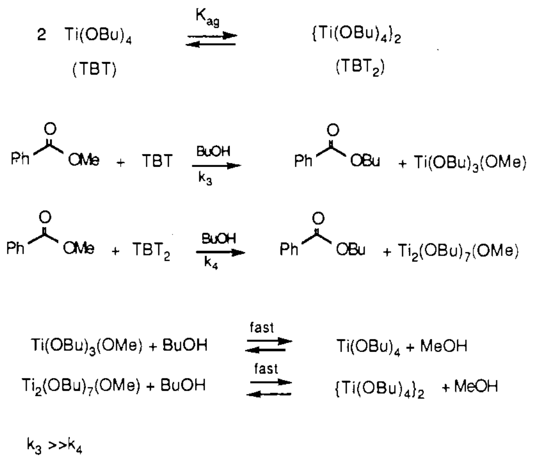
Scheme I. Proposed Mechanism of Transesterification[a]



[a] Reaction is fractional order in titanate catalyst and independent of alcohol concentration.

Table I. Temperature and Rate Data for Titanate-Monomer-Catalyzed Transesterification of Methyl Benzoate to Butyl Benzoate

temp, K (±0.5 K)	$10^{-2}k_3$, L mol^{-1} s^{-1}	temp, K (±0.5 K)	$10^{-2}k_3$, L mol^{-1} s^{-1}
333	1.72 ± 0.16	373	13.00 ± 1.27
353	4.72 ± 0.37	388	16.88 ± 1.40

thought to act as Lewis acids in polytransesterification reactions;[12] for example, Ca^{2+} catalysis of condensation polymerization of dimethyl terephthalate with ethylene glycol is first order in glycol, ester, and catalyst. Antimony oxide is believed to catalyze polytransesterification by ligand exchange within the antimony coordination sphere.[13]

In conclusion, we have examined some basic mechanistic features of the Ti(IV)-catalyzed transesterification and have found that, unlike some other transesterification reactions, the titanate-catalyzed process is independent of alcohol concentration. Catalyst structure is important: catalysts that maintain minimum aggregation throughout the reaction while still providing adequate coordination sites for the transesterification seem to be most active. Comparison of our results to those of Uri and Tuulmets[1] suggests that ligand structure plays an important role in determining the transition state of the reaction. Further studies of ligand structure influence will not only help in understanding transesterification catalysis, but may help elucidate other titanate-catalyzed processes as well. Toward this end, we are studying the steric and electronic effects of other ligands on transesterification and are employing spectroscopic techniques to better understand the reactions which take place in the coordination sphere of the metal.

Acknowledgment. I thank Drs. H. E. Bryndza and P. L. Watson for many valuable discussions and M. J. Grovola for expert technical assistance.

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(14) Contribution No. 4661.

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Polyoxomolybdate–*o*-Benzoquinone Interactions. Synthesis and Structure of a Diacetal Derivative, $[Mo_4O_{15}(OH)(C_{14}H_8)]^{3-}$, from 9,10-Phenanthrenequinone Carbonyl Insertion. Comparison to the Reaction Products with Tetrachloro-1,2-benzoquinone, the Ligand-Bridged Binuclear Complexes $[(MoO_2Cl_2)_2L]^{2-}$, L = $(C_6Cl_2O_4)^{2-}$ and $(C_2O_4)^{2-}$, Formed via Carbonyl Insertion and Chloride Transfer

Sir:

The structural relationship of polyoxoanions to solid oxides has prompted a number of investigations of the interactions between poly oxometalate clusters and substrate organic molecules.[1-4] Investigations of polyoxomolybdate–carbonyl interactions have demonstrated that carbonyl insertion into a Mo–O bond is a common feature of this chemistry,[5,6] resulting in a class of tetranuclear polyoxomolybdate acetal structures for which $[RCHMo_4O_{15}H]^{3-}$ provides the prototype.[5] In the course of our continuing investigations of the chemistry of polyoxomolybdates with catechol and *o*-quinone ligand types,[7,8] we have examined the reaction chemistries of 9,10-phenanthrenequinone and tetrachloro-1,2-benzoquinone with $(Bu_4N)_2[Mo_2O_7]$ and found that, although carbonyl insertion occurs in both instances, dramatically different structural types are formed as a consequence of chloride transfer in the latter case.

