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New Paramagnetic Re(II) Compounds with Nitrile and Cyanide Ligands Prepared by Homolytic Scission of Dirhenium Complexes

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The preparation and characterization of three new paramagnetic complexes of the 17-electron Re^{II} ion are reported. The salts [Re(triphos)(CH_3CN)$_3$)][X]$_2$, X = $[BF_4]^-$ (**1**), $[PF_6]^-$ (**2**), and $[Et_4N]$[Re(triphos)(CN)$_3$] (**3**) were prepared by homolytic cleavage of the Re–Re bond in $[Re_2(CH_3CN)_{10}][BF_4]_4$ or by disruption of the chlorine bridges in [(triphos)Re(μ-Cl)$_3$Re(triphos)]Cl (**1**) (triphos = 1,1,1-tris(diphenylphosphino-methyl)ethane) and characterized by single-crystal X-ray diffraction, infrared and ^{1}H NMR spectroscopies, cyclic voltammetry, and magnetic susceptibility measurements. Compound **2** undergoes reversible reduction and irreversible oxidation processes while **3** undergoes a reversible reduction, an irreversible oxidation, and a reversible oxidation. The magnetic susceptibility data for **2** and **3** exhibit a strong temperature independent paramagnetic component which is in accord with a highly anisotropic $S = {}^1/_2$ magnetic ground state. The results of this study indicate that dinuclear $Re_2^{II,II}$ starting materials are viable precursors for producing unusual mononuclear Re^{II} complexes.

Supramolecular chemistry involving transition metal ions is a powerful entry into the design of molecular materials with tunable magnetic,[1] electronic,[2] and photophysical properties.[3] Such studies require a steady influx of new precursors to investigate properties of both discrete molecules and polymeric architectures. As part of our interest in this area, we are focusing on coordination complexes of Re which exhibit rich electrochemistry and photochemistry and offer the potential for engendering unusual anisotropic magnetic properties.

Mononuclear 17-electron complexes of Re^{II} are attractive prospects for applications in molecular magnetism due to strong spin−orbit coupling effects arising from the low-spin d^5 configuration. The main literature of mononuclear Re^{II} compounds consists of phosphine and carbonyl complexes[4] and electrochemically generated species, but the development of convenient synthetic routes for such compounds with a diversity of ligand types has been hindered by the tendency for Re^{II} to engage in metal−metal multiple bonding.[5] In spite of this obstacle, work by Walton and others[6] has demonstrated the feasibility of using bulky ligands to induce homolytic scission of the metal−metal bond of dirhenium $Re_2^{II,II}$ complexes to form stable mononuclear Re^{II} species. Herein we report the synthesis and characterization of new mixed-ligand Re^{II} compounds prepared by reacting triphos with two different dirhenium staring materials.

The cation $[Re(triphos)(CH_3CN)_3]^{2+}$ was synthesized from the M_2L_{10} complex $[Re_2^{II,II}(CH_3CN)_{10}][BF_4]_4$ prepared in our laboratories,[7] as well as from the face-sharing bioctahedral complex [(triphos)Re(μ-Cl)$_3$Re(triphos)]Cl originally reported by Walton and co-workers (triphos = 1,1,1-tris(diphenyl-

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(1) (a) Sessoli, R.; Tsai, H. L.; Schake, A. R.; Wang, S. Y.; Vincent, J. B.; Folting, K.; Gatteschi, D.; Christou, G.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1993**, *115*, 1804−1816. (b) Gatteschi, D.; Sessoli, R. *Angew. Chem., Int. Ed.* **2003**, *42*, 268−297. (c) Coronado, E.; Galán-Mascarós J. R.; Gomez-Garcia, C. J.; Laukhin, V. *Nature* **2000**, *408*, 447−449. (d) Entley, W. R.; Girolami, G. S. *Science* **1995**, *268*, 397−400.

(2) (a) Cotton, F. A.; Dikarev, E. V.; Petrukhina, M. A.; Schmitz, M.; Stang, P. J. *Inorg. Chem.* **2002**, *41*, 2903−2908. (b) Cotton, F. A.; Lin, C.; Murillo, C. A. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4810−4813. (c) Bera, J. K.; Angaridis, P.; Cotton, F. A.; Petrukhina, M. A.; Fanwick, P. E.; Walton, R. A. *J. Am Chem. Soc.* **2001**, *123*, 1515−1516.

