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Mononuclear and Binuclear Rhenium Carbonyl Nitrosyls: Comparison with Their Manganese Analogues

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The structures and energetics of $Re(NO)(CO)_n$ ($n = 5, 4, 3, 2$) and $Re_2(NO)_2(CO)_n$ ($n = 7, 6$) have been investigated using density functional theory. For $Re(NO)(CO)_4$ the preferred structure is an equatorially substituted trigonal bipyramid analogous to the known structure of the manganese analogue. The lowest energy structures for the unsaturated $Re(NO)(CO)_n$ ($n = 3, 2$) species can be derived from this structure by removal of carbonyl groups. A structure is found for $Re(NO)(CO)_5$ in which the NO ligand has attached to one of the CO ligands by forming a C−N bond to give an unprecedented η^2-OCNO ligand. However, this structure is predicted to undergo exothermic CO loss to give $Re(NO)(CO)_4$. The preferred structures for the binuclear derivatives $Re_2(NO)_2(CO)_n$ ($n = 7, 6$) are structures unprecedented for the manganese analogues and consist of a $Re(CO)_5$ unit linked to a $Re(NO)_2(CO)_{n-5}$ unit. However, only slightly higher in energy are structures of the type $Re_2(\mu\text{-}NO)_2(CO)_n$ with two bridging nitrosyl groups, similar to the global minima for the manganese analogues. These results predict extensive areas of new rhenium carbonyl nitrosyl chemistry. Thus the synthesis of $Re(NO)(CO)_4$ by methods related to the synthesis of the manganese analogue appears to be feasible. In addition, the existence of an extensive series of $Re(NO)_2(CO)_2X$ derivatives, as well as a $Re_2(NO)_4(CO)_4$ dimer, is predicted.

1. Introduction

A number of first row transition metal carbonyl nitrosyls are known which are isoelectronic with homoleptic metal carbonyl derivatives.[1,2] These include the sequence of tetrahedral molecules $Co(NO)(CO)_3 \rightarrow Fe(NO)_2(CO)_2 \rightarrow Mn(NO)_3CO \rightarrow Cr(NO)_4$ isoelectronic and isostructural with $Ni(CO)_4$ and the less extensive series of five-coordinate molecules $Mn(NO)(CO)_4 \rightarrow Cr(NO)_2(CO)_3$ isoelectronic with $Fe(CO)_5$. However, analogous metal carbonyl nitrosyls of the second or third row transition metals have never been synthesized.

One of the most promising candidates for a third row transition metal carbonyl nitrosyl is $Re(NO)(CO)_4$, isoelectronic with $Os(CO)_5$. The manganese analogue, $Mn(NO)(CO)_4$, has been known since 1961[3] and is readily prepared by reaction of $HMn(CO)_5$ with the nitrosylating agent N-nitroso-N-methyl-*p*-toluenesulfonamide ("Diazald") according to the following equation (Ts = p-toluenesulfonyl):

$$HMn(CO)_5 + TsN(NO)Me \rightarrow Mn(NO)(CO)_4 + CO + TsN(H)Me \quad (1)$$

Since $HRe(CO)_5$ is readily synthesized, an analogous reaction would appear to be possible for the synthesis of $Re(NO)(CO)_4$. However, one possible difficulty might be the need for the liberation of one equivalent of carbon monoxide to form $Re(NO)(CO)_4$. In this connection the metal−carbonyl bond is often found to be more difficult to break for third row transition metals relative to first and second row transition metals. Thus, the nitrosylation of $HRe(CO)_5$ might only go as far as $Re(NO)(CO)_5$ and stop there. The pentacarbonyl $Re(NO)(CO)_5$ could in principle be a stable

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18-electron octahedral complex if the nitrosyl group is a bent formal one-electron donor rather than the usual linear formal three-electron donor. A metal carbonyl nitrosyl with a bent nitrosyl group and no ligands besides carbonyl and nitrosyl would be unprecedented.

The rhenium carbonyl nitrosyl system has some other features of interest. One feature of the metal pentacarbonyls $M(CO)_5$ ($M = Fe, Os$), to which $Re(NO)(CO)_4$ would be isoelectronic, is their tendency to undergo facile conversion to the corresponding binuclear derivatives $M_2(CO)_9$. In this connection the structures of the iron and osmium derivatives are distinctly different. Thus, the iron derivative $Fe_2(CO)_6(\mu\text{-}CO)_3$ has three bridging carbonyl groups[4,5] whereas the osmium derivative $Os_2(CO)_8(\mu\text{-}CO)$ has only a single bridging carbonyl group.[6,7] The manganese derivative $Mn_2(NO)_2(CO)_7$ is unknown but is predicted[8] to prefer a structure with two bridging nitrosyl groups.

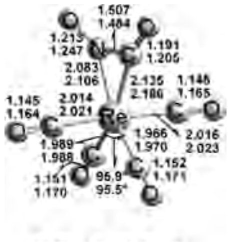
This paper describes the use of density functional theory (DFT) to investigate the chemistry of mononuclear and binuclear rhenium nitrosyl carbonyl derivatives with the following more specific objectives:

(1) Examination of the structures of $Re(NO)(CO)_4$ and any possible $Re(NO)(CO)_5$ intermediates in the nitrosylation of $HRe(CO)_5$;

(2) Examination of the most likely binuclear derivatives including $Re_2(NO)_2(CO)_7$ isoelectronic with $M_2(CO)_9$ ($M =$ Fe, Os) as well as the unsaturated $Re_2(NO)_2(CO)_6$.

2. Theoretical Methods

Electron correlation effects were considered by employing DFT, which has evolved as a practical and effective computational tool, especially for organometallic compounds.[9−17] In this work, the two DFT methods BP86 and MPW1PW91 were used. The BP86 method is a pure DFT method combining Becke's 1988 exchange functional with Perdew's 1986 correlation functional.[18,19] The MPW1PW91 method[20] is a so-called second-generation[21] functional, namely a combination of the modified Perdew−Wang exchange functional with the Perdew−Wang 91 gradient-correlation functional.[22] The MPW1PW91 method has been found to be more suitable for the structures and energetics of second and third row transition metal systems while the BP86 method usually provides better vibrational frequencies.[23,24]



5S-1 (C_1)

Figure 1. Optimized structure of $Re(NO)(CO)_5$. In the figures the bond distances are reported in Å with the figures on the top being the result obtained by the MPW1PW91 method and those on the bottom by the BP86 method.

For the third row transition metals, the large numbers of electrons can increase exponentially the computational efforts. To reduce the cost, relativistic effective core potential (ECP) basis sets were employed. In this study the SDD (Stuttgart-Dresden ECP plus DZ)[25] ECP basis set was used for the rhenium atoms. For the C, N, and O atoms, double-ζ plus polarization (DZP) basis sets were used. They are the Huzinaga−Dunning contracted double-ζ sets[26,27] plus a set of spherical harmonic d polarization functions with orbital exponents $\alpha_d(C) = 0.75$, $\alpha_d(N) = 0.80$, and $\alpha_d(O) = 0.85$ and designated as (9s5p1d/4s2p1d).

The geometries of the structures were fully optimized using the two selected DFT methods with the SDD ECP basis set. The vibrational frequencies were determined by evaluating analytically the second derivatives of the energy with respect to the nuclear coordinates at the same levels. The corresponding infrared intensities were also evaluated analytically. All of the computations were carried out with the Gaussian 03 program.[28] The fine grid (75, 302) was the default for evaluating integrals numerically, and the tight (10^{-8} hartree) designation is the default for the energy convergence. The finer grid (120, 974) was used only for investigating the small imaginary vibrational frequencies.[29] All of the predicted triplet structures are found to have negligible spin contamination, that is, the values of $S(S + 1)$ are very close to the ideal outcome value of 2.

3. Results

3.1. Mononuclear Derivatives. 3.1.1. $Re(NO)(CO)_5$. The global minimum of $Re(NO)(CO)_5$ (**5S-1** in Figure 1 and Table 1) is predicted to be a genuine minimum with four linear CO groups and an unprecedented OCNO ligand obtained by forming a C−N bond between one carbonyl group and the nitrosyl group. The length of this C−N bond is 1.507 Å (MPW1PW91) or 1.484 Å (BP86) suggesting a single bond. In this OCNO ligand the Re−N−O and Re−C−O angles are predicted to be 148.4° and 162.1°

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Table 1. Total Energies (E, in Hartree), Number of Imaginary Vibrational Frequencies (Nimag), Angles Re−N−O and Re−C−O, and the Dihedral Angle O−N−C-O for **5S-1**

5S-1 (C_1)	E	Nimag	Re−N−O	Re−C−O	dihedral O−N−C−O
MPW1PW91	−774.93566	0	148.4°	162.1°	33.5°
BP86	−775.27262	0	141.9°	155.1°	44.1°

(MPW1PW91) or 141.9° and 155.1° (BP86), respectively. The Re−C and Re−N distances to the OCNO ligand in **5S-1** are predicted to be ~0.12 Å longer than usual Re−C and Re−N distances to terminal carbonyl and nitrosyl groups, respectively. The N−O and C−O bond lengths in the OCNO ligand are also predicted to be longer than those in the usual terminal CO or NO groups, suggesting lower bond orders. Assuming that the OCNO ligand is a formal three-electron donor, the rhenium atom in **5S-1** has the favored 18-electron configuration. The alternative structure of Re(CO)$_5$(NO) with all linear carbonyls and a bent NO group without N−C bonding is found, but at the very high energy of ~125 kcal/mol above **5S-1.**