Reaction of 1 equiv of 9,10-phenthrenequinone with 2 equiv of $(Bu_4N)_2[Mo_2O_7]$ in moist CH_3OH followed by addition of ether results in precipitation of a yellow product that is analyzed as $(Bu_4N)_3[Mo_4O_{15}(OH)(C_{14}H_8)]$ (I)[9] after recrystallization from CH_2Cl_2/ether. As shown in Figure 1, (I) exhibits a tetranuclear core, related to those previously described for $[(CH_3)_2AsMo_4O_{15}H]^{2-}$,[10] $[CH_2Mo_4O_{15}H]^{3-}$, and $[HCCHMo_4O_{15}X]^{3-}$. As a consequence of both carbonyl residues inserting into the cluster core, the complex may be described as a diacetal derivative, with the $(C_{14}H_8O_4)^{4-}$ unit capping the $[Mo_4O_{11}(OH)]^+$ framework, providing terminal (O3 and O4) and bridging (O1 and O2) oxygen donor interactions. The most unusual features of the structure are the triply bridging hydroxy group, O16, and the single five-coordinate molybdenum center, Mo1. These features contrast with the exclusively six-coordinate molybdenum sites observed for $[CH_2Mo_4O_{15}H]^{3-}$ and $[HCCHMo_4O_{15}F]^{3-}$ and the quadruply bridging mode assumed by the hydroxyl group of $[CH_2Mo_4O_{15}H]^{3-}$.

The contrast between the chemistry of glyoxal and that of 9,10-phenanthrenequinone with $[Mo_2O_7]^{2-}$ was not anticipated. Whereas the α-dialdehyde glyoxal initially yields the isolable formylated methylenedioxomolybdate $[OHCCHMo_4O_{15}H]^{3-}$, which undergoes intramolecular insertion of the second carbonyl

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(9) Anal. Calcd for $(Bu_4N)_3[Mo_4O_{15}(OH)(C_{14}H_8)]$, $C_{62}H_{117}N_3O_{16}Mo_4$ (I): C, 48.2; H, 7.58; N, 2.72. Found: C, 48.6; H, 7.63; N, 2.83. IR (KBr pellet, cm^{-1}): 2960 (s), 2875 (ms), 1490 (s), 1380 (m), 1260 (m), 1155 (m), 1070 (m), 1030 (m), 1000 (m), 920 (vs), 905 (vs), 800 (m), 755 (m), 692 (s). Crystal data: tetragonal space group $I4_1/a$, with a = 48.129 (6) Å, c = 13.057 (2) Å, V = 30 246.2 (12) Å^3, Z = 16, and D_{calcd} = 1.35 g cm^{-3}. Structure solution and refinement based on 5554 reflections with $F_o \geq 6\sigma(F_o)$ (Mo Kα, λ = 0.71073 Å) converged at a conventional discrepancy factor of 0.0545.
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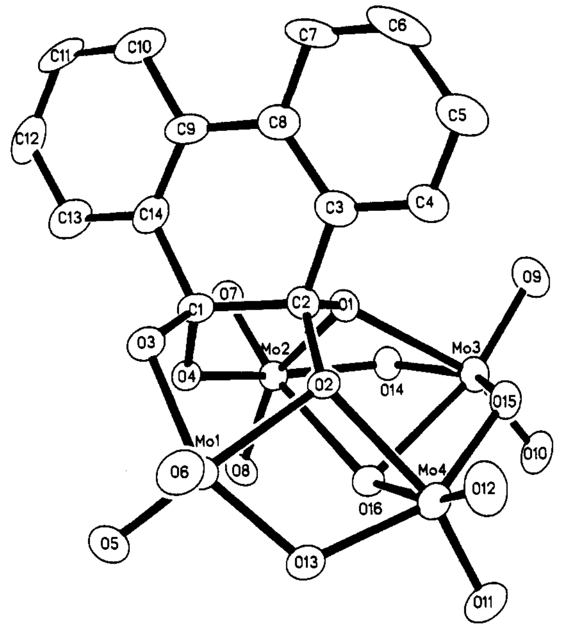