(3) (a) Serroni, S.; Campagna, S.; Puntoriero, F.; Juris, A.; Denti, G.; Balzani, V.; Venturi, M. *Inorg. Synth.* **2002**, *33*, 10−18. (b) Vicinelli, V.; Ceroni, P.; Maestri, M.; Balzani, V.; Gorka, M.; Vogtle, F. *J. Am. Chem. Soc.* **2002**, *124*, 6461−6468. (c) Baudin, H. B.; Davidsson, J.; Serroni, S.; Juris, A.; Balzani, V.; Campagna, S.; Hammarstrom, L. *J. Phys. Chem. A* **2002**, *106*, 4312−4319.

(4) (a) Bond, A. M.; Colton, R.; McDonald, M. E. *Inorg. Chem.* **1978**, *17*, 2842−2847. (b) Bond, A. M.; Colton, R.; Gable, R. W.; Mackay, M. F.; Walter, J. N. *Inorg. Chem.* **1997**, *36*, 1181−1193. (c) Bond, A. M.; Colton, R.; Humphrey, D. G.; Mahon, P. J.; Snook, G. A.; Tedesco, V.; Walter, J. N. *Organometallics* **1998**, *17*, 2977−2985. (d) Bond, A. M.; Colton, R.; van der Bergen, A.; Walter, J. N. *Inorg. Chem.* **2000**, *39*, 4696−4703. (e) Costello, M. T.; Fanwick, P. E.; Green, M. A.; Walton, R. A. *Inorg. Chem.* **1992**, *31*, 2359−2365. (f) Crabtree, R. H.; Hlatky, G. G.; Holt, E. M. *Inorg. Chim. Acta* **1987**, *130*, 5−7.

(5) (a) Cotton, F. A.; Walton, R. A. *Multiple Bonds between Metal Atoms*, 2nd ed.; Clarendon Press: Oxford, 1993. See references therein. (b) Rouchias, G. *Chem. Rev.* **1974**, *74*, 560.

(6) (a) Nimry, T.; Walton, R. A. *Inorg. Chem.* **1977**, *16*, 2829−2834. (b) Hertzer, C. A.; Myers, R. E.; Brant, P.; Walton, R. A. *Inorg. Chem.* **1978**, *17*, 2383−2389. (c) Allison, J. D.; Wood, T. E.; Wild, R. E.; Walton, R. A. *Inorg. Chem.* **1982**, *21*, 3540−3546. (d) Allison, J. D.; Fanwick, P. E.; Walton, R. A. *Organometallics* **1984**, *3*, 1515−1520. (e) Bakir, M.; Fanwick, P. E.; Walton, R. A. *Polyhedron* **1987**, *6*, 907−913.

(7) Bernstein, S. N.; Dunbar, K. R. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1360−1362.

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phosphino-methyl)ethane).[8] Reactions of $[Re_2(CH_3CN)_{10}][BF_4]_4$ with excess triphos in a refluxing solution of CH_3CN/CH_2Cl_2 for 4 days produce $[Re(triphos)(CH_3CN)_3][BF_4]_2$ (**1**) in 30% yield.[9] The long time required for obtaining the mononuclear product is not surprising in view of the robustness of Re−Re triple bonds. The persistent green color of the reaction mixture, even after refluxing for 4 days, indicates that cleavage of the M−M bond is still incomplete. A green intermediate, as yet uncharacterized, is significantly less soluble in CH_3CN/Et_2O than is **1**, and was therefore separated by filtration. The yield of **1** is increased by employing longer reaction times and by using excess triphos ligand.

Although it proved to be possible to prepare **1** from $[Re_2(CH_3CN)_{10}][BF_4]_4$, the low yields and long reaction times led us to explore analogous chemistry of the face-sharing bioctahedral complex $[(triphos)Re(\mu\text{-}Cl)_3Re(triphos)]Cl$. Reactions of $[(triphos)Re(\mu\text{-}Cl)_3Re(triphos)]Cl$ with 4 equiv of $TlPF_6$ in the presence of acetonitrile lead to the formation of $[Re(triphos)(CH_3CN)_3][PF_6]_2$ (**2**) in good yields (76%) after 12 h of reflux.[10]