3.1.2. Re(NO)(CO)$_4$. Four singlet and one triplet energetically low lying structures are found for Re(NO)(CO)$_4$ (Figure 2 and Table 2). The rhenium atom in all of the singlet structures is predicted to have the favored 18-electron configuration, assuming that the nitrosyl group is a three-electron donor. The global minimum **4S-1** (Figure 2 and Table 2) of Re(NO)(CO)$_4$ is predicted to be a C_{2v} trigonal bipyramid singlet structure analogous to the known Mn(NO)(CO)$_4$ (ref 30) as well as Fe(CO)$_5$ (ref 31) and the isoelectronic Os(CO)$_5$ (refs 32, 33). This structure **4S-1** has all linear Re−C−O and Re−N−O bonds and shows the nitrosyl group in an equatorial position. A C_{4v} square pyramid structure **4S-2** at ~7 kcal/mol above **4S-1** (Figure 2 and Table 2) is a transition state with an imaginary vibrational frequency at 79i cm^{-1} (BP86 in Table 2). Following the corresponding normal mode leads to the global minimum **4S-1**. Structure **4S-2** is predicted to have all linear Re−C−O and Re−N−O bonds. A singlet C_{3v} trigonal bipyramidal structure **4S-3** (Figure 2 and Table 2) at ~12 kcal/mol above **4S-1** has a pair of degenerate imaginary vibrational frequencies at 28i cm^{-1} (BP86 in Table 2), which cannot be removed by using a finer integration grid (120, 974). Following the corresponding normal mode leads to structure **4S-1**.

A singlet structure **4S-4** of Re(NO)(CO)$_4$ with an unusual η^2-NO group (Figure 2 and Table 2) lies ~18 kcal/mol in energy above the global minimum **4S-1** and has all real vibrational frequencies. The Re−N−O angle is predicted to be ~80°, while the Re−N, Re−O, and N−O bond distances in **4S-4** are predicted to be 2.084 Å, 2.208 Å, and 1.221 Å (MPW1PW91) or 2.086 Å, 2.247 Å, and 1.246 Å (BP86), respectively. The η^2-NO nitrosyl group in **4S-4** appears to be a formal three-electron donor, thereby giving the rhenium atom the favored 18-electron configuration.

The only triplet structure found for Re(CO)$_4$(NO) within 25 kcal/mol of the global minimum **4S-1**, namely **4T-1** (Figure 2 and Table 2), is predicted to be a genuine minimum at ~14.5 kcal/mol (MPW1PW91) or ~21.2 kcal/mol (BP86) higher in energy than the global minimum **4S-1.** The Re−N−O angle in **4T-1** is predicted to be ~143°, suggesting a bent one-electron donor nitrosyl, thereby giving the rhenium atom a 16-electron configuration consistent with a triplet electronic state.

3.1.3. Re(NO)(CO)$_3$. Six low lying structures (three singlet and three triplet structures) were found for Re(NO)(CO)$_3$ (Figure 3 and Table 3). The global minimum of Re(NO)(CO)$_3$ is predicted to be a singlet or a triplet structure depending on the method. The MPW1PW91 method predicts a C_s triplet structure **3T-1** as the global minimum, with the lowest lying singlet structure **3S-1** at ~3.4 kcal/mol higher in energy than **3T-1**. However, the BP86 method predicts the singlet structure **3S-1** (C_s) to be the global minimum with the triplet structure **3T-1** lying energetically at ~3.1 kcal/mol above **3S-1.** Both structures are predicted to be genuine minima, having all real vibrational frequencies. The structures of **3S-1** and **3T-1** can be derived from those found in previous DFT studies on the isoelectronic Os(CO)$_4$ by replacing one carbonyl group with a nitrosyl group.

Another singlet structure **3S-2** (C_s) of Re(NO)(CO)$_3$ with all linear CO and NO groups is predicted to be almost degenerate in energy with **3S-1** by 0.1 kcal/mol (MPW1PW91) or 3.5 kcal/mol (BP86) with all real vibrational frequencies. Structures **3S-1** and **3S-2** can be derived from the trigonal bipyramidal structure **4S-1** (Figure 2) by removing an equatorial or an axial carbonyl group, respectively.

A structure with an η^2-NO group is also found for Re(CO)$_3$(NO) (**3S-3** in Figure 3 and Table 3), which is predicted to lie 15.2 kcal/mol (MPW1PW91) or 17.0 kcal/mol (BP86) in energy above **3S-1** with all real vibrational frequencies. The Re−N−O angle in **3S-3** is predicted to be 89.6° (MPW1PW91) or 95.3° (BP86), while the Re−N, Re−O, and N−O bond lengths are predicted to be 1.928 Å, 2.279 Å, and 1.228 Å (MPW1PW91) or 1.929 Å, 2.393 Å, and 1.249 Å (BP86), respectively. The Re−N distance to the η^2-NO group in **3S-3** is predicted to be ~0.15 Å shorter than that for **4S-4**. This shortening of the Re−N distance could arise if the η^2-NO group is a formal five-electron donor in **3S-3** and only a three-electron donor in **4S-4**. A formal five-electron donor η^2-NO group in the Re(η^2-NO)(CO)$_3$ structure **3S-3** would give the rhenium atom the favored 18-electron configuration.

A C_{3v} triplet structure **3T-2** of Re(NO)(CO)$_3$ (Figure 3 and Table 3) with all linear CO and NO groups is predicted to lie at 1.4 kcal/mol (MPW1PW91) or 3.0 kcal/mol (BP86) in energy above **3T-1** with a small degenerate e″ imaginary vibrational frequency at 72i cm^{-1} (BP86 in Table 3). Following one of the corresponding normal modes leads to the triplet global minimum **3T-1.** Another triplet C_s structure **3T-3** of Re(NO)(CO)$_3$ (Figure 3 and Table 3) with all linear CO and NO groups lies 11.8 kcal/mol (MPW1PW91) or 8.1 kcal/mol (BP86) higher in energy than **3T-1** and has no imaginary vibrational frequencies. All of the triplet structures of Re(CO)$_3$(NO) are consistent with 16-electron configura-

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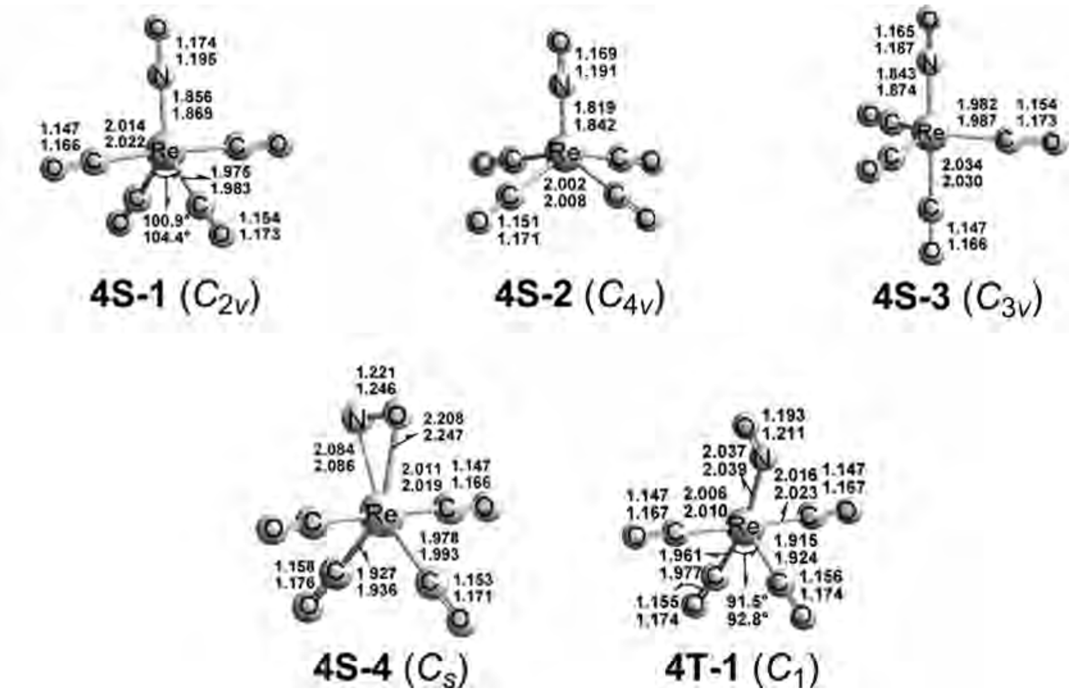

Figure 2. Five optimized $Re(NO)(CO)_4$ structures.