Figure 1. Perspective view of the structure of $[Mo_4O_{15}(OH)(C_{14}H_8)]^{3-}$ (I), showing the atom-labeling scheme and omitting hydrogen atoms. Selected bond lengths (Å) and angles (deg): Mo1–O2, 2.123 (7); Mo1–O3, 1.962 (8); Mo2–O1, 2.156 (7); Mo2–O4, 1.976 (8); Mo2–O16, 2.513 (8); Mo3–O1, 2.322 (8); Mo3–O16, 2.294 (8); Mo4–O2, 2.207 (7); Mo4–O16, 2.294 (8); Mo–O_t(av), 1.707 (11); Mo–O_{2b}(av), 1.886 (9) and 1.941 (10); Mo1···O16, 3.702 (8); O2–Mo1–O5, 143.7 (4); O3–Mo1–O13, 145.1 (3); O6–Mo1–O(av), 106.3 (10); O4–Mo2–O14, 148.4 (3); O1–Mo2–O8, 149.8 (4); O1–Mo3–O10, 158.4 (4); O2–Mo4–O11, 158.2 (4). Abbreviations: O_t, terminal oxo group; O_{2b}, doubly bridging oxo group.

only upon addition of HF to give $[HCCHMo_4O_{15}F]^{3-}$,[6] complex I forms without the necessity of anion substitution and further cluster expansion, although initial formation of a monoacetal intermediate is likely. Furthermore, the ^{17}O NMR spectrum of I exhibits two resonances in an approximately 2:1 ratio in the 400–420 ppm region associated with bridging MoOMo oxo groups, although the structure of I presents three chemically distinct MoOMo bond types: O13, O14, and O15. As the temperature is lowered, the downfield resonances broadens and finally resolves into two peaks of equal intensity at −60 °C. Thus, in the low-temperature limit three distinct resonances assigned to doubly bridging oxo groups are observed, consistent with the unsymmetrically bridged structure presented by the solid state. The room-temperature equivalence of O13 and O14 may suggest rapid intramolecular exchange of the triply bridging hydroxy group O16 between equivalent sites bridging Mo2–Mo3–Mo4 and Mo1–Mo3–Mo4, indicating that the anion cavity of I allows a degree of OH^- group migration as a consequence of its expanded volume relative to that of $[(CH_2)Mo_4O_{15}H]^{3-}$, where the OH^- is rigidly held. Alternatively, the ^{17}O NMR behavior may simply reflect anion symmetry.

The reaction of $(Bu_4N)_2[Mo_2O_7]$ with a 2-fold excess of tetrachloro-1,2-benzoquinone in methanol/acetonitrile, followed by careful addition of ether, yields dark blue crystals of $(Bu_4N)_2[(MoO_2Cl_2)_2(C_6Cl_2O_4)]\cdot 0.5CH_3CN$ (II; yield 30%).[11] Upon further addition of ether and standing at 4 °C for 2 weeks, yellow crystals of $(Bu_4N)_2[(MoO_2Cl_2)_2(C_2O_4)]$ (III) deposit in 25% yield.