Reactions of **1** with 3 equiv of anhydrous $[Et_4N]CN$ in acetonitrile proceed with an immediate color change from yellow-orange to dark orange, but invariably the substituion product is contaminated with the $[Et_4N][BF_4]$ byproduct. Direct reaction of $[(triphos)Re(\mu\text{-}Cl)_3Re(triphos)]Cl$ with 6 equiv of anhydrous $[Et_4N]CN$ leads to homolytic scission of the Re_2^{4+} core to yield pure $[Et_4N][Re(triphos)(CN)_3]$ (**3**) in 33% yield.[11]

Infrared spectroscopy performed on a Nujol mull of **2** confirmed the presence of coordinated acetonitrile ligands with weak $\nu(C\equiv N)$ stretches appearing at 2274 cm^{-1} (s) and 2319 cm^{-1} (s). The shifts of the $\nu(C\equiv N)$ stretching modes to higher energies in **2** versus that of free acetonitrile (2252 cm^{-1}) are consistent with primarily σ-donation from the cyanide ligand to the metal ion.[12] The $\nu(C\equiv N)$ stretches for the cations in the salts **1** and **2** are essentially identical. The infrared spectrum of a microcrystalline sample of **3** contains two intense $\nu(C\equiv N)$ stretches at 2060 and 2070 cm^{-1}, which are shifted by 10 and 20 cm^{-1}, respectively, from that of tetraethylammonium cyanide (2050 cm^{-1}).

Single crystals of $[Re(triphos)(CH_3CN)_3][BF_4]_2$ (**1**) and $[Re(triphos)(CH_3CN)_3][PF_6]_2$ (**2**) were grown by slow diffusion of Et_2O into saturated solutions of the compounds in acetonitrile.[13] Single crystals of $[Et_4N][Re(triphos)(CN)_3]$ were grown by chilling a saturated solution of **3** in Et_2O/CH_3CN (50/50 v/v) for 12 h.[11] Structures were determined using single-crystal X-ray diffraction methods.[14]

The coordination geometry of the Re^{II} ions in compounds **1**−**3** (Figures 1 and 2) is pseudo-octahedral with only slight deviations of the coordination angles from the ideal values. Three sites are occupied by acetonitrile molecules or cyanide ligands while the other three positions are filled by P atoms of the capping triphos ligand. The *cis*-P−Re−N angles in **1** (90.88(8)−99.78(7)°) and *cis*-P−Re−C angles in **3** (90.6(3)−98.8(2)°) are all greater than 90° due to steric interactions between the triphos and other ligands. Selected bond distances and angles are provided in the figure captions.

The cyclic voltammograms of compounds **2** and **3** were recorded in 0.1 M *n*-$[Bu_4NPF_6]/CH_3CN$.[15] Complex **2** shows a reversible reduction couple at $E_{1/2} = +0.09$ V presumed to be due to Re^{II}/Re^{I}, an irreversible oxidation at $E_{p,a} = +1.17$ V assigned to Re^{II}/Re^{III}, and a corresponding irreversible

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[8] Costello, M. T.; Schrier, P. W.; Fanwick, R. E.; Walton, R. A. *Inorg. Chim. Acta* **1993**, *212*, 157−163.

[9] Synthesis of $[Re(triphos)(CH_3CN)_3)][BF_4]_2$ (**1**): $[Re_2(CH_3CN)_{10}][BF_4]_4$ (0.251 g, 0.22 mmol) and triphos (0.491 g, 0.81 mmol) were refluxed in a 20 mL solution of CH_3CN/CH_2Cl_2 (3/1) for 3 days, during which the color of the solution changed from dark blue to dark green and finally yellow-green. The yellow-green solution was concentrated to 10 mL, 20 mL of Et_2O was added, and the resulting mixture was placed in a refrigerator at 0 °C for 12 h. The yellow solution was collected by filtration, concentrated to an oily residue, and redissolved in a minimal volume of CH_2Cl_2. The addition of 40 mL of Et_2O resulted in a yellow solid, which was collected by filtration, washed with fresh Et_2O (2×10 mL), and recrystallized from CH_3CN/Et_2O. Yield: 0.134 g (30%).

[10] Preparation of $[Re(triphos)(CH_3CN)_3][PF_6]_2$ (**2**): $[(triphos)Re(\mu\text{-}Cl)_3Re(triphos)]Cl\cdot 9EtOH$ (1.01 g, 0.464 mmol) and $TlPF_6$ (0.650 g, 1.85 mmol) were refluxed in 15 mL of CH_3CN for 12 h. The resulting bright orange mixture was filtered through Celite to give a clear, orange solution, which was concentrated to ∼5 mL and treated with 40 mL of Et_2O to effect the precipitation of a flocculent orange solid. The supernatant was removed, the orange solid was washed successively with 3×10 mL portions of Et_2O, and the solid was dried in vacuo for 3 h. Yield: 0.845 g (76%).

