ion adopts a distorted octahedral geometry with the following angles: N1–Co–N4 = 100.3°, N2–Co–N3 = 176.7°, and O1–Co–O2 = 71.8°. The large N1–Co–N4 angle, similar to that observed in $RuCl(\eta^2\text{-}SO_4)(NO)(PPh_3)_2$, reflects the strain in the contiguous four-membered ring.[10] A slightly deformed tetrahedral configuration was found for the sulfate ligand with O–S–O angles of 99.4, 109.4, 112.0, and 113.4°. The exocyclic S–O bonds are about 0.07 Å shorter than the endocyclic ones. "Short-long" trans effects are seen clearly: N4–Co (1.949 (4) Å) vs O1–Co (1.974 (4) Å); N1–Co (1.983 (4) Å) vs O2–Co (1.950 (3) Å). The two axial N–Co bonds are almost identical (1.971 (4) and 1.977 (4) Å). Finally, an interesting hydrogen-bonded network[11] exists between N4–H, water, and ClO_4^-. One is remained of the S_N1CB mechanism[12] in which hydroxide attacks an NH_2R coordinated to Co(III).

Hydrolysis of I was monitored by the absorbance decrease at 548 nm observed when a 10.2 mM aqueous solution of I was added to 0.2 M *N*-ethylmorpholine buffer (I = 1.0 M with $NaClO_4$) thermostated at 25.0 °C in a stopped-flow spectrophotometer. First-order rate constants of 0.19, 0.21, and 0.22 s^{-1} were obtained at pH values of 7.24, 7.89, and 8.20, respectively. This is about 65 times faster[2] than $[(en)_2Co(\mu\text{-}SO_4)]_2^{2+}$, where ring strain is not a factor, and almost 10 times faster than $[(trpn)Co(\eta^2\text{-}OAc)]^{2+}$. Binding of SO_4^{-2} to $[(trpn)Co(OH_2)_2]^{3+}$, followed from the 548-nm absorbance increase at pH 2.9 ([Co] = 5.04 mM; $NaClO_4$, I = 1.0 M; 0.023–0.24 M $NaSO_4$; 25°C), gave a second-order rate constant of 0.11 M^{-1} s^{-1}. *p*-Nitrophenyl sulfate, a weak ligand, was not hydrolyzed by $[(trpn)Co(OH_2)(OH)]^{2+}$.

Acknowledgment. This work was supported by the National Institutes of Health and the Army Research Office. We also greatly appreciate the assistance of Professors K. S. Hagen and C. G. Trowbridge with the X-ray and stopped-flow analyses, respectively.

Supplementary Material Available: Details of the crystal structure determination for $[(trpn)Co(\eta^2\text{-}SO_4)]ClO_4\cdot H_2O$, including crystallographic experimental procedures, ORTEP drawings, and tables of crystal data (Table S1), atomic positional parameters (Table S2), bond distances (Table S3), bond angles (Table S4), anisotropic thermal parameters (Table S5), and hydrogen atom positions (Table S6) (10 pages); a listing of observed and calculated structure factors for $[(trpn)Co(\eta^2\text{-}SO_4)]ClO_4\cdot H_2O$ (7 pages). Ordering information is given on any current masthead page.

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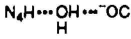
(11) The following distances pertain to the hydrogen-bonded network



$$N_4H\cdots \underset{H}{O}H\cdots{}^{-}OClO_4$$

(see also Tables S2 and S6 and S6 of the supplementary data): N_4–O_w and O_w–O_p (2.856 Å); N_4H–O_w (1.941 Å); and O_wH–O_p (1.855 Å).

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A Triply Bonded Dirhenium Complex Containing a Nitrosyl Ligand

The reactions of nitric oxide with multiply bonded dimetal complexes can, like those with carbon monoxide and organic isocyanides, lead to cleavage of the metal–metal bond and the formation of products in which a metal–metal interaction is no longer present.[1,2] Examples include the conversions of $Mo_2X_4(PR_3)_4$ (X = Cl, Br; PR_3 = PEt_3, P-*n*-Bu_3, $PEtPh_2$) to $Mo(NO)_2X_2(PR_3)_2$,[3] $Mo_2(O\text{-}i\text{-}Pr)_6$ to $Mo_2(\mu\text{-}O\text{-}i\text{-}Pr)_2(O\text{-}i\text{-}Pr)_4(NO)_2$,[4] and $W_2(O\text{-}t\text{-}Bu)_6$ to $W(O\text{-}t\text{-}Bu)_3(NO)(py)$.[5] A few instances are also known where nitric oxide forms adducts with multiply bonded dimetal species, such as the case of the diruthenium complexes $Ru_2(\mu\text{-}O_2CR)_4(NO)_2$ and $Ru_2(\mu\text{-}N_3Ph_2)_4(NO)_2$.[6] Structure determinations on the carboxylate complexes where R = Et or CF_3 show that the Ru–Ru bonds are much longer and weaker than in the parent $Ru_2(\mu\text{-}O_2CR)_4$ compounds.[6,7] Quite different behavior is encountered with the nitrosonium cation NO^+, which we have found can serve as a one-electron oxidant in converting triply bonded dirhenium(II) species to their dirhenium(III,II) congeners.[8-10] We now describe a previously unreported reaction course in which NO^+ first behaves as a one-electron oxidant, followed by the incorporation of NO into the final reaction product without a net change in the metal–metal bond order.