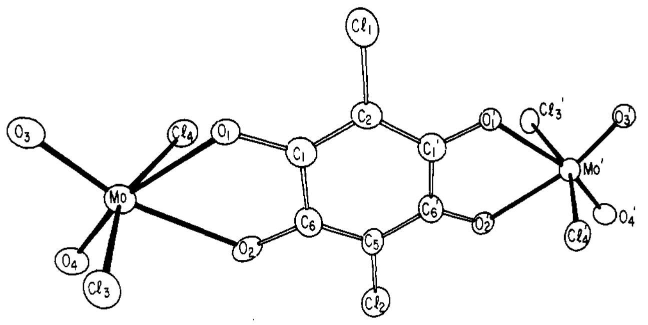

Figure 2. ORTEP view of the structure of $[(MoO_2Cl_2)_2(C_6O_4Cl_2)]^{2-}$ (anion of II), showing the atom-labeling scheme. Selected bond lengths (Å) and angles (deg): Mo–Cl3, 2.353 (5); Mo–Cl4, 2.348 (6); Mo–O1, 2.24 (1); Mo–O2, 2.24 (1); Mo–O3, 1.64 (1); Mo–O4, 1.66 (1); C1–O1, 1.27 (2); C6–O2, 1.27 (2); Cl3–Mo–Cl4, 158.3 (2); O3–Mo–O4, 104.5 (7); O1–Mo–O4, 162.2 (5); O2–Mo–O3, 163.4 (6); O1–Mo–O2, 70.3 (4).

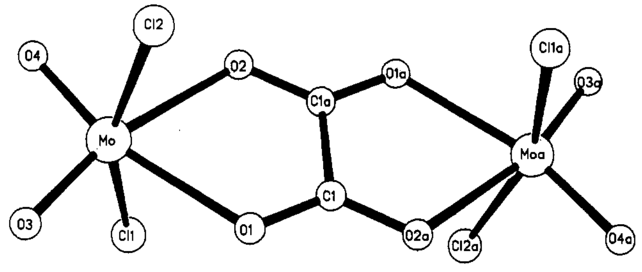

Figure 3. ORTEP view of the structure of $[(MoO_2Cl_2)_2(C_2O_4)]^{2-}$ (anion of III), showing the atom-labeling scheme. Selected bond lengths (Å) and angles (deg): Mo–Cl1, 2.382 (1); Mo–Cl2, 2.368 (1); Mo–O1, 2.231 (2); Mo–O2, 2.253 (2); Mo–O3, 1.685 (3); Mo–O4, 1.688 (3); C1–C1a, 1.545 (5); Cl1–Mo–Cl2, 159.8 (1); O1–Mo–O2, 72.8 (1); O3–Mo–O4, 105.0 (1); O1–C1–C1a, 116.5 (4); O1–C1–O2a, 126.7 (4); C1a–C1–O2a, 116.8 (4).

As illustrated in Figure 2, the structure of II consists of discrete $[(MoO_2Cl_2)_2(C_6Cl_2O_4)]^{2-}$ anions possessing a crystallographic 2-fold axis passing through Cl1, C2, C5, and Cl2. The two *cis*-dioxodichloromolybdenum(VI) units are bridged by a chloranilate dianion $(Cl_2C_6O_4)^{2-}$, formed as a consequence of chloride transfer from the tetrachloro-1,2-benzoquinone to a molybdate center, coupled to oxo addition to the quinone ligand.

Compound III, depicted in Figure 3, presents a similar bridged binuclear structure, $[(MoO_2Cl_2)_2L]^{2-}$, with L = oxalate.[12] Although the formation of the bridging oxalate ligand from tetrachloro-1,2-benzoquinone requires that carbonyl insertion occur as a step in the chemical transformation, the coupled chloride-transfer reaction and C–C bond cleavage complicate the interpretation of the chemical sequence. The ability of molybdate to abstract chloride from chlorohydrocarbons has precedents in the synthesis of $[Mo_2O_2Cl_5(SPh)_2]^-$ via chloride abstraction from chloroform[13] and in the reaction of $[MoO_4]^{2-}$ with CH_2Cl_2 to yield $[CH_2Mo_4O_{15}H]^{3-}$.[14] Although II may also be prepared from the reaction of $[MoO_2Cl_2(dmf)_2]$ with chloranilic acid, we have been unable to isolate III under similar conditions from $[MoO_2Cl_2(dmf)_2]$ and oxalate.

