)]^+$ exists as a pair of enantiomers[21] that can carry into the crystal during packing. If we assume the two enantiomers are present in a ratio different from 1:1, then we can understand the elongated Re−NO bond in terms of the disorder created by packing the mixture of enantiomers. Using a back-calculation analysis, similar to the methods used to compensate for the elongated Re−NO bond lengths in **I** and **II**, an approximate ratio of the two enantiomers in the crystal is 1:3. The 1:3 ratio of enantiomers generates Re−NO and Re−CO bond lengths that closely match theoretical values reported in the international tables.[18] The presence of disorder in the structure of $[(\eta^5\text{-}C_5H_5)Re(CO)(NO)(PPh_3)]_2[W_6O_{19}]$ was not recognized at the time of publication, but the authors carefully refined the NO position in order to obtain the best structure.

Since $[(\eta^5\text{-}C_5H_5)Re(CO)(NO)(PPh_3)]^+$ is chiral, and the $[(\eta^5\text{-}C_5H_5)Re(CO)(NO)(PPh_3)]_2[W_6O_{19}]$ complex is racemic, a nondisordered crystal would form in one of two *meso*-diastereomeric forms, RS or SR (for example, RS/RS/RS/RS/RS/RS). However, the approximate crystal packing disorder of 25% indicates a nonrandom packing imperfection of the two *meso*-diastereomeric forms in the single-crystal lattice, for example RS/RS/RS/SR/RS/RS). Therefore, the observation of the elongated Re−NO and the shortened Re−CO bond lengths can be explained by this imperfection during the formation of the crystal lattice, and the level of disorder may vary from crystal to crystal. This type of analysis may also be applied to other chiral rhenium compounds to determine the extent of packing disorder and imperfection.

Working with the achiral $[(\eta^5\text{-}C_5Me_5)Re(CO)_2(NO)]I$ and $[(\eta^5\text{-}C_5Me_5)Re(CO)_2(NO)]BF_4$ complexes, Hubbard reported Re−NO and Re−CO bond lengths similar to those observed in **I** and **II**.[41] The nitrosyl ligand in $[(\eta^5\text{-}C_5Me_5)Re(CO)_2(NO)]^+$ is reported to sit on the crystallographic mirror, but because of the isostructural similarities of the carbonyl and nitrosyl ligands, a crystallographic differentiation between the CO and NO ligands is not definitive. Observed Re−NO bond lengths in $[(\eta^5\text{-}C_5Me_5)Re(CO)_2(NO)]I$ (1.90 Å) and $[(\eta^5\text{-}C_5Me_5)Re(CO)_2(NO)]BF_4$ (1.855 Å; Table 1)[41] are substantially lengthened,[18] whereas the carbonyls in the isomorphous structures were observed to be similar in length and shorter than expected (1.89 Å; Table 1). The lengths of the Re−CO and Re−NO bonds in $[(\eta^5\text{-}C_5Me_5)Re(CO)_2(NO)]^+$ are quite similar and are likely due to a random positional disorder as observed in **I** and **II**.

In this study, we have only examined complexes that contain both Re−CO and Re−NO bonds. There is no reason to believe that this behavior is unique to Re, and it is likely that analogously disordered CO/NO structures are seen with many other transition metal complexes.

In conclusion, with the preparation of **I** and **II** we have complexes that clearly exhibit unambiguous crystallographic disorder. The recognition of this disorder has allowed us to analyze all structures in the literature that contain both Re−NO and Re−CO moieties. During this analysis, we have found a significant number of structures with unreported or unrecognized disorder.

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Supporting Information Available: Details of X-ray structure determinations, including final coordinates, thermal parameters, bond distances, and bond angles. Table of all complexes containing both Re−NO and Re−CO bonds reported in the Cambridge Crystallographic Data Center.

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