Table 2. Total Energies (*E*, in Hartree), Relative Energies (Δ*E*, in kcal/mol), Number of Imaginary Vibrational Frequencies (Nimag), Re−N−O Angles, and $\langle S^2 \rangle$ of the $Re(NO)(CO)_4$ Structures

	MPW1PW91					BP86				
	E	Δ*E*	Nimag	Re−N−O	$\langle S^2 \rangle$	*E*	Δ*E*	Nimag	Re−N−O	$\langle S^2 \rangle$
4S-1 (C_{2v})	−661.66133	0	0	180.0	0	−661.96793	0	0	180.0	0
4S-2 (C_{4v})	−661.64750	8.7	1(104*i*)	180.0	0	−661.95929	5.4	1(79*i*)	180.0	0
4S-3 (C_{3v})	−661.63873	14.2	2(52*i*,52*i*)	180.0	0	−661.95101	10.6	2(28*i*,28*i*)	180.0	0
4S-4 (C_s)	−661.63526	16.4	0	79.1	0	−661.93615	19.9	0	80.5	0
4T-1 (C_1)	−661.63685	14.5	0	142.6	2.02	−661.93410	21.2	0	143.6	2.01

tions required by the triplet electronic states, assuming that the linear NO group is a formal three-electron donor.

3.1.4. $Re(NO)(CO)_2$. Three low-lying singlet and two low-lying triplet structures were found for $Re(NO)(CO)_2$. All of the structures are predicted to be genuine minima, having all real vibrational frequencies.

The global minimum found for $Re(CO)_2(NO)$ is a singlet structure **2S-1** (Figure 4 and Table 4) with a bent NO group. The Re−N−O angle is predicted to be 156.3° (MPW1PW91) or 155.3° (BP86). The singlet structure **2S-2** (Figure 4 and Table 4) with a η^2-NO group is predicted to lie in energy above **2S-1** by only 2.8 kcal/mol (MPW1PW91) or 4.0 kcal/mol (BP86). Conceptually, structure **2S-2** can be derived from structure **3S-3** by removing a carbonyl group. The Re−N−O angle in **2S-2** is predicted to be 82.2° (MPW1PW91) or 81.3° (BP86), while the Re−N and Re−O bond lengths are predicted to be shorter than those in **3S-3** (Figure 3) by ~0.05 Å and ~0.16 Å, respectively. A relatively long N−O distance is found for **2S-2**, namely 1.272 Å (MPW1PW91) or 1.308 Å (BP86). This long N−O bond is even ~0.05 Å longer than that of **3S-3**, suggesting an N−O single bond. This is supported by an exceptionally low predicted ν(NO) vibrational frequency of 1199 cm^{-1} (BP86 in Table 5). The formal N−O bond order of 1 in the η^2-NO group in **2S-2** suggests a formal NO^{3-} ligand derived from hydroxylamine, NH_2OH by complete deprotonation.

A T-shaped singlet structure **2S-3** for $Re(NO)(CO)_2$ (Figure 4 and Table 4) with all linear CO and NO groups is predicted to lie 11.4 kcal/mol (MPW1PW91) or 11.9 kcal/mol (BP86) higher in energy than **2S-1.** The Re−N bond distance in **2S-3** is found to be the shortest of all the predicted rhenium carbonyl nitrosyl complexes, namely 1.737 Å (MPW1PW91) or 1.758 Å (BP86).

Two triplet structures **2T-1** (C_s) and **2T-2** (C_1) with different arrangements of the one NO and two CO groups were found for $Re(NO)(CO)_2$. These structures have very similar energies within ~2 kcal/mol. Structure **2T-1** lies 6.2 kcal/mol (MPW1PW91) or 8.7 kcal/mol (BP86) above the global minimum **2S-1** whereas structure **2T-2** lies 7.0 kcal/mol (MPW1PW91) or 10.8 kcal/mol (BP86) above **2S-1**.

3.1.5. Vibrational Frequencies. The theoretical ν(CO) and ν(NO) vibrational frequencies together with their infrared intensities for all the mononuclear rhenium carbonyl nitrosyl derivatives $Re(NO)(CO)_n$ are shown in Table 5. In general the BP86 results are found to be most reliable for ν(CO) and ν(NO) frequencies[23] and therefore are those discussed below.

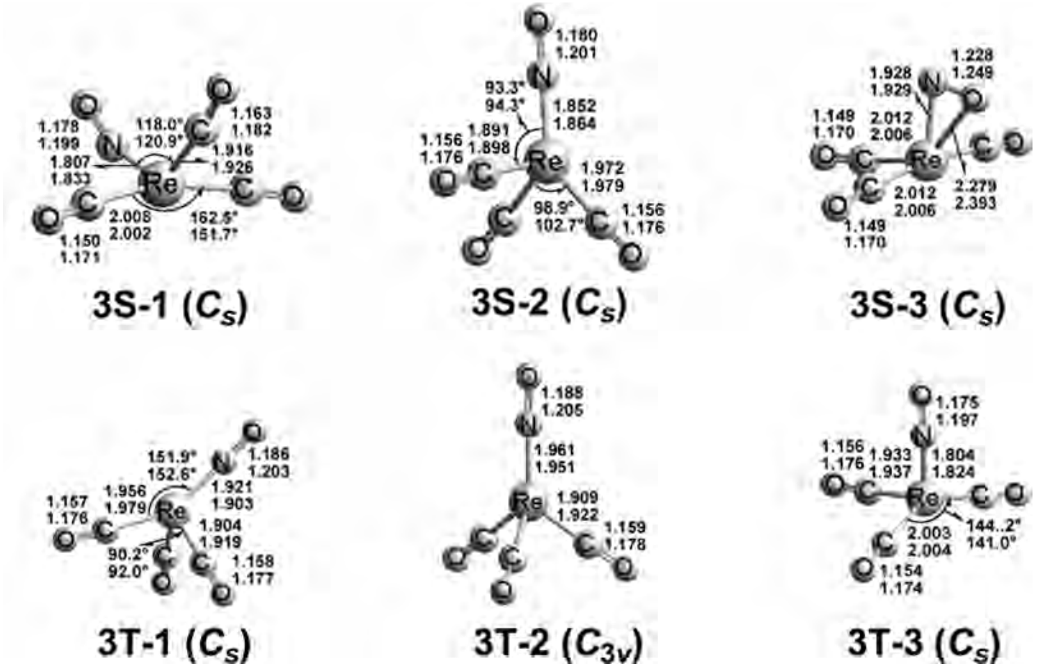

Figure 3. Six optimized $Re(NO)(CO)_3$ structures.

Table 3. Total Energies (*E*, in Hartree), Relative Energies (Δ*E*, in kcal/mol), Number of Imaginary Vibrational Frequencies (Nimag), Re−N−O Angles, and ⟨S²⟩ of the $Re(CO)_3(NO)$ Structures

	MPW1PW91					BP86				
	E	Δ*E*	Nimag	Re−N−O	⟨S²⟩	*E*	Δ*E*	Nimag	Re−N−O	⟨S²⟩
3S-1 (C_s)	−548.28302	0.0	0	159.4	0	−548.56147	0.0	0	158.0	0
3S-2 (C_s)	−548.28283	0.1	0	178.8	0	−548.55588	3.5	0	176.9	0
3S-3 (C_s)	−548.25884	15.2	0	89.6	0	−548.53438	17.0	0	95.3	0
3T-1 (C_s)	−548.28837	−3.4	0	179.1	2.05	−548.55646	3.1	0	177.4	2.01
3T-2 (C_{3v})	−548.28626	−2.0	2(37*i*,37*i*)	180.0	2.02	−548.55178	6.1	2(72*i*,72*i*)	180.0	2.01
3T-3 (C_s)	−548.26965	8.4	0	178.0	2.02	−548.54368	11.2	0	178.4	2.00

The terminal ν(CO) frequencies (Table 5) fall in the ranges 1988−2074 cm^{-1}, 1961−2077 cm^{-1}, 1934−2036 cm^{-1}, and 1900−1983 cm^{-1}, for the $Re(NO)(CO)_5$, $Re(NO)(CO)_4$, $Re(NO)(CO)_3$, and $Re(NO)(CO)_2$ structures, respectively. The decreasing ν(CO) frequencies with decreasing numbers of carbonyl groups relates to increased π* back bonding to the remaining carbonyl groups because of less competition. The carbonyl group in the unusual OCNO ligand in $Re(NO)(CO)_5$ (**5S-1**) exhibits a ν(CO) frequency at 1781 cm^{-1}, which is in the range of bridging ν(CO) vibrational frequencies.

The typical terminal ν(NO) frequencies predicted for the $Re(NO)(CO)_n$ molecules fall in the range 1683−1803 cm^{-1} (Table 5). The one-electron donor bent NO group in **4T-1** (Figure 2) exhibits a lower ν(NO) frequency at 1634 cm^{-1} (Table 5). A still lower ν(NO) frequency predicted at 1467 cm^{-1} (Table 5) arises from the OCNO ligand in **5S-1.** The η^2-NO groups in **4S-4** and **3S-3** are predicted to exhibit even lower ν(NO) frequencies at 1431 cm^{-1} and 1397 cm^{-1} (Table 5), respectively. The lowest ν(NO) frequency found in this work, namely 1199 cm^{-1}, is found in **2S-2**. There the N−O bond is long enough to be a single bond, and the ligand is formally NO^{3-}, derived from hydroxylamine by complete deprotonation.