Solutions of the dirhenium(II) complex $Re_2Cl_4(\mu\text{-}dmpm)_3$ (**1**; dmpm = $Me_2PCH_2PMe_2$) in 0.1 M *n*-Bu_4NPF_6/CH_2Cl_2 exhibit two one-electron oxidations at $E_{1/2}$ = +0.53 V and $E_{p,a}$ = +1.30 V vs Ag/AgCl.[11] The reversible oxidation can be accessed both electrochemically and chemically, the latter with the use of $NOPF_6$ as the oxidant. A mixture of **1** (0.10 g, 0.108 mmol) and $NOPF_6$ (0.023 g, 0.130 mmol) in 10 mL of dichloromethane was stirred at room temperature for 15 min, the purple solution evaporated to dryness, and ethanol added to the residue to afford the microcrystalline complex $[Re_2Cl_4(\mu\text{-}dmpm)_3]PF_6$ (**2**), yield 0.08 g (70%). Anal. Calcd for $C_{15}H_{42}Cl_4F_6P_7Re_2$: C, 16.88; H, 3.95. Found: C, 16.36; H, 4.14. The identity of **2** was further established by its electrochemical and spectroscopic properties.[12]

A different reaction product is obtained if **1** is reacted with $NOPF_6$ by using 1:2 molar proportions of these reagents. The reaction between **1** (0.21 g, 0.228 mmol) and $NOPF_6$ (0.080 g, 0.455 mmol) in dichloromethane (15 mL) for 4 h at room temperature led to a color change from red to purple to brown. The reaction mixture was filtered and evaporated to dryness and the residue treated with ethanol to give dark red-brown $Re_2Cl_5(dmpm)_2(NO)$ (**3**), yield 0.08 g (41%). Anal. Calcd for $C_{10}H_{28}Cl_5NOP_4Re_2$: C, 14.10; H, 3.29. Found: C, 14.62; H, 3.08. This same product was formed when acetone was used as the reaction solvent in place of dichloromethane and was also formed by the reaction of **2** with 1 equiv of $NOPF_6$ in dichloromethane.

The diamagnetic nitrosyl complex **3**, which is the first triply bonded dimetal species to contain a NO ligand, shows a single intense ν(NO) mode at 1750 cm^{-1} in its IR spectrum (Nujol mull). Its ^1H NMR spectrum (recorded in $CDCl_3$ at room temperature) exhibits a broad resonance (unresolved multiplet) at δ +4.13 (P–CH_2–P) and multiplets at δ +2.46, +2.00, and +1.60, in an intensity ratio of ca. 1:1:2, which are assigned to CH_3–P. The resonance at δ +1.60 is composed of two overlapping multiplets. Overall, these results indicate the presence of four inequivalent pairs of CH_3–P groups in the structure of **3**. The cyclic voltammograms of solutions of **3** in 0.1 M *n*-Bu_4NPF_6/CH_2Cl_2 show a

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(12) Cyclic voltammogram (0.1 M *n*-$BuNPF_6/CH_2Cl_2$): $E_{1/2}$(red) = +0.54 V and $E_{p,a}$ = +1.28 V vs Ag/AgCl. IR spectrum (Nujol mull): 840 s cm^{-1} (ν(P–F) of PF_6^-). X-Band ESR spectrum (CH_2Cl_2 at −160 °C): $g \simeq 2.2$ (broad signal showing some hyperfine).