Although carbonyl insertion into Mo–O bonds is a dominant theme of polyoxomolybdate–carbonyl chemistry, there appears to be considerable variability in the details of the structural types adopted and in the influence of ligand substituents. We are currently examining the chemistry of related *o*-quinone ligands,

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(11) Anal. Calcd for $(Bu_4N)_2[(MoO_2Cl_2)_2(C_6Cl_2O_4)]\cdot 0.5CH_3CN$, $C_{39}H_{73.5}N_{2.5}O_8Cl_6Mo_2$ (II): C, 42.2; H, 6.63; N, 3.16. Found: C, 42.1; H, 6.53; N, 3.01. IR (KBr pellet, cm^{-1}): 2960 (s), 2890 (ms), 1545 (vs), 1475 (s), 1390 (s), 954 (vs), 920 (vs), 860 (vs), 485 (vs), 345 (s). Electronic spectrum (CH_3CN; λ, nm [ε, M^{-1} cm^{-1}]): 563 [8.26 × 10^2], 367 [2.14 × 10^4], 305 [8.6 × 10^3]. ^{17}O NMR ($CDCl_3$, ppm): 338, 1005. Crystal data: orthorhombic space group *P*222, with $a = 9.804$ (2) Å, $b = 15.465$ (3) Å, $c = 18.951$ (3) Å, $V = 2873.3$ (11) $Å^3$, $Z = 2$, and $D_{calcd} = 1.28$ g cm^{-3}. Structure solution and refinement based on 1304 reflections with $F_o \geq 6\sigma(F_o)$ (Mo Kα, λ = 0.71073 Å) converged at $R = 0.0602$.

(12) Anal. Calcd for $(Bu_4N)_2[(MoO_2Cl_2)_2(C_2O_4)]$, $C_{34}H_{72}N_2O_8Cl_4Mo_2$ (III): C, 42.1; H, 7.43; N, 2.89. Found: C, 42.2; H, 7.34; N, 2.76. IR (KBr pellet, cm^{-1}): 2965 (s), 2878 (vs), 1550 (vs), 1470 (s), 1385 (s), 945 (vs), 910 (vs), 850 (vs), 340 (s). Crystal data: monoclinic space group $P2_1/n$, with $a = 9.916$ (2) Å, $b = 17.701$ (3) Å, $c = 13.513$ (3) Å, $\beta = 90.20$ (1)°, $V = 2393.3$ (7) $Å^3$, $Z = 2$, and $D_{calcd} = 1.35$ g cm^{-3}. Structure solution and refinement based on 2989 reflections with $F_o \geq 6\sigma(F_o)$ (Mo Kα, λ = 0.71073 Å) converged at 0.0338.

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such as 1,2-naphthoquinone, 3,5-dibutylbenzoquinone, and tetrabromo-1,2-benzoquinone, to establish general patterns of product structure.

Acknowledgment. This work was supported by a grant from the National Science Foundation to Jon Zubieta (CHE8514634).

Supplementary Material Available: Tables of non-hydrogen atom coordinates, bond lengths, bond angles, thermal parameters, and hydrogen atom coordinates for I-III (17 pages); tables of observed and calculated structure factors for the complexes (47 pages). Ordering information is given on any current masthead page.

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Carbon-Carbon Bond Formation in the Reductive Coupling of Nitriles at a Multiply Bonded Dirhenium Center

Sir:

Compounds that contain metal-metal multiple bonds can display a rich and varied redox chemistry.[1] However, the use of these metal-metal-bonded complexes as sources of electrons in organic coupling reactions is very limited. Previous examples include the recently reported coupling of ethylene by triply bonded $W_2(O\text{-}i\text{-}Pr)_6$,[2] the reductive coupling of ketones by doubly bonded $W_2Cl_4(\mu\text{-}OR)_2(OR)_2(ROH)_2$,[3] and the coupling between nitriles and the coordinated alkyne ligand in adducts such as $W_2(O\text{-}t\text{-}Bu)_6(py)(\mu\text{-}C_2H_2)$.[4] We report here the first examples of the reductive coupling of nitriles by multiply bonded dimetal compounds in which the dimetal unit is retained and the coupled nitrile ligand exhibits a novel bonding mode. The reducing equivalents needed in these coupling reactions are provided by the dimetal unit.

