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]

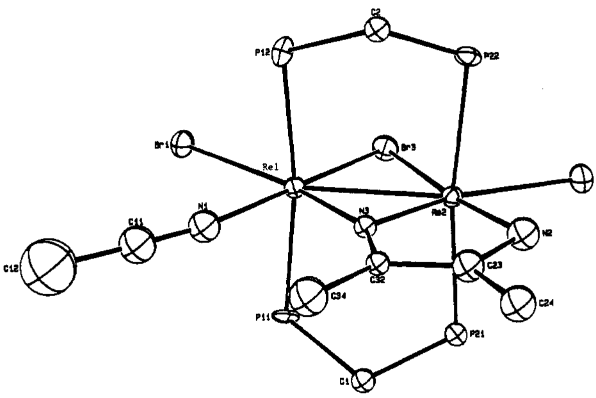

Figure 1. ORTEP view of the structure of the $[Re_2Br_3(\mu\text{-dppm})_2(\mu\text{-}HN_2C_2Me_2)(NCMe)]^+$ cation with phenyl carbon atoms of the dppm ligands omitted. The thermal ellipsoids are drawn at the 50% probability level except those for the methylene carbon atoms, which are shown as circles 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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(1) (a) Cotton, F. A.; Walton, R. A. *Multiple Bonds Between Metal Atoms*; Wiley: New York, 1982. (b) Cotton, F. A.; Walton, R. A. *Struct. Bonding (Berlin)* **1985**, *62*, 1.

(2) Chisholm, M. H.; Hampden-Smith, M. *J. Am. Chem. Soc.* **1987**, *109*, 5871.

(3) Anderson, L. B.; Cotton, F. A.; DeMarco, D.; Falvello, L. R.; Tetrick, S. M.; Walton, R. A. *J. Am. Chem. Soc.* **1984**, *106*, 4743.

(4) Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *Chem. Soc. Rev.* **1985**, *14*, 69 and references cited therein.

(5) (a) Ebner, J. R.; Tyler, D. R.; Walton, R. A. *Inorg. Chem.* **1976**, *15*, 833. (b) Barder, T. J.; Cotton, F. A.; Dunbar, K. R.; Powell, G. L.; Schwotzer, W.; Walton, R. A. *Inorg. Chem.* **1985**, *24*, 2550.

(6) (a) Price, A. C.; Walton, R. A. *Polyhedron* **1987**, *6*, 729 and references cited therein. (b) Fanwick, P. E.; Price, A. C.; Walton, R. A. *Inorg. Chem.* **1987**, *26*, 3920. (c) Fanwick, P. E.; Price, A. C.; Walton, R. A. *Inorg. Chem.* **1987**, *26*, 3086.

(7) Barder, T. J.; Cotton, F. A.; Falvello, L. R.; Walton, R. A. *Inorg. Chem.* **1985**, *24*, 1258.

(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: Λ_M = 121 Ω^{-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, α = 99.53 (2)°, β = 113.35 (2)°, γ = 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 (λ = 0.71073 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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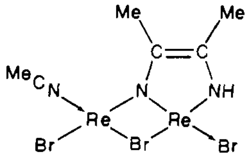

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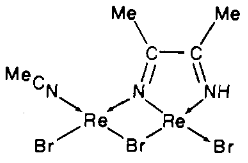

II

if either, is the better description in view of the relatively low precision of the present structure determination. Work is underway to obtain crystals of other derivatives that do not exhibit a disorder between the nitrile and $HN_2C_2R_2$ ligands, so as to permit a more accurate structure determination.

The corresponding 1:2 salts $[Re_2X_3(\mu\text{-dppm})_2(\mu\text{-}HN_2C_2R_2)(NCR)](PF_6)_2$ can be prepared by oxidizing the green 1:1 salts with $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ in acetone or $NOPF_6$ in CH_2Cl_2.[14] In addition, the red acetonitrile complex $[Re_2Cl_3(\mu\text{-dppm})_2(\mu\text{-}HN_2C_2Me_2)(NCMe)](PF_6)_2$ can be isolated from mixtures in acetonitrile of $(n\text{-}Bu_4N)_2Re_2Cl_8$, dppm, and KPF_6 that have been refluxed for several days. The ^1H NMR spectrum (CD_2Cl_2, 25 °C) of this complex is of particular interest. In addition to the resonances associated with the coordinated dppm, there is a broad N–*H* resonance at $\delta = +7.90$ and three methyl resonances at $\delta = +1.74$ (s), +3.02 (s), and +6.05 (s). It is unclear at this time why two of the methyl resonances appear so far downfield, but this may reflect diamagnetic anisotropy effects or some degree of contact shifting.[15] The methyl resonances remain unchanged when this solution is cooled to −50 °C.