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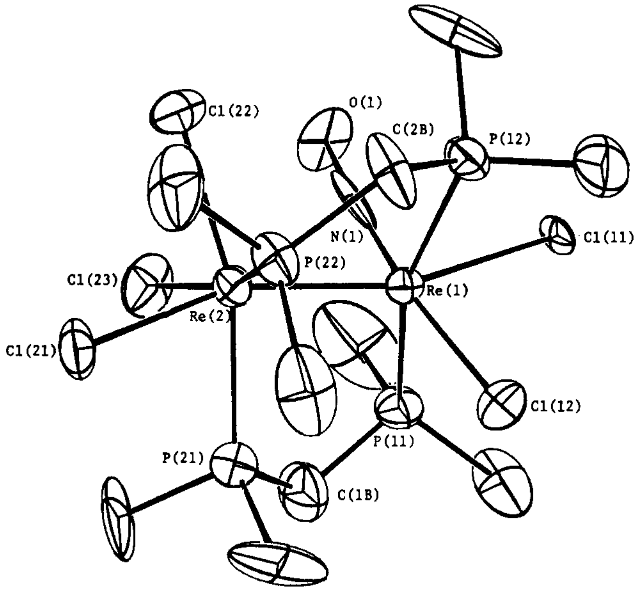

Figure 1. ORTEP view of the structure of $\mathrm{Re_2Cl_5(dmpm)_2(NO)}$ (3) with the hydrogen atoms of the dmpm ligands omitted. The thermal ellipsoids are drawn at the 50% probability level. Some representative and important distances (Å) and angles (deg) are as follows: Re(1)–Re(2) = 2.379 (1), Re(1)–Cl(11) = 2.622 (4), Re(1)–Cl(12) = 2.373 (6), Re(1)–P(11) = 2.431 (6), Re(1)–P(12) = 2.455 (6), Re(1)–N(1) = 1.68 (3), Re(2)–Cl(21) = 2.461 (6), Re(2)–Cl(22) = 2.406 (6), Re(2)–Cl(23) = 2.408 (6), Re(2)–P(21) = 2.446 (6), Re(2)–P(22) = 2.414 (6), N(1)–O(1) = 1.28 (3); Re(2)–Re(1)–Cl(11) = 158.2 (1), Re(2)–Re(1)–Cl(12) = 112.1 (2), Re(2)–Re(1)–P(11) = 98.2 (2), Re(2)–Re(1)–P(12) = 98.5 (1), Re(2)–Re(1)–N(1) = 75.3 (6), Re(1)–Re(2)–Cl(21) = 152.9 (2), Re(1)–N(1)–O(1) = 174 (1), P(11)–Re(1)–P(12) = 162.7 (2), P(21)–Re(2)–P(22) = 107.7 (2).

reversible oxidation at $E_{1/2} = +0.95$ V and an irreversible reduction at $E_{p,c} = -0.82$ V vs Ag/AgCl.

The X-ray crystal structure of **3** was determined on a crystal grown by the slow diffusion of hexane vapor into a dichloromethane solution of the complex.[13-15] The important features of the structure are shown in Figure 1. The complex, which contains a linearly bound nitrosyl ligand (Re(1)–N(1)–O(1) = 174 (1)°), is formed from **1** through loss of one dmpm ligand. The remaining dmpm ligands are bound such that there is a rarely encountered cis, trans disposition of phosphorus donor atoms at the two metal centers;[16] the angles P(22)–Re(2)–P(21) and P(12)–Re(1)–P(11) are 107.7 (2) and 162.7 (2)°, respectively. While this molecule possesses no crystallographically imposed symmetry, there is a virtual plane of symmetry containing the NO ligand and the atoms C(11), Cl(12), Re(1), Re(2), and Cl(21) that bisects the angles P(22)–Re(2)–P(21) and P(12)–Re(1)–P(11); this is shown in Figure S1, which is an ORTEP representation of the structure as viewed down the Re–Re axis. If we treat the nitrosyl ligand as being formally $\mathrm{NO^+}$, then **3** can be considered as a derivative of $\mathrm{Re_2^{4+}}$. The Re–Re bond distance of 2.379 (1) Å accords with this being a Re$\equiv$Re bond, although it is longer than the comparable distance in $\mathrm{Re_2Cl_4(\mu\text{-}dmpm)_3}$ (2.3157 (4) Å), a complex that also contains two axial Re–Cl bonds.[11] This bond lengthening is probably a consequence of a weakening of the π and/or δ components of the Re$\equiv$Re bond through Re → NO(π^*) back-bonding. Indeed, the Re(1)–N(1) bond distance of 1.68 (3) Å appears to be somewhat shorter than the Re–N bond distances normally associated with mononuclear mononitrosyl complexes of rhenium halides,[17] although, in view of the relatively large esd's associated with the nitrosyl unit in the structure determination of **3**, this difference may not be significant. However, the relative shortness of the Re–Cl bond that is trans to the nitrosyl ligand may support the occurrence of some degree of Re → NO(π^*) back-bonding since this could enhance any Cl(p_π) → Re(d) contribution to the Re(1)–Cl(12) bond as well as the σ-bonding interaction. The disparity in the axial and equatorial Re–Cl bond distances at Re(1) (2.622 (4) and 2.373 (6) Å, respectively) is comparable to that seen in $\mathrm{Re_2Cl_4(\mu\text{-}dmpm)_3}$.[11] However, a much smaller difference exists between the Re–Cl bonds about Re(2); in particular, the axial bond Re(2)–Cl(21) is surprisingly short (2.461 (6) Å). Although the reason for this is not obvious, it may reflect a disparity in charges at the two Re centers that renders Re(2) more positively charged and therefore leads to a shortening of this axial bond.