3.2. Binuclear Derivatives. 3.2.1 $Re_2(NO)_2(CO)_7$. Seven singlet structures with zero, one, two, or three bridging groups were found for $Re_2(NO)_2(CO)_7$ (Figure 5 and Table 6). The two lowest lying structures **7S-1** and **7S-2** are unsymmetrical structures derived from the known[34,35] $Re_2(CO)_{10}$ by replacing three CO groups on one of the rhenium atoms with two NO groups. This leads to unbridged $(OC)_5Re{-}Re(CO)_2(NO)_2$ structures consisting of an $Re(CO)_5$ unit and an $Re(CO)_2(NO)_2$ unit connected by a single Re−Re bond, with different arrangements of CO and NO groups in the $Re(CO)_2(NO)_2$ unit. These structures are almost degenerate in energy. Thus, **7S-1** is predicted to be the global minimum with **7S-2** lying only 0.9 kcal/mol (MPW1PW91) or 3.1 kcal/mol (BP86) higher. The Re−Re distances in the two structures are predicted to be in the range of 3.006−3.143 Å, consistent with experimental values for the Re−Re single bond in $Re_2(CO)_{10}$ of 3.02 Å[34] and 3.041 Å.[35] All of the rhenium atoms have the favored 18-electron configuration. A structure closely related to that of **7S-1** and **7S-2** for the isoelectronic $Os_2(CO)_9$ was found in previous work but only at a significantly higher energy than the global minimum structure.

Structure **7S-3**, of C_s symmetry with two unsymmetrical bridging NO groups (Figure 5 and Table 6) is another local minimum lying above **7S-1** by 7.8 kcal/mol (MPW1PW91)

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(35) Churchill, M. R.; Amoh, K. N.; Wasserman, H. J. *Inorg. Chem.* **1981**, *20*, 1609.

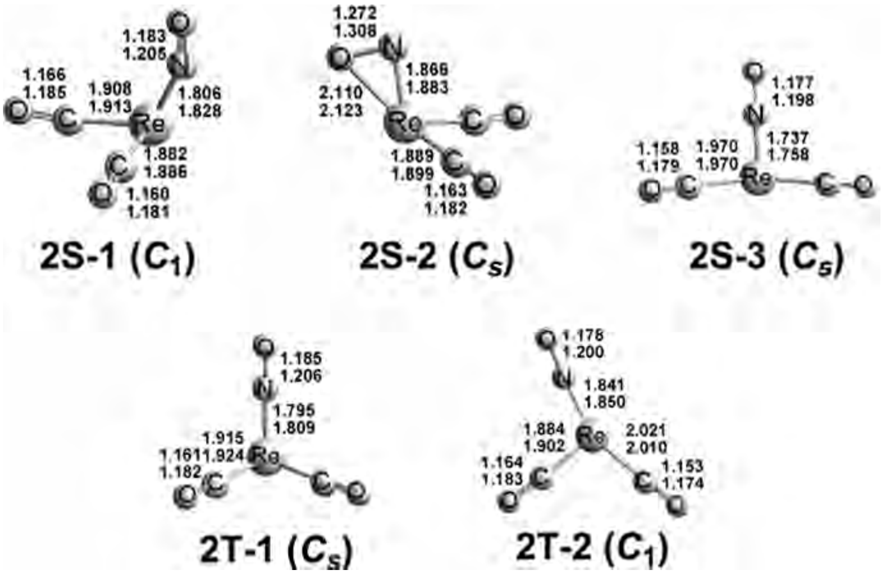


Figure 4. Five optimized $Re(NO)(CO)_2$ structures.

Table 4. Total Energies (E, in Hartree), Relative Energies (ΔE, in kcal/mol), Number of Imaginary Vibrational Frequencies (Nimag), Re−N−O Angles, and $\langle S^2 \rangle$ of the $Re(NO)(CO)_2$ Structures

	MPW1PW91					BP86				
	E	ΔE	Nimag	Re−N−O	$\langle S^2 \rangle$	E	ΔE	Nimag	Re−N−O	$\langle S^2 \rangle$
2S-1 (C_1)	−434.90740	0	0	156.3	0	−435.14928	0	0	155.3	0
2S-2 (C_s)	−434.90288	2.8	0	82.2	0	−435.14298	4.0	0	81.3	0
2S-3 (C_s)	−434.88919	11.4	0	177.3	0	−435.13028	11.9	0	176.7	0
2T-1 (C_s)	−434.89752	6.2	0	168.7	2.04	−435.13538	8.7	0	168.7	2.00
2T-2 (C_1)	−434.89630	7.0	0	179.1	2.04	−435.13206	10.8	0	172.1	2.01

or 12.3 kcal/mol (BP86). The Re−N bond lengths to the unsymmetrical bridging NO groups are predicted to be 2.010 Å and 2.200 Å (MPW1PW91) or 2.003 Å and 2.265 Å (BP86). The predicted Re−Re bond distance at 2.925 Å (MPW1PW91) or 2.962 Å (BP86) corresponds to the single bond required by the 18-electron rule, assuming the bridging NO groups to be three-electron donors. An analogous structure was found to be the global minimum for the manganese analogue $Mn_2(NO)_2(CO)_7$ in a previous DFT study.[8]

The triply bridged structure **7S-4** for $Re_2(NO)_2(CO)_7$ with two symmetrical bridging NO groups and one bridging CO group (Figure 5 and Table 6) is found at 12.5 kcal/mol (MPW1PW91) or 18.2 kcal/mol (BP86) higher in energy than the global minimum **7S-1**. Structure **7S-4** is clearly a transition state rather than a global minimum, since it has a significant imaginary vibrational frequency at $112i$ cm^{-1} (MPW1PW91) or $106i$ cm^{-1} (BP86). Following the corresponding normal mode leads to **7S-3** with two unsymmetrical bridging nitrosyl groups. An attempt to optimize a triply bridging carbonyl structure of $Re_2(NO)_2(CO)_7$ analogous to the known $Fe_2(CO)_9$ structure[4,5] led to the singly CO bridged structure **7S-6** and the unbridged structure **7S-7** (Figure 5 and Table 6). Structure **7S-6** is predicted to lie in energy at 22 kcal/mol above the global minimum **7S-1**. The isoelectronic $Os_2(CO)_9$ system has predicted structures similar to **7S-4** and **7S-6**. However, the $Os_2(CO)_9$ structure analogous to **7S-6** is predicted to be the global minimum and is known experimentally.[6,7]

A singly nitrosyl bridged structure **7S-5** for $Re_2(NO)_2(CO)_7$ (Figure 5 and Table 6) is found at 12.9 kcal/mol (MPW1PW91) or 15.9 kcal/mol (BP86) above the global minimum **7S-1** and has all real vibrational frequencies. The Re−Re distance of 2.942 Å (MPW1PW91) or 2.970 Å (BP86) in **7S-5** suggests the single bond required to give each of the Re atoms the favored 18-electron configuration, assuming that the bridging NO group as well as the terminal NO group is a formal three-electron donor.

3.2.2 $Re_2(NO)_2(CO)_6$. Twenty structures were found for $Re_2(NO)_2(CO)_6$, namely twelve singlets and eight triplets. This plethora of $Re_2(NO)_2(CO)_6$ structures includes structures with zero, one, or two bridging groups, indicating a complicated potential energy surface. Among these 20 structures found for $Re_2(NO)_2(CO)_6$, nine structures, lying more than 20 kcal/mol in energy above the global minimum, are not discussed in this paper but are reported in the Supporting Information.

The global minimum found for $Re_2(NO)_2(CO)_6$ is a C_s unbridged singlet structure **6S-1** (Figure 6 and Table 7) consisting of an $Re(CO)_5$ unit joined to a $Re(NO)_2(CO)$ unit by an unbridged rhenium−rhenium bond. This structure is derived from structure **7S-1** (Figure 5) by removal of one carbonyl group from its $Re(NO)_2(CO)_2$ unit. The Re−Re distance decreases from 3.092 Å to 2.819 Å (MPW1PW91), suggesting the dipolar $(OC)_5Re^+{=}Re^-(NO)_2(CO)$ double bond required to give both rhenium atoms the favored 18-electron configurations.

Two doubly nitrosyl bridged *cis*- and *trans*- structures **6S-2** (C_{2v}) and **6S-3** (C_{2h}) for $Re_2(NO)_2(CO)_6$ (Figure 6 and Table 7) have nearly degenerate energies within ~0.5 kcal/mol at

Table 5. Infrared ν(CO) and ν(NO) Vibrational Frequencies (cm^{-1})^a Predicted for Re(NO)(CO)$_n$ Using the More Reliable BP86 method[23,24]

	BP86
5S-1 (C_1)	**1467(290)**^{b}, **1781(611),** 1988(1444), 1991(1120), 2000(403), 2074(323)
4S-1 (C_{2v})	1756(980)^b, 1963(1309), 1988(295), 2004(1552), 2077(74)
4S-2 (C_{4v})	1773(1077)^b, 1974(1584), 1974(1584), 1979(0), 2063(159)
4S-3 (C_{3v})	1803(993)^b, 1961(1373), 1961(1373), 1994(290), 2058(265)
4S-4 (C_s)	**1431(268)**^{b}, 1963(1089), 1991(473), 1991(1692), 2074(104)
4T-1 (C_1)	**1634(616)**^{b}, 1964(978), 1980(688), 1986(1630), 2070(97)
3S-1 (C_s)	1728(1028)^b, 1935(959), 1962(1614), 2035(141)
3S-2 (C_s)	1722(959)^b, 1936(1279), 1956(773), 2024(347)
3S-3 (C_s)	**1397(461)**^{b}, 1939(936), 1962(1645), 2036(169)
3T-1 (C_s)	1706(887)^b, 1946(1008), 1948(1099), 2013(406)
3T-2 (C_{3v})	1683(662)^b, 1942(1026), 1942(1026), 2012(413)
3T-3 (C_s)	1745(892)^b, 1934(1648), 1946(893), 2008(171)
2S-1 (C_1)	1699(974)^b, 1908(966), 1979(582)
2S-2 (C_s)	**1199(222)**^{b}, 1919(998), 1983(673)
2S-3 (C_s)	1782(764)^b, 1919(1688), 1983(183)
2T-1 (C_s)	1701(917)^b, 1900(1340), 1953(520)
2T-2 (C_1)	1731(1152)^b, 1923(1222), 1983(519)

[a] Infrared intensities in parentheses are in km/mol, bent ν(NO) or ν(CO) are in **bold**. [b] ν(NO) frequency.