The coupling of two acetonitrile molecules by $(Re{\equiv}Re)^{4+}$, as is present in $Re_2X_4(\mu\text{-dppm})_2$, to give I and II, can formally be represented as redox processes that involve oxidation of the dirhenium core to Re_2^{6+} and Re_2^{8+}, respectively, depending upon the description of the resulting $Re_2(\mu\text{-}NC(CH_3)C(CH_3)NH)$ dimetallacycle. We can envision the reactions as first giving the dicationic species $[Re_2X_3(\mu\text{-dppm})_2(\mu\text{-}HN_2C_2R_2)(NCR)]^{2+}$ (these are formally Re_2^{6+} or Re_2^{8+} derivatives depending upon the ligand formulation, i.e. I or II, respectively) that then undergo a one-electron reduction in the reaction mixture to afford the monocations (correspondingly formulated as Re_2^{5+} or Re_2^{7+}). The origin of the reductant for the latter step is not known. The structure determination on $[Re_2Br_3(\mu\text{-dppm})_2(\mu\text{-}HN_2C_2Me_2)(NCMe)]^+$ (Figure 1) has shown the Re–Re distance to be 2.666 (1) Å, a value that does not easily distinguish between a Re_2^{5+} and Re_2^{7+} core in such an edge-sharing bioctahedral structure.[16]

The intramolecular multielectron redox process that gives rise to the nitrile coupling is accompanied by the "protonation" of the terminal nitrogen atom of the coupled ligand. Experiments using CD_3CN in place of CH_3CN show that the source of this hydrogen is the acetonitrile ligand itself. This hydrogen is very labile and exchanges with deuterium when the complex is treated with CH_3CN/D_2O. The resulting product has its IR-active ν(N–D) mode at 2493 m cm^{-1}.

Along with the bonding mode of the coupled ligand,[17] these reactions have several other important features; viz., they do not require the use of an extraneous reducing agent, the dimetal core remains in the final product, and both alkyl and aryl nitriles have been successfully coupled. Although there are a few examples of the stabilization of reductively coupled nitriles at mononuclear transition-metal centers,[18-22] no systems have shown the combination of features displayed by these dirhenium species, which represent the most versatile reactions of their type to date. An examination of the scope of this chemistry is underway.

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Supplementary Material Available: A listing of representative elemental microanalyses, experimental details relating to the crystal structure determination, listings of crystallographic data and data collection parameters (Table S1), atomic positional parameters (Table S2), anisotropic thermal parameters (Table S3), complete bond distances (Table S4), and complete bond angles (Table S5), and a figure showing the full atomic numbering scheme and disorder for the $[Re_2B_3(\mu\text{-dppm})_2(\mu\text{-}HN_2C_2Me_2)(NCMe)]^+$ cation (Figure S1) (24 pages); a table of observed and calculated structure factors (42 pages). Ordering information is given on any current masthead page.

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(14) These complexes are not ESR-active and display well-defined NMR spectra. Magnetic moment determinations at room temperature by the Faraday method show a weak paramagnetism after allowance has been made for diamagnetic corrections; e.g., $\chi_g = -0.212 \times 10^{-6}$ cgsu and $\mu_{eff} = 1.20\ \mu_B$ for $[Re_2Br_3(\mu\text{-dppm})_2(\mu\text{-}HN_2C_2Me_2)(NCMe)](PF_6)_2$. They behave as 1:2 electrolytes in acetone and have electrochemical properties in 0.1 M $(n\text{-}Bu_4N)PF_6\text{–}CH_2Cl_2$ that accord with their being the one-electron-oxidized congeners of $[Re_2X_3(\mu\text{-dppm})_2(\mu\text{-}HN_2C_2R_2)(NCR)]PF_6$; e.g. $E_{1/2}(\text{red}) = +0.19$ V and $E_{1/2}(\text{red}) = -0.80$ V for X = Cl and R = Me.