The formation of $\mathrm{Re_2Cl_5(\mu\text{-}dmpm)_2(NO)}$ (**3**) from $\mathrm{Re_2Cl_4(\mu\text{-}dmpm)_3}$ (**1**) is unusual in that it requires the loss of a dmpm ligand from the latter complex. Since **1** is normally very stable and shows little tendency to undergo ligand dissociation, it is apparently the attack of $\mathrm{NO^+}$ upon the more reactive oxidized species $\mathrm{[Re_2Cl_4(\mu\text{-}dmpm)_3]^+}$ that leads to the formation of **3**. However, this is obviously a complex reaction since some proportion of the dirhenium species must be sacrificed to provide the extra chloride ligand that becomes incorporated into the final product **3**. Interestingly, when the reaction is carried out in the presence of added chloride ion (as in $\mathrm{[(Ph_3P)_2N]Cl}$) we observed no discernible increase in the yield of **3**, implying that free $\mathrm{Cl^-}$ is not required. The mechanism and scope of this reaction are under further investigation, and attempts are being made to prepare other multiply bonded dimetal complexes that contain the NO ligand.

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Supplementary Material Available: A listing of atomic positional parameters for the structure of $\mathrm{Re_2Cl_5(dmpm)_2(NO)}$ (Table S1) and a figure (Figure S1) showing a view of the structure down the Re–Re axis (5 pages). Ordering information is given on any current masthead page.

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(13) Dark red crystals of **3** are orthorhombic, space group *Iba*2 (No. 45), with $a = 14.278$ (3) Å, $b = 23.966$ (3) Å, $c = 13.880$ (3) Å, $V = 4749$ (3) Å^3, $Z = 8$, $d_{calcd} = 2.383$ g/cm^3. X-ray data were collected at 20 °C on a 0.38 × 0.17 × 0.13 mm crystal for 1743 independent reflections having $4 < 2\theta < 45°$ on an Enraf-Nonius diffractometer using graphite-crystal-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Lorentz and polarization corrections were applied to the data. The structure was solved by the use of the Patterson heavy-atom method, which revealed the positions of the Re atoms. The remaining non-hydrogen atoms were identified in succeeding difference Fourier syntheses. Hydrogen atoms of the dmpm ligands were included at fixed positions. An empirical absorption correction was applied,[14] but no correction for extinction was made. The non-hydrogen atoms of the dirhenium complex were refined anisotropically; corrections for anomalous scattering were applied to these atoms.[15] The final residuals were $R = 0.036$ ($R_w = 0.047$) and GOF = 1.399 for 1427 data with $I > 3\sigma(I)$. Refinement in the other enantiomorph gave $R = 0.040$ ($R_w = 0.052$) and GOF = 1.544.

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(16) See, for example, the case of the isomer *mer,fac*-$\mathrm{Mn_2(CO)_6(\mu\text{-}dmpm)_2}$. A cis, trans coordination is more common with a pair of bridging $\mathrm{Ph_2PCH_2PPh_2}$ ligands. Lemke, F. R.; Kubiak, C. P. *Inorg. Chim. Acta* **1986**, *113*, 125 and references cited therein.

(17) For example, in the structures of $\mathrm{(Et_4N)[Re(NO)Cl_4(py)]}$, $\mathrm{(Et_4N)[Re(NO)Br_4L]}$ (L = EtOH or MeCN), and $\mathrm{[Re(NO)F(CO)(PPh_3)_3]ClO_4}$ the Re–N distances occur in the range 1.72 (2)–1.76 (2) Å. (a) Ciani, G.; Giusto, D.; Manassero, M.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* **1975**, 2156. (b) Ciani, G.; Giusto, D.; Manassero, M.; Sansoni, M. *J. Chem. Soc., Dalton Trans.* **1978**, 798. (c) Cameron, T. S.; Grundy, K. R.; Robertson, K. N. *Inorg. Chem.* **1982**, *21*, 4149.

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