[11] Synthesis of $[Et_4N][Re(triphos)(CN)_3)]$ (**3**): $[(triphos)Re(\mu\text{-}Cl)_3Re(triphos)]Cl$ (0.656 g, 0.301 mmol) and $[Et_4N]CN$ (0.283 g, 1.81 mmol) were stirred in 25 mL of CH_3CN. The resulting dark green solution was concentrated to 10 mL, and a bright yellow-green solid was isolated by filtration. The solid was recrystallized from 15 mL of a 2/1 mixture of THF/CH_3CN to which had been added 5 mL hexanes. After chilling for 12 h at 10 °C, bright yellow crystals were obtained, which were collected by filtration. Yield: 0.203 g, 33%.

[12] Storhoff, B. N.; Lewis, H. C., Jr. *Coord. Chem. Rev.* **1977**, *23*, 1−29.

[13] Crystal data for $\mathbf{1}\cdot CH_3CN$: $C_{49}H_{51}B_2F_8N_4P_3Re$, $M = 1148.67$, monoclinic, $P2_1/n$ (No. 14), $a = 13.368(3)$ Å, $b = 18.656(4)$ Å, $c = 19.765(4)$ Å, $\beta = 91.08(3)°$, $V = 4928.4(2)$ Å^3, $Z = 4$, $d_c = 1.548$ g cm^{-3}, $\mu = 2.632$ mm^{-1}, 31196 reflections (11749 unique, $R_{int} = 0.0319$) with $2\theta = 56.6°$, 608 variables, $R = 0.0279$, $R_w(F_o^2) = 0.0647$ [9057 data, $I > 2\sigma(I)$], GOF = 0.962. Crystal data for **2**: $C_{47}H_{48}F_{12}N_3P_5Re_1$, $M = 1223.95$, monoclinic, $P2_1/c$ (No. 14), $a = 13.429(3)$ Å, $b = 18.750(4)$ Å, $c = 19.823(4)$ Å, $\beta = 106.67(3)°$, $V = 4781.5(19)$ Å^3, $Z = 4$, $d_c = 1.700$ g cm^{-3}, $\mu = 2.794$ mm^{-1}, 27516 reflections (10783 unique, $R(int) = 0.0749$) with $2\theta = 54.98°$, 539 variables, $R = 0.0870$, $R_w(F_o^2) = 0.1575$ [7398 data, $I > 2\sigma(I)$], GOF = 1.024. Crystal data for $\mathbf{3}\cdot 2CH_3CN\cdot Et_2O$: $C_{60}H_{65}N_6OP_3Re$, $M = 1165.29$, monoclinic, $P2_1/c$ (No. 14), $a = 18.587(6)$ Å, $b = 14.115(5)$ Å, $c = 21.662(8)$ Å, $\beta = 94.375(6)°$, $V = 5667(3)$ Å^3, $Z = 4$, $d_c = 1.366$ g cm^{-3}, $\mu = 2.274$ mm^{-1}, 35519 reflections (13537 unique, $R_{int} = 0.0860$) with $2\theta = 56.8°$, 543 variables, $R = 0.0593$, $R_w(F_o^2) = 0.1485$ [6678 data, $I > 2\sigma(I)$], GOF = 0.981. X-ray data were measured at 110(2) K on a Siemens SMART CCD diffractometer with graphite-monochromated Mo Kα ($\lambda_\alpha = 0.71073$ Å) radiation. Structures **1** and **3** were solved and refined using the Bruker SHELXTL v5.1 software package (Siemens. *SHELXTL v5.1: Structure Solution, Refinement and Analysis Software*; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1999). Structure **2** was solved and refined using SHELX97 (Sheldrick, G. M. *SHELXL97: Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997) with the graphical interface X-SEED (Barbour, L. J. 1999 X-Seed, Graphical interface to SHELX-97 and POV-Ray). The $P(C_6H_5)$ groups of **2** were disordered and were modeled by refining two components with distances restrained. The $[PF_6]^-$ ions of **2** were also disordered, and were modeled using two components with P−F and F−F distances restrained. The disordered components of structure of **2** resulted in high *R* values. Hydrogen atoms were placed in calculated positions and refined with displacement parameters 1.2 or 1.5 times that of the heavy atoms to which they were bonded.