~2 kcal/mol above **6S-1**. Both structures are predicted to have a negligible imaginary vibrational frequency of $7i$ cm^{-1} (BP86), which is removed by using a finer integration grid (120, 974). The Re═Re bond lengths of the two structures are predicted to fall in the range 2.706−2.770 Å, consistent with the Re═Re double bonds required to give both rhenium atoms 18-electron configurations. An $Mn_2(NO)_2(CO)_6$ structure analogous to **6S-2** was found to be the global minimum in a previous DFT study.[8]

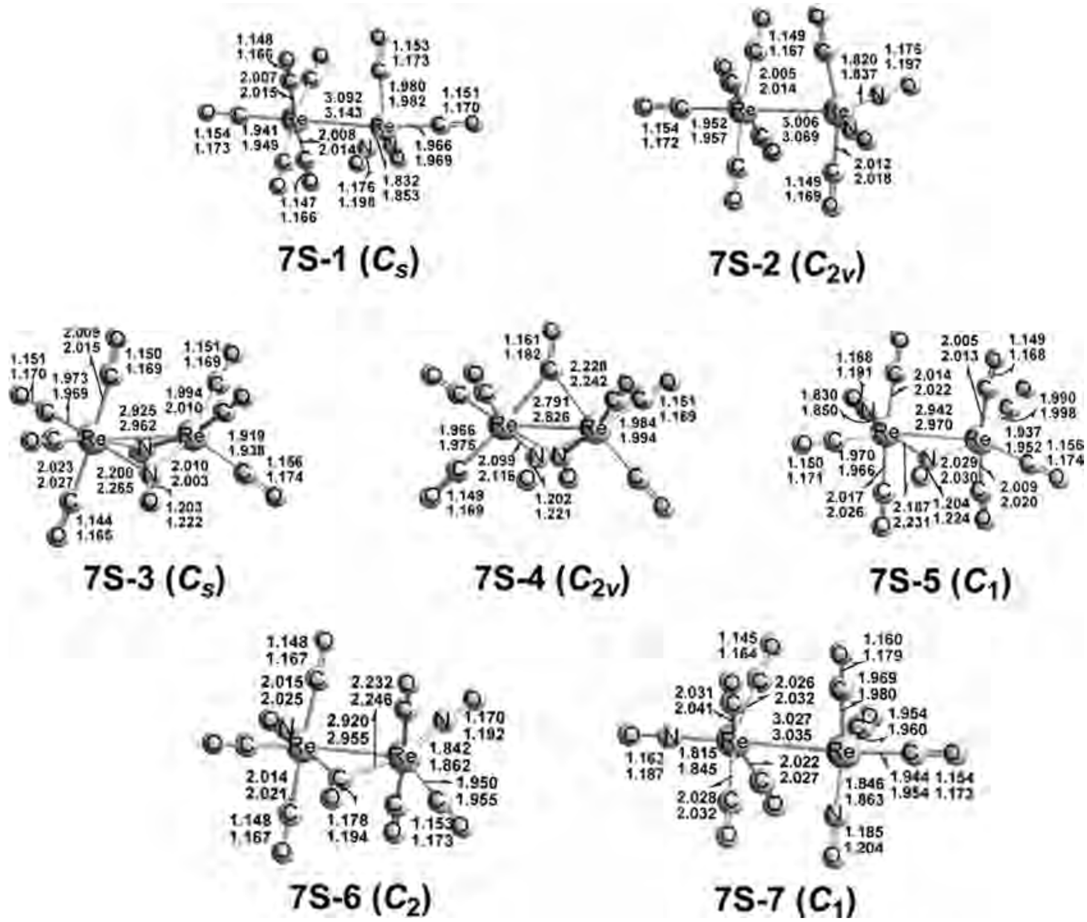
The C_1 structure **6S-4** for $Re_2(NO)_2(CO)_6$ (Figure 6 and Table 7) with one bridging nitrosyl group and one semibridging carbonyl group is predicted to have nearly the same energy within ±0.7 kcal/mol as **6S-3**, with all real vibrational frequencies. The Re═Re distance in **6S-4** of 2.742 Å (MPW1PW91) or 2.783 Å (BP86) suggests the formal double bond needed to give each of the two rhenium atoms the favored 18 electron configuration. A similar $Mn_2(NO)_2(CO)_6$ structure was predicted previously.[8]

Two additional $Re_2(NO)_2(CO)_6$ structures **6S-5** (*trans*) and **6S-8** (*cis*) of C_{2h} and C_{2v} symmetry, respectively, (Figure 6 and Table 7) are predicted to lie in energy above **6S-1** by 14.2 kcal/mol (MPW1PW91) or 8.6 kcal/mol (BP86) for **6S-5** and 19.9 kcal/mol (MPW1PW91) or 13.1 kcal/mol (BP86) for **6S-8**. Both are unbridged structures having a very small imaginary vibrational frequency at $10i$ cm^{-1}(**6S-5**) or $15i$ cm^{-1} (**6S-8**) with BP86. This small imaginary vibrational frequency decreases slightly to $8i$ cm^{-1} (**6S-5**) or $11i$ cm^{-1} (**6S-8**) when the finer integration grid (120, 974) is used. The corresponding normal mode is related to the internal rotation around the Re═Re bond. The Re═Re distances in the two structures are predicted to fall in the range of 2.743−2.862 Å, consistent with double bonds, in spite of the fact that the Re═Re distance in the *cis* structure **6S-8** is 0.07 Å longer than that in the *trans* structure **6S-5**. A C_{2v} structure of $Mn_2(NO)_2(CO)_6$ similar to **6S-8** was found in a previous DFT study[8] to have a relatively high energy at ~25 kcal/mol above its global minimum.

The C_2 unbridged $Re_2(NO)_2(CO)_6$ structure **6S-9** (Figure 6 and Table 7) is predicted to have an energy nearly identical to **6S-8** within ~2.0 kcal/mol and has all real vibrational frequencies. The Re═Re distance of 2.746 Å (MPW1PW91) or 2.769 Å (BP86) suggests the double bond required for the favored 18-electron configuration.

A pair of doubly bridged C_{2v} $Re_2(NO)_2(CO)_6$ structures **6S-6** and **6S-7** (Figure 6 and Table 7) is predicted at 14.6 kcal/mol (MPW1PW91) or 9.3 kcal/mol (BP86) for **6S-6** and 14.9 kcal/mol (MPW1PW91) or 4.4 kcal/mol for **6S-7**. Structure **6S-6** with two unsymmetrical bridging NO groups has an imaginary vibrational frequency at $50i$ cm^{-1} by the BP86 method, while the MPW1PW91 method predicts all real vibrational frequencies. By using a finer integration grid (120, 974), the imaginary vibrational frequency increases in magnitude to $60i$ cm^{-1}. The corresponding normal mode consists of a rotation of the two units around the Re−Re metal bond. Structure **6S-7** for $Re_2(NO)_2(CO)_6$, with two unsymmetrical bridging CO groups, is predicted to have an imaginary vibrational frequency at $64i$ cm^{-1} by the MPW1PW91 method. Following the normal mode of the imaginary vibrational frequency leads to **6S-1** through a C_s intermediate. The BP86 method predicts no imaginary vibrational frequency for **6S-7**. The Re−Re length in **6S-6** is predicted to be 0.07 Å longer than that in **6S-7.** The predicted Re−Re bond distances of 2.960 Å (MPW1PW91) or 2.998 Å (BP86) for **6S-6** and 2.892 Å (MPW1PW91) or 2.938 Å (BP86) for **6S-7** is consistent with a Re−Re single bond, giving one rhenium atom (the “left” rhenium in Figure 6) the favored 18 electron configuration but the other rhenium atom (the “right” rhenium in Figure 6) only a 16-electron configuration.

Two low-lying C_s triplet structures **6T-1** and **6T-2** (Figure 6 and Table 7) are found for $Re_2(NO)_2(CO)_6$, with all real vibrational frequencies. The lower energy structure **6T-1**, at 9.9 kcal/mol (MPW1PW91) or 13.4 kcal/mol (BP86) above **6S-1**, is an unbridged structure consisting of a $Re(CO)_5$ unit and a $Re(NO)_2(CO)$ unit joined by a Re−Re bond. The predicted Re−Re distance of 2.863 Å (MPW1PW91) or 2.867 Å (BP86) in **6T-1** appears to be a short Re−Re single bond, thereby giving the rhenium atom in the $Re(CO)_5$ unit the favored 18-electron configuration but the rhenium atom in the $Re(NO)_2(CO)$ unit only a 16-electron configuration.