The triply bonded dirhenium(II) complexes $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl,Br; dppm = $Ph_2PCH_2PPh_2$)[5] react with carbon monoxide, nitriles, and isocyanides to coordinate up to three of these ligands and give products in which a metal-metal bond is retained.[6] When the preformed bis(nitrile) complex $[(EtCN)_2ClRe(\mu\text{-dppm})_2ReCl_2]PF_6$[7] is reacted in refluxing acetonitrile for 2 days, the green, paramagnetic complex $[Re_2Cl_3(\mu\text{-dppm})_2(\mu\text{-}HN_2C_2Me_2)(NCMe)]PF_6$ can be isolated in 67% yield.[8] The $HN_2C_2Me_2$ ligand is formed from the reductive coupling of two acetonitrile ligands. The reaction seems general in that acetonitrile, propionitrile, isobutyronitrile, and benzonitrile have all been coupled by this means to give analogous species. The corresponding bromo complexes have also been prepared for the acetonitrile and propionitrile derivatives.[9]

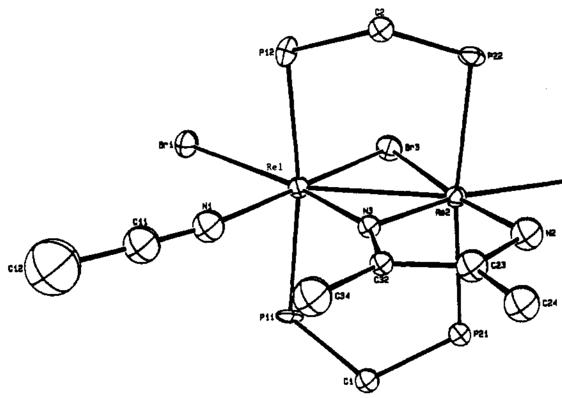

Figure 1. ORTEP view of the structure of the $[Re_2Br_3(\mu\text{-dppm})_2(\mu\text{-}HN_2C_2Me_2)(NCMe)]^+$ cation with phenyl carbon atoms of the dppm ligands omitted. The thermal ellipsoids are drawn at the 50% probability level except those for the methylene carbon atoms, which are shown as circles of arbitrary radius. This view represents half of the disorder associated with the cation. Important bond lengths (Å) and angles (deg) are as follows: $Re_1-Re_2 = 2.6656\ (8)$, $Re_1-Br_1 = 2.580\ (2)$, $Re_1-Br_3 = 2.540\ (2)$, $Re_1-P_{11} = 2.449\ (3)$, $Re_1-P_{12} = 2.447\ (4)$, $Re_1-N_1 = 2.04\ (1)$, $Re_1-N_3 = 1.98\ (1)$, $Re_2-Br_2 = 2.571\ (2)$, $Re_2-Br_3 = 2.545\ (2)$, $Re_2-P_{21} = 2.463\ (4)$, $Re_2-P_{22} = 2.446\ (3)$, $Re_2-N_2 = 2.03\ (1)$, $Re_2-N_3 = 1.96\ (1)$, $N_1-C_{11} = 1.18\ (3)$, $N_2-C_{23} = 1.45\ (4)$, $N_3-C_{32} = 1.32\ (4)$, $C_{11}-C_{12} = 1.49\ (5)$, $C_{23}-C_{24} = 1.58\ (4)$, $C_{23}-C_{32} = 1.41\ (5)$, $C_{32}-C_{34} = 1.49\ (4)$; $Re_1-Br_3-Re_2 = 63.22\ (4)$, $Br_1-Re_1-Br_3 = 90.59\ (5)$, $Br_2-Re_2-Br_3 = 90.17\ (5)$, $Br_1-Re_1-N_1 = 83.3\ (3)$, $Br_2-Re_2-N_2 = 84.8\ (3)$, $N_1-Re_1-N_3 = 80.8\ (5)$, $N_2-Re_2-N_3 = 79.2\ (5)$, $Re_2-N_2-C_{23} = 109\ (2)$, $N_2-C_{23}-C_{32} = 120\ (3)$, $C_{23}-C_{32}-N_3 = 108\ (3)$, $Re_2-N_3-C_{32} = 123\ (2)$, $Re_1-N_3-C_{32} = 151\ (2)$.