[14] Elemental analysis of **2** and **3** confirmed the molecular formula established by the crystallography experiments. Anal. Calcd for **2**, $C_{47}H_{48}N_3F_{12}P_5Re$: C, 46.12; H, 3.95; N, 3.43. Found: C, 46.10; H, 4.04; N, 3.47. Anal. Calcd for **3**, $C_{52}H_{59}N_4P_3Re$: C, 61.28; H, 5.83; N, 5.50. Found: C, 61.10; H, 6.63; N, 5.76.

[15] Pt working electrode, Pt wire auxiliary, scan rate 200 mV s^{-1}, potentials vs Ag/AgCl.

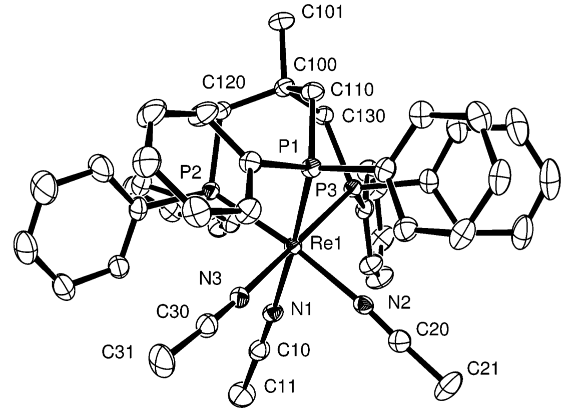

Figure 1. Thermal ellipsoid plot of the cationic unit in **1** with important atoms labeled. Hydrogen atoms were omitted for the sake of clarity. Selected bond distances (Å) and bond angles (deg): Re(1)−P(1) 2.3991(10), Re(1)−P(2) 2.3841(9), Re(1)−P(3) 2.3907(9), Re(1)−N(1) 2.096(3), Re(1)−N(2) 2.095(3), Re(1)−N(3) 2.094(3), N(1)−C(10) 1.154(4), N(2)−C(20) 1.137(4), N(3)−C(30) 1.134(4), P(1)−Re(1)−P(2) 88.11(3), P(1)−Re(1)−P(3) 85.16(3), P(2)−Re(1)−P(3) 88.84(3), N(1)−Re(1)−N(2) 82.88(10), N(1)−Re(1)−N(3) 84.20(10), N(2)−Re(1)−N(3) 85.02(10), N(1)−Re(1)−P(2) 91.25(8), N(1)−Re(1)−P(3) 94.12(7), N(1)−Re(1)−P(3) 175.80(8).

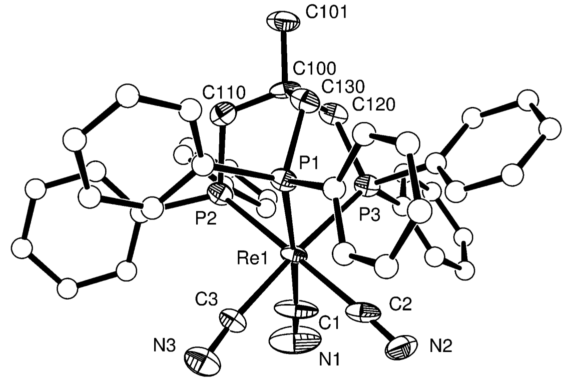

Figure 2. Thermal ellipsoid plot of the anionic unit in **3** with important atoms labeled. The thermal ellipsoids are drawn at the 50% level except for the carbon atoms of the phenyl rings, which are represented as arbitrary size spheres of arbitrary radius. Hydrogen atoms were omitted for the sake of clarity. Selected bond distances (Å) and bond angles (deg): Re(1)−P(1) 2.429(2), Re(1)−P(2) 2.422(2), Re(1)−P(3) 2.425(2), Re(1)−C(1) 2.038(9), Re(1)−C(2) 2.110(9), Re(1)−C(3) 2.109(8), C(1)−N(1) 1.162(10), C(2)−N(2) 1.153(10), C(3)−N(3) 1.148(10), P(1)−Re(1)−P(2) 84.53(7), P(1)−Re(1)−P(3) 84.87(7), P(2)−Re(1)−P(3) 87.32(7), C(1)−Re(1)−C(2) 86.1(3), C(1)−Re(1)−C(3) 85.3(3), C(2)−Re(1)−C(3) 83.8(3), C(1)−Re(1)−P(1) 175.1(3), C(1)−Re(1)−P(2) 90.6(3), C(1)−Re(1)−P(3) 95.4(3), Re(1)−C(1)−N(1) 176.1(9), Re(1)−C(2)−N(2) 175.8(7), Re(1)−C(3)−N(3) 173.9(8).