(15) Similar features are seen in the ^1H NMR spectra of the propionitrile derived complexes. For example, the spectrum of $[Re_2Cl_3(\mu\text{-dppm})_2(\mu\text{-}HN_2C_2Et_2)(NCEt)](PF_6)_2$ (recorded in CD_2Cl_2) has resonances at δ +7.96 (s, N-*H*), −0.05 (t, C*H*$_3$), +0.44 (t, C*H*$_3$), +1.56 (t, C*H*$_3$), +2.07 (q, C*H*$_2$), +4.20 (q, C*H*$_2$), and +4.66 (q, C*H*$_2$).

(16) Anderson, L. B.; Cotton, F. A.; Dunbar, K. R.; Falvello, L. R.; Price, A. C.; Reid, A. H.; Walton, R. A. *Inorg. Chem.* **1987**, *26*, 2717.

(17) Note that this complex possesses a structural analogy with $W_2(\mu\text{-}NC(Ph)CHCH)(O\text{-}i\text{-}Pr)_6$ formed by coupling of the PhC≡N and HC≡CH ligands. Chisholm, M. H.; Hoffman, D. M.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 6815.

(18) Harris, T. V.; Rathke, J. W.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 6966.

(19) Bercaw, J. E.; Davies, D. L.; Wolczanski, P. T. *Organometallics* **1986**, *5*, 443.

(20) DeBoer, E. J. M.; Teuben, J. H. *J. Organomet. Chem.* **1978**, *153*, 53.

(21) (a) Finn, P. A.; King, M. S.; Kilty, P. A.; McCarley, R. E. *J. Am. Chem. Soc.* **1975**, *97*, 220. (b) Cotton, F. A.; Hall, W. T. *Inorg. Chem.* **1978**, *17*, 3525.

(22) Cotton, F. A.; Hall, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 5094.

A Novel Hexairon(III) Aggregate Prepared from a Basic Iron(III) Benzoate. Possible Building Blocks in Ferritin Core Formation

Sir:

Ferritin is the iron storage protein found in most life forms. Up to 4500 high-spin iron(III) centers can be accommodated in the hollow core of the apoprotein,[1] but few structural details are known about their aggregation and placement. We have been investigating the oligomerization of mononuclear and oxo-bridged binuclear iron(III) units under hydrolytic conditions that might occur during ferritin core formation.[2] Studies of this kind have uncovered a fascinating array of new Fe_3,[3] Fe_4,[4] Fe_6,[5] Fe_8,[6] and

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(1) (a) Clegg, G. A.; Fitton, J. E.; Harrison, P. M.; Treffry, A. *Prog. Biophys. Mol. Biol.* **1980**, *36*, 53–86. (b) Crichton, R. R. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 57. (c) Theil, E. C. *Annu. Rev. Biochem.* **1987**, *56*, 289.

(2) Lippard, S. J. *Angew. Chem.* **1988**, *100*, 353 and references cited therein.

(3) Gorun, S. M.; Papaefthymiou, G. C.; Frankel, R. B.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 4244.

(4) (a) Stukan, R. A.; Ponomarev, V. I.; Nifontov, V. P.; Turtě, K. I.; Atovmyan, L. O. *J. Struct. Chem.* (*Engl. Transl.*) **1985**, *26*, 197. (b) Jameson, D. L.; Xie, C.-L.; Hendrickson, D. N.; Potenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1987**, *109*, 740. (c) Armstrong, W. H.; Roth, M. E.; Lippard, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 6318. (d) Murch, B. P.; Bradley, F. C.; Boyle, P. D.; Que, L., Jr.; Papaefthymiou, V. *J. Am. Chem. Soc.* **1987**, *109*, 7993. (e) Gorun, S. M.; Lippard, S. J. *Inorg. Chem.* **1988**, *27*, 149.

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