7S-1 (C_s) **7S-2 (C_{2v})**

7S-3 (C_s) **7S-4 (C_{2v})** **7S-5 (C_1)**

7S-6 (C_2) **7S-7 (C_1)**

Figure 5. Seven optimized $Re_2(NO)_2(CO)_7$ structures.

Table 6. Total Energies (E, in Hartree), Relative Energies (ΔE, in kcal/mol), Re−Re Bond Distances (Å), and Numbers of Imaginary Vibrational Frequencies (Nimag) of $Re_2(NO)_2(CO)_7$

	MPW1PW91				BP86			
	E	ΔE	Nimag	Re−Re	E	ΔE	Nimag	Re−Re
7S-1 (C_s)	−1210.02132	0	1(13i)	3.092	−1210.59750	0	0	3.143
7S-2 (C_{2v})	−1210.01994	0.9	0	3.006	−1210.59252	3.1	0	3.069
7S-3 (C_s)	−1210.00892	7.8	0	2.925	−1210.57787	12.3	0	2.962
7S-4 (C_{2v})	−1210.00135	12.5	1(112i)	2.791	−1210.56847	18.2	1(106i)	2.826
7S-5 (C_1)	−1210.00070	12.9	0	2.942	−1210.57223	15.9	0	2.970
7S-6 (C_2)	−1209.98182	24.8	0	2.920	−1210.56132	22.7	0	2.955
7S-7 (C_1)	−1209.98066	25.5	0	3.027	−1210.55885	24.3	0	3.035

The other triplet structure of $Re_2(NO)_2(CO)_6$, namely **6T-2**, has an unsymmetrical bridging CO group and lies 15.0 kcal/mol (MPW1PW91) or 17.7 kcal/mol (BP86) higher in energy than **6S-1.** The Re−C distances to the unsymmetrical bridging carbonyl group in **6T-2** are 1.995 Å and 2.351 Å (MPW1PW91) or 2.022 Å and 2.362 Å (BP86). The Re−Re bond distance at 2.943 Å (MPW1PW91) or 2.966 Å (BP86) in **6T-2** corresponds to a Re−Re single bond. This gives each rhenium atom in **6T-2** the 17-electron configuration required for a triplet dimeric molecule assuming that the bridging carbonyl group donates one electron to each rhenium atom.

3.2.3. Vibrational Frequencies. The infrared ν(CO) and ν(NO) vibrational frequencies together with the infrared intensities predicted for the dinuclear rhenium carbonyl nitrosyl derivatives $Re_2(NO)_2(CO)_n$ (n = 7,6) are reported in Table 8 from the BP86 method, which is known to be more reliable for ν(CO) and ν(NO) frequencies.[23] The terminal ν(CO) frequencies fall in the expected range 1918−2091 cm^{-1}. The five lower ν(CO) frequencies predicted in the range 1823−1887 cm^{-1} in Table 8 are in the range of bridging ν(CO) frequencies and correspond to the bridging CO groups in structures **7S-4**, **7S-6**, **6S-7** (two bridging CO groups), and **4T-2**.

For the NO groups, the typical terminal ν(NO) frequencies predicted for $Re_2(NO)_2(CO)_n$ (n = 7, 6) fall in the 1699−1797 cm^{-1} range (Table 8). The bridging NO groups exhibit lower ν(NO) frequencies in the 1496−1589 cm^{-1} range (Table 8).

3.3. Dissociation Energies. Table 9 reports some dissociation energies involving the binuclear rhenium carbonyl derivatives $Re_2(NO)_2(CO)_n$ (n = 7, 6). In this connection there are at least two different pathways for the dissociation for each binuclear $Re_2(NO)_2(CO)_n$ (n = 7, 6) derivative, namely dissociation of a carbonyl group

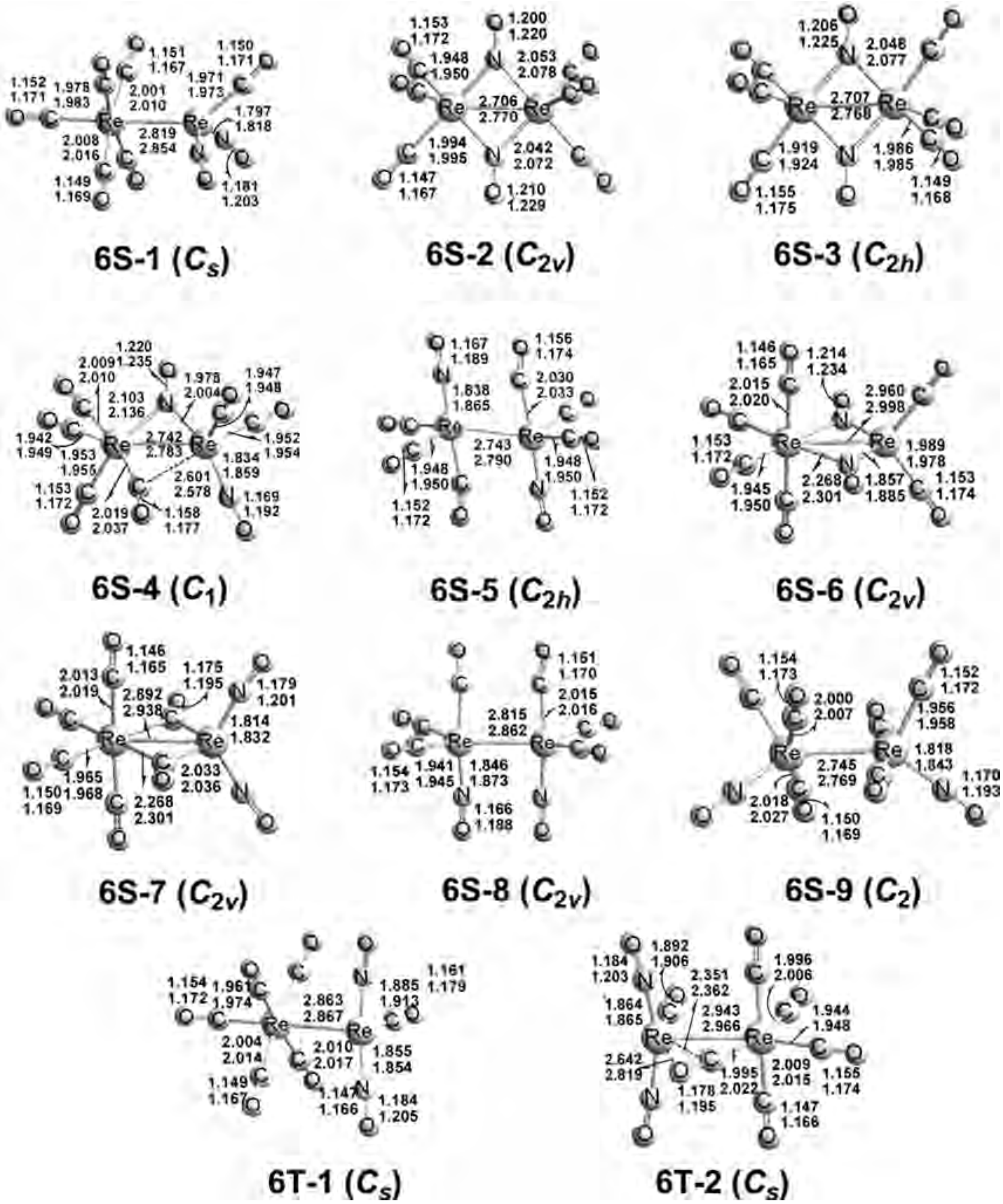


Figure 6. Eleven optimized $Re_2(NO)_2(CO)_6$ structures.

Table 7. Total Energies (*E*, in Hartree), Relative Energies (Δ*E*, in kcal/mol), Number of Imaginary Vibrational Frequencies (Nimag), and Re−Re Bond Distances (Å) in $Re_2(CO)_6(NO)_2$

	MPW1PW91				BP86			
	E	Δ*E*	Nimag	Re−Re	*E*	Δ*E*	Nimag	Re−Re
6S-1 (C_s)	−1096.66418	0	0	2.819	−1097.20546	0	0	2.854
6S-2 (C_{2v})	−1096.66031	2.4	1(3*i*)	2.706	−1097.20261	1.8	1(7*i*)	2.770
6S-3 (C_{2h})	−1096.65971	2.8	1(9*i*)	2.707	−1097.20213	2.1	1(7*i*)	2.768
6S-4 (C_1)	−1096.65865	3.5	0	2.742	−1097.20312	1.5	0	2.783
6S-5 (C_{2h})	−1096.64149	14.2	0	2.743	−1097.19180	8.6	1(10*i*)	2.790
6S-6 (C_{2v})	−1096.64097	14.6	0	2.960	−1097.19058	9.3	1(50*i*)	2.998
6S-7 (C_{2v})	−1096.64048	14.9	1(64*i*)	2.892	−1097.19843	4.4	0	2.938
6S-8 (C_{2v})	−1096.63249	19.9	1(18*i*)	2.815	−1097.18466	13.1	1(15i)	2.862
6S-9 (C_2)	−1096.63079	21.0	0	2.745	−1097.18149	15.0	0	2.769
6T-1 (C_s)	−1096.64837	9.9	0	2.863	−1097.18408	13.4	0	2.867
6T-2 (C_s)	−1096.64023	15.0	0	2.943	−1097.15416	17.7	0	2.966

or dissociation into two different pairs of mononuclear $Re(NO)(CO)_m$ units. The CO dissociation energies from $Re_2(NO)_2(CO)_n$ ($n = 7, 6$) to give $Re_2(NO)_2(CO)_{n-1}$ are predicted to be much less than that for the dissociation of