reduction of the oxidized Re^{III} product at $E_{p,c} = -0.30$ V. The wave at $E_{p,c} = -0.30$ V is not present when the potential is swept first from 0 to +1 V, an indication that this is a chemical product wave generated by the irreversible process occurring at +1.17 V.

The electrochemistry of **3** consists of an irreversible, one-electron oxidation assigned to Re^{II}/Re^{III} at $E_{p,c} = +0.19$ V, a reversible oxidation attributed to Re^{III}/Re^{IV} at $E_{1/2} = +1.12$ V, and a reversible reduction (Re^{II}/Re^{I}) at $E_{1/2} = -0.74$ V (Figure 3). The presence of a completely irreversible process at an intermediate potential between two reversible processes is unusual; nevertheless it is reproducible and invariable under a variety of experimental conditions including variation of the scan rate, the use of coordinating or noncoordinating solvents, and at Pt as well as glassy carbon working electrodes. Additional details on the electrochemistry of **3** are available in the Supporting Information.

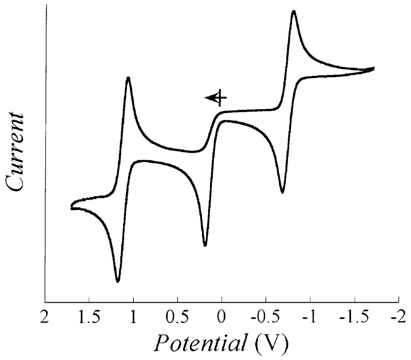

Figure 3. Cyclic voltammogram of compound **3** in 0.1 M [n-Bu_4N][PF_6]/CH_3CN at a Pt disk electrode versus Ag/AgCl.

The magnetic properties of compounds **1** and **3** were examined over the temperature range 2−300 K. The $\chi_m T$ versus T plot of **1** is in reasonable accord with one unpaired electron ($C = 0.289$) and a large temperature independent paramagnetic contribution (TIP) ($\chi_{TIP} = 1.796 \times 10^{-3}$). Compound **3** exhibits magnetic behavior similar to that of **1** with $C = 0.208$ and $\chi_{TIP} = 1.363 \times 10^{-3}$. The values of C for **1** and **3** are lower than expected and are attributed to strong spin−orbit coupling in this unquenched d^5 system (λ values for Re are reported to be in the range 2000−3000 cm^{-1}). A model for the magnetic behavior of these compounds is currently being developed.[16]

The compounds reported in this study are new examples of 17-electron mononuclear Re^{II} complexes suitable for the preparation of clusters and supramolecular architectures. Although the preparation of **1** from [$Re_2(CH_3CN)_{10}$][BF_4]$_4$ requires long reaction times, these experiments demonstrate the utility of dirhenium complexes as convenient precursors for mononuclear Re^{II} complexes. Efforts are underway to incorporate **2** and **3** into larger assemblies to probe the effects of strong spin−orbit coupling on magnetic clusters containing both 3d and 5d ions.

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Supporting Information Available: Molar magnetic susceptibility versus temperature data for **1** and **3**, electrochemical data for **2**. Discussion of the electrochemical data for **3** and discussion of the ^{1}H NMR for **2** and **3**. Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) (a) Dunbar, K. R.; Schelter, E. J.; Tsukerblat, B. S.; Palii, A. V.; Ostrovsky, S. M.; Mirovitskii, V. Y. *Polyhedron*, in press. (b) Dunbar, K. R.; Schelter, E. J.; Tsukerblat, B. S.; Palii, A. V.; Ostrovsky, S. M.; Mirovitskii, V. Y.; Klokishner, S. I. *Adv. Quantum Chem.*, in press. (c) Dunbar, K. R.; Schelter, E. J.; Palii, A. V.; Ostrovsky, S. M.; Mirovitskii, V. Y.; Klokishner, S. I.; Tsukerblat, B. S. *J. Phys. Chem.*, submitted.