An X-ray crystal structure determination on a salt of the $[Re_2Br_3(\mu\text{-dppm})_2(\mu\text{-}HN_2C_2Me_2)(NCMe)]^+$ cation has confirmed the structure,[10] clearly showing the presence of coupled nitriles (Figure 1). The *all-cis* arrangement of halide ligands and other features of the structure are normal.[6b] This coupling gives rise to a delocalized, planar, five-membered metallocycle. The $HN_2C_2Me_2$ ligand can be considered formally as having contributions from the ligand forms shown in I and II (the dppm ligands have been omitted). It is not clear at this time which ligand form,

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(8) Anal. Calcd for $C_{56}H_{54}Cl_3F_6N_3P_5Re_2$: C, 44.35; H, 3.59; Cl, 7.01. Found: C, 44.36; H, 3.55; Cl, 6.99. IR spectrum (Nujol mull): ν(N—H) 3354 m cm^{-1}; $\nu(C\equiv N)$ 2286 w cm^{-1}. Cyclic voltammetric half-wave potentials (recorded in 0.1 M $(n\text{-}Bu_4N)PF_6-CH_2Cl_2$ with a Pt-bead electrode at $v = 200$ mV s^{-1}): $E_{1/2}(ox) = +0.19$ V and $E_{1/2}(red) = -0.80$ V vs Ag/AgCl. Conductivity in acetone: $\Lambda_M = 121\ \Omega^{-1}\ cm^2\ mol^{-1}$ for $c \sim 1 \times 10^{-3}$ M. Magnetic moment (Faraday method): 2.05 (±0.1) μ_B. X-Band ESR spectrum (CH_2Cl_2, −160 °C): complex pattern from 1.5 to 4.5 kG centered at $g \simeq 2.14$.

(9) These compounds gave satisfactory elemental analyses (see Supplementary Material) and had properties very similar to those shown by the rhenium chloride–acetonitrile coupled product.[8]

(10) Green crystals of $[Re_2Br_3(\mu\text{-dppm})_2(\mu\text{-}HN_2C_2Me_2)(NCMe)](PF_6)_{0.8}(Br)_{0.2}\cdot{}^1/_2Et_2O\cdot Me_2CO$, which were grown by diffusion of diethyl ether vapor into an acetone solution of the complex, are triclinic, space group $P\bar{1}$, with $a = 13.150\ (3)$ Å, $b = 21.227\ (5)$ Å, $c = 12.592\ (2)$ Å, $\alpha = 99.53\ (2)°$, $\beta = 113.35\ (2)°$, $\gamma = 74.72\ (2)°$, $V = 3160\ (2)$ Å^3, $Z = 2$, and $d_{calcd} = 1.852$ g/cm^3. X-ray diffraction data were collected at −150 °C on a 0.20 × 0.11 × 0.08 mm crystal for 8065 independent reflections having $4 < 2\theta < 45°$ on an Enraf-Nonius CAD4 diffractometer using graphite-crystal-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). Data collection and reduction methods are the same as described elsewhere.[11] An empirical absorption correction was applied,[12] but no correction for extinction was made. There are three separate disorders present in the crystal: the nitrile ligand is disordered with the $HN_2C_2Me_2$ ligand, the molecule of Et_2O is disordered on an inversion center, and the anion refines as 0.2 Br^- and 0.8 PF_6^-. Owing to these disorder problems, only the Re, Br, P, and F atoms were refined anisotropically, and corrections for anomalous scattering were applied to these atoms.[13] All other non-hydrogen atoms were refined isotropically. The final residuals were $R = 0.066$ and $R_w = 0.092$ for 6019 data with $I > 3\sigma(I)$.

(11) Fanwick, P. E.; Harwood, W. S.; Walton, R. A. *Inorg. Chim. Acta* **1986**, *122*, 7.

(12) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A: Found Crystallogr.* **1983**, *A39*, 158.

(13) (a) Cromer, D. T. *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.3.1. (b) For the scattering factors used in the structure solution see Cromer, D. T.; Waber, J. T. *Ibid.* Table 2.2B.

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