Table 8. Infrared ν(CO) Vibrational Frequencies (cm^{-1})^a Predicted for $Re_2(NO)_2(CO)_n$ ($n = 7, 6$) Using the More Reliable BP86 Method[23,24]

	BP86
7S-1 (C_s)	1724(918)^b, 1750(335)^b, 1957(281), 1984(633), 2000(1326), 2001(1322), 2014(1636), 2024(0), 2091(205)
7S-2 (C_{2v})	1742(937)^b, 1766(932)^b, 1965(27), 1982(628), 1991(1447), 2003(2270), 2013(0), 2015(335), 2088(233)
7S-3 (C_s)	**1553(652)**^{b}, **1575 (160)**^{b}, 1966(408), 1982(205), 1987(1332), 1987(1374), 2004(771), 2026(1911), 2073 (173)
7S-4 (C_{2v})	**1566(560)**^{b}, **1589(360)**^{b}, **1887(387),** 1981(0), 1987(6), 1989(1674), 1994 (1513), 2023(2705), 2061(16)
7S-5 (C_1)	**1540(406)**^{b}, 1776(942)^b, 1966(690), 1972(367), 1984(1089), 1989(11), 2002(2233), 2030(1173), 2073(51)
7S-6 (C_2)	1760(742)^b, 1766(1599)^b, **1816(28),** 1975(41), 1976(1141), 1984(625), 2002(2198), 2026(780), 2070(91)
7S-7 (C_1)	1699(736)^b, 1797(1318)^b, 1918(664), 1940(162), 2004(1147), 2010(1102), 2016(1391), 2031(232), 2085(94)
6S-1 (C_s)	1705(811)^b, 1740(557)^b, 1982(732), 1984(1255), 1986(1162), 1998(1397), 2010(118), 2076(244)
6S-2 (C_{2v})	**1512(574)**^{b}, **1576(218)**^{b}, 1968(0), 1977(2010), 1990(49), 1995(1272), 2028(2264), 2055(20)
6S-3 (C_{2h})	**1527(792)**^{b}, **1557(0)**^{b}, 1969 (0), 1973(1957), 1995(0), 1997(1307), 2027(2424), 2054(0)
6S-4 (C_1)	**1496(452)**^{b}, 1767(826)^b, 1935(506), 1972(486), 1981(1412), 2000(840), 2024(1433), 2063(419)
6S-5 (C_{2h})	1780(0)^b, 1780(1492)^b 1957(851), 1968(0), 1974(0), 1976(2060), 2015(2256), 2041(0)
6S-6 (C_{2v})	**1502(792)**^{b}, **1532(78)**^{b}, 1942(826), 1983(1379), 1983(865), 1997(1702), 2002(489), 2084(279)
6S-7 (C_{2v})	1711(961)^b, 1727(1420)^b, **1823(867)**, **1832(27)**, 1992(878), 2002(1396), 2009(499), 2079(590)
6S-8 (C_{2v})	1743(91)^b, 1810(1358)^b, 1965(9), 1966(0), 1967(2121), 1993(461), 2007(2496), 2048(388)
6S-9 (C_2)	1755(1428)^b, 1765(649)^b, 1950(65), 1967(664), 1975(1113), 1981(1210), 2003(1539), 2050(88)
6T-1 (C_s)	1668(1001)^b, 1719(491)^b, 1946(544), 1982(844), 1994(1289), 1996(1646), 2019(15), 2084(273)
6T-2 (C_s)	1680(998)^b, 1730(469)^b, **1834(636)**, 1965(1), 1980(1414), 1995(1345), 2002(529), 2074(410)

[a] Infrared intensities in parentheses are in km/mol, bridging ν(CO) and ν(NO) frequencies are in **bold**. [b] ν(NO) frequency.

Table 9. Dissociation Energies (kcal/mol) for $Re_2(NO)_2(CO)_n$^{a}

	MPW1PW91	BP86
$Re_2(NO)_2(CO)_7 \rightarrow Re_2(NO)_2(CO)_6 + CO$	36.4	37.6
$Re_2(NO)_2(CO)_7 \rightarrow Re(NO)(CO)_4 + Re(NO)(CO)_3$	48.3	42.7
$Re_2(NO)_2(CO)_7 \rightarrow Re(NO)(CO)_5 + Re(NO)(CO)_2$	111.9	110.2
$Re_2(NO)_2(CO)_6 \rightarrow Re_2(NO)_2(CO)_5 + CO$	37.0	31.9
$Re_2(NO)_2(CO)_6 \rightarrow 2Re(NO)(CO)_3$	61.6	51.8
$Re_2(NO)_2(CO)_6 \rightarrow Re(NO)(CO)_4 + Re(NO)(CO)_2$	59.9	55.4

[a] All results reported refer to the lowest energy structures of reactant and products.

Table 10. Carbonyl Dissociation Energies (kcal/mol) for $Re(NO)(CO)_n$^{a}

	MPW1PW91	BP86
$Re(NO)(CO)_5 \rightarrow Re(NO)(CO)_4 + CO$	−15.6	−17.3
$Re(NO)(CO)_4 \rightarrow Re(NO)(CO)_3 + CO$	49.6	46.6
$Re(NO)(CO)_3 \rightarrow Re(NO)(CO)_2 + CO$	48.0	50.2

[a] All results reported refer to the lowest energy structures.

$Re_2(NO)_2(CO)_n$ ($n = 7, 6$) into mononuclear fragments $Re(NO)(CO)_m$ indicating the strength of the rhenium−rhenium interactions in all of these structures.

The CO dissociation energies for the global minima of the mononuclear rhenium carbonyl nitrosyl $Re(NO)(CO)_n$ ($n = 5, 4, 3$) have also been investigated (Table 10). The dissociation of one carbonyl group from the global minimum of $Re(NO)(CO)_5$ to give $Re(NO)(CO)_4$ is an exothermic process by 15.6 kcal/mol (MPW1PW91) or 17.3 kcal/mol (BP86). This necessarily implies that $Re(NO)(CO)_5$ is not thermodynamically stable. This further suggests that the nitrosylation of $HRe(CO)_5$ is likely to lead directly to $Re(NO)(CO)_4$, without an isolable $Re(NO)(CO)_5$ intermediate.

The energy for the subsequent dissociation of carbonyl groups from $Re(NO)(CO)_4$, as indicated by the 48 ± 2 kcal/mol CO dissociation energy from $Re(NO)(CO)_4$ and $Re(CO)_3(NO)$, is on the high side of the normal range for CO dissociation from metal carbonyls and somewhat higher than the CO dissociation energy of 38 ± 2 kcal/mol for the isoelectronic $Os(CO)_5$ predicted by DFT and the reported[36] CO dissociation energy of 41 ± 2 kcal/mol for $Fe(CO)_5$.

4. Discussion

4.1. Mononuclear Derivatives. A pentacarbonyl derivative $Re(NO)(CO)_5$ (**5S-1** in Figure 1) was found in which the NO ligand has joined one of the CO ligands to give a novel η^2-OCNO ligand by formation of a direct C−N bond in an unprecedented process. This process can be considered as a nucleophilic attack by the nitrogen lone pair of a bent nitrosyl group on an adjacent carbonyl carbon. The resulting $Re(NO)(CO)_5$ structure (**5S-1**) could be an initial product from the nitrosylation of $HRe(CO)_5$, similar to the known[3] preparation of $Mn(NO)(CO)_4$ by nitrosylation of $HMn(CO)_5$. However, dissociation of $Re(NO)(CO)_5$ (**5S-1**) to give the most stable structure of $Re(NO)(CO)_4$ (**4S-1** in Figure 2) is

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(36) Ehlers, A. W.; Frenking, G. *Organometallics* **1995**, *14*, 423.

predicted to be an exothermic process (Table 10). Our study thus suggests that nitrosylation of $HRe(CO)_5$ under typical reaction conditions will go directly to the tetracarbonyl $Re(NO)(CO)_4$ with immediate loss of one carbonyl group and without an isolable pentacarbonyl intermediate.

The tetracarbonyl $Re(NO)(CO)_4$ is the direct analogue of the known $Mn(NO)(CO)_4$, as well as being isoelectronic with $Os(CO)_5$. The expected trigonal dipyramidal structures were found for $Re(NO)(CO)_4$ with an energetic preference of the NO group for an equatorial position in structure **4S-1** rather than for an axial position in structure **4S-3** (Figure 2), just as is the case for the manganese analogue.[30] A square pyramidal transition state **4S-2** was found for $Re(NO)(CO)_4$ at a low enough energy (<10 kcal/mol above the global minimum) to predict $Re(NO)(CO)_4$ to be a typical fluxional five-coordinate system undergoing the Berry pseudorotation.[37]

The lowest energy structures for the tricarbonyl $Re(NO)(CO)_3$ can be derived from the lowest energy structure for $Re(NO)(CO)_4$ (**4S-1**) by removal of either an equatorial or axial carbonyl group to give **3S-1** or **3S-2**, respectively. The lowest energy triplet structure for $Re(NO)(CO)_3$ (**3T-1**) is similarly derived from **4S-1** by removal of an equatorial carbonyl group. A higher energy singlet structure **3S-3** for $Re(NO)(CO)_3$ has the NO group bonded to the metal in a η^2 manner involving the oxygen as well as the nitrogen atom. This special type of NO group, considered as a neutral ligand, is a formal five electron donor using two electron pairs for the ligand−metal bonding after giving up a fifth electron to the metal by formal oxidation to the nitrosonium cation, NO^+. A higher energy triplet structure of $Re(NO)(CO)_3$ (**3T-2**) has tetrahedral rhenium coordination and is thus a 16-electron complex.

Several T-shaped or nearly T-shaped structures are found for $Re(NO)(CO)_2$ including the global minimum **2S-1** (Figure 4). The most unusual structure for $Re(NO)(CO)_2$ is **2S-2**, which has an η^2-NO group with an unusually long bond around 1.30 Å. This relatively long N−O bond in **2S-2** suggests that all of the π-bonding electrons have been removed from the NO ligand, considered as NO^+, and transferred to the metal. In this way the oxygen atom as well as the nitrogen atom of the η^2-NO group is involved in the rhenium−ligand bonding, as indicated by a short Re−O distance of ~2.1 Å. This type of NO ligand may also be derived from hydroxylamine, NH_2OH, which has a formal N−O single bond, by complete deprotonation leading to the formal NO^{3-} trianion isoelectronic with F_2.

4.2. Binuclear Structures. The two lowest energy structures for $Re_2(NO)_2(CO)_7$, namely **7S-1** and **7S-2** in Figure 5, have an unusual feature not found in any metal carbonyl nitrosyl structures of the first row transition metals, namely, one metal atom with both NO groups and the other metal atom with only CO groups. Thus, the **7S-1** and **7S-2** structures simply consist of an $-Re(CO)_5$ and a $-Re(NO)_2(CO)_2$ group linked together with an Re−Re single bond without any bridging carbonyl or nitrosyl groups. Structures **7S-1** and **7S-2** differ only in the arrangements of the NO groups in the $Re(NO)_2(CO)_2$ unit relative to the $Re(CO)_5$ unit. Thus, the lower energy structure **7S-1** has an approximately linear OC−Re−Re−CO unit whereas the higher energy structure **7S-2** has an approximately linear OC−Re−Re−NO unit.

The $Re(CO)_5$ unit is well-known to form very stable rhenium carbonyl derivatives, as exemplified by $Re_2(CO)_{10}$ itself as well as numerous $Re(CO)_5X$ derivatives (X = Cl, Br, I, Me, etc.). However, the $Re(NO)_2(CO)_2$ unit is unknown in rhenium chemistry. Its presence in the lowest energy structure of $Re_2(NO)_2(CO)_7$ suggests that there might be an extensive, but still unknown, very rich chemistry of $Re(NO)_2(CO)_2X$ derivatives waiting to be discovered.

The lowest energy structure for $Mn_2(NO)_2(CO)_7$ is predicted in a previous study[8] to have two bridging NO groups. A similar structure **7S-3** is found for $Re_2(NO)_2(CO)_7$, but at higher energy than the two $(OC)_5Re-Re(NO)_2(CO)_2$ structures discussed above. A triply bridged $Mn_2(NO)_2(CO)_7$ structure **7S-4**, with a CO bridge in addition to the two NO bridges analogous to the well-known structure[4,5] of $Fe_2(CO)_9$, appears to be a transition state rather than a true minimum. This transition state leads to the structure **7S-3** without the bridging carbonyl but retaining the two bridging nitrosyls (Figure 5).

The global minimum and experimentally known structure for $Os_2(CO)_9$ has a single bridging carbonyl group.[6,7] Related $Re_2(NO)_2(CO)_7$ structures are found with a single bridging nitrosyl group (**7S-5**) and a single bridging carbonyl group (**7S-6**). The structure **7S-5** with a single bridging nitrosyl group is significantly lower in energy than structure **7S-6** with a single bridging carbonyl group. This, as well as the observation of structure **7S-3** with two bridging nitrosyl groups as the lowest energy bridged structure of $Re_2(NO)_2(CO)_7$, indicates the preference of rhenium for bridging nitrosyl groups over bridging carbonyl groups as was previously noted for analogous manganese systems.[8]

The potential energy surface for the unsaturated $Re_2(NO)_2(CO)_6$ was found to be very complicated with a total of twenty structures located. Therefore, only the 11 structures within 20 kcal/mol of the global minimum were considered in detail. The lowest energy structure for $Re_2(NO)_2(CO)_6$ is an unbridged structure $(OC)_5Re-Re(NO)_2(CO)$ (**6S-1** in Figure 6) derived from the global minimum of $Re_2(NO)_2(CO)_7$ by removal of one of the carbonyl groups in the $Re(NO)_2(CO)_2$ unit while retaining the $Re(CO)_5$ unit intact. This, in itself, shows the stability of the $Re(CO)_5$ unit. However, two doubly nitrosyl bridged $Re_2(NO)_2(CO)_6$ structures (**6S-2** and **6S-3** in Figure 6) were found less than 3 kcal/mol above the global minimum **6S-1**. An analogous doubly nitrosyl bridged structure was predicted[8] to be the global minimum for the manganese analogue $Mn_2(NO)_2(CO)_6$.

A comparison of the lowest energy predicted structures of the binuclear manganese and rhenium derivatives $M_2(NO)_2(CO)_n$ (M = Mn, Re; n = 7, 6) suggests the following:

(1) Manganese prefers structures in which both nitrosyl groups are bridging groups. Thus the lowest energy structures

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[37] Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.

for both $Mn_2(NO)_2(CO)_7$ and $Mn_2(NO)_2(CO)_6$ were found to have two bridging nitrosyl groups and all terminal carbonyl groups.[8]

(2) Rhenium prefers unbridged structures in which a $Re(CO)_5$ unit is bonded to a $Re(NO)_2(CO)_n$ group as demonstrated by the lowest energy structures found for both $Re_2(NO)_2(CO)_7$ (**7S-1** in Figure 5) and $Re_2(NO)_2(CO)_6$ (**6S-1** in Figure 6).

5. Conclusion

These theoretical studies suggest that there should be no inherent difficulty in preparing $Re(NO)(CO)_4$ by the nitrosylation of $Re(CO)_5X$ derivatives such as the reaction of $HRe(CO)_5$ with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide, analogous to the reported[3] synthesis of $Mn(NO)(CO)_4$. The only $Re(NO)(CO)_5$ structure that we found, namely **5S-1**, was shown to undergo exothermic decarbonylation to $Re(NO)(CO)_4$. We therefore suspect that the only reason that $Re(NO)(CO)_4$ has not been reported is that no one has studied the nitrosylation of $HRe(CO)_5$ or other suitable rhenium precursor in sufficient detail.

These theoretical studies also suggest some interesting chemistry of more highly nitrosylated rhenium carbonyl derivatives. Thus the $-Re(NO)_2(CO)_2$ unit appears to be a favorable building block for binuclear rhenium carbonyl nitrosyls, as indicated by the structure $(OC)_5Re-Re(NO)_2(CO)_2$ for the global minimum of $Re_2(NO)_2(CO)_7$. This suggests the existence of a variety of dinitrosylrhenium derivatives of the type $Re_2(NO)_2(CO)_2X$ (X = H, Cl, Br, I, alkyl, aryl, etc.), as well as possibly an interesting dimer $Re_2(NO)_4(CO)_4$. Such derivatives might be synthesized by further nitrosylation of $Re(NO)(CO)_4$ with $NO^+PF_6^-$ to give the cation $Re(NO)_2(CO)_3^+$ followed by further reaction with a suitable metal hydride to give $HRe(NO)_2(CO)_2$. The hydride $HRe(NO)_2(CO)_2$ could then be converted to the tetrahedral anion $Re(NO)_2(CO)_2^-$ by deprotonation; mild oxidation of this anion might give the dimer $Re_2(NO)_4(CO)_4$. In addition further nitrosylation of $HRe(NO)_2(CO)_2$ with *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide or similar reagent might give the trinitrosyl $Re(NO)_3(CO)$ analogous to the known[38,39] $Mn(NO)_3(CO)$.

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Supporting Information Available: Tables S1−S15: theoretical harmonic vibrational frequencies for $Re(CO)_5(NO)$ (2 structures), $Re(CO)_4(NO)$ (7 structures), $Re(CO)_3(NO)$ (6 structures), $Re(CO)_2(NO)$ (6 structures), $Re_2(CO)_7(NO)_2$ (8 structures), and $Re_2(CO)_6(NO)_2$ (22 structures) using the BP86 method; Tables S16-S66: theoretical Cartesian coordinates for $Re(CO)_5(NO)$ (2 structures), $Re(CO)_4(NO)$ (7 structures), $Re(CO)_3(NO)$ (6 structures), $Re(CO)_2(NO)$ (6 structures), $Re_2(CO)_7(NO)_2$ (8 structures), and $Re_2(CO)_6(NO)_2$ (22 structures) using the MPW1PW91 method; complete Gaussian reference (ref 28). This material is available free of charge via the Internet at http://pubs.acs.org.

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