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Inorganic Chemistry Article

Multielectron Donors Based on TTF–Phosphine and Ferrocene–Phosphine Hybrid Complexes of a Hexarhenium(III) Octahedral Cluster Core

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Electroactive molecular materials precursors are obtained through coordination chemistry of the hexarhenium cluster core $[Re_6Se_8]^{2+}$ on the six available apical positions with redox-active phosphines bearing tetrathiafulvalene- or ferrocene-based moieties. Single-crystal X-ray diffraction study and electrospray mass spectrometry ascertain the synthesis of these hexasubstituted electroactive clusters, containing up to 12 redox active sites. Cyclic voltammetry experiments demonstrate that these compounds can be reversibly oxidized at rather low potentials, thus allowing an easy access to the corresponding radical species which should provide new conducting and/or magnetic molecular materials.

Introduction

All six apical, μ-coordination sites of the octahedral, $[Re_6Q_8]^{2+}$ (Q = S, Se, Te) core of the molecular forms of Re(III) chalcohalides[1] (Chart 1) can be functionalized with various ligands, starting either from the halogenated tetraanion $[Re_6Q_8X_6]^{4-}$ (X = Cl, Br, I)[2] or from the more reactive "naked", yet solvated, dicationic precursor $[Re_6Q_8(MeCN)_6]^{2+}$.[3] This strategy, all the more sound when considering the electroactive nature of these clusters and their luminescent character,[4] allowed the preparation of a large variety of hybrid mineral−coordination compounds, such as porous magnetic materials,[5] coordination polymers,[3] hexaporphyrin substituted clusters,[6] star-shaped complexes,[7] and dendrimers supported by a $[Re_6Q_8]^{2+}$ metal cluster core.[8] Furthermore, it has been recently demonstrated that these cluster cores allow electronic communication between ligands in apical position,[9] since stepwise reduction of pyridine-based ligands was nicely evidenced within a series of substituted clusters.[2b] Electron donors such as tetrathiafulvalene- (TTF) or ferrocene- (Fc) based derivatives, capable to provide stable paramagnetic species upon one-electron oxidation, have been the object of much deserved attention in the field of molecular materials. Indeed, tetrathiafulvalenes are versatile building blocks for the construction of radical cation salts displaying a wealth of electronic properties and low-dimensional physics,[10] and they stand out as molecules of

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(1) Gabriel, J.-C.; Boubekeur, K.; Uriel, S.; Batail, P. *Chem. Rev.* **2001**, *101*, 2037−2066.

(2) (a) Yoshimura, T.; Umakoshi, K.; Sasaki, Y.; Sykes, A. G. *Inorg. Chem.* **1999**, *38*, 5557−5564. (b) Yoshimura, T.; Umakoshi, K.; Sasaki, Y.; Ishizaka, S.; Kim, H.-B.; Kitamura, N. *Inorg. Chem.* **2000**, *39*, 1765−1772. (c) Chen, Z. N.; Yoshimura, T.; Abe, M.; Tsuge, K.; Sasaki, Y.; Ishisaka, S.; Kim, S.; Kitamura, H. B. *Chem.*—*Eur. J.* **2001**, *7*, 20, 4447−4455. (d) Gray, T. G.; Holm, R. H. *Inorg. Chem.* **2002**, *41*, 4211.

(3) (a) Selby, H. D.; Roland, B. K.; Zheng, Z. *Acc. Chem. Res.* **2003**, *36*, 933−944. (b) Zheng, Z.; Long, J. R.; Holm, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 2163−2171.

(4) (a) Guilbaud, C.; Deluzet, A.; Domercq, B.; Molinié, P.; Coulon, C.; Boubekeur, K.; Batail, P. *Chem. Commun.* **1999**, 1867−1868. (b) Gray, T. G.; Rudzinski, C. M.; Nocera, D.; Holm, R. H. *Inorg. Chem.* **1999**, *38*, 5932−5933. (c) Yoshimura, T.; Ishizaka, S.; Sasaki, Y.; Kim, H. B.; Kitamura, N.; Naumov, N.; Sokolov, M.; Fedorov, V. *Chem. Lett.* **1999**, 1121.

(5) (a) Bennett, M. V.; Beauvais, L. G.; Shores, M. P.; Long, J. R. *J. Am. Chem. Soc.* **2001**, *123*, 8022−8032. (b) Beauvais, L. G.; Shores, M. P.; Long, J. R. *J. Am. Chem. Soc.* **2000**, *122*, 2763−2772. (c) Naumov, N. G.; Virovets, A. V.; Sokolov, N. S.; Artemkina, S. B.; Fedorov, V. E. *Angew. Chem., Int. Ed.* **1998**, *37*, 1943−1945.

(6) Itasaka, A.; Abe, M.; Yoshimura, T.; Tsuge, K.; Suzuki, M.; Imamura, T.; Sasaki, Y. *Angew. Chem., Int. Ed.* **2002**, *41*, 3, 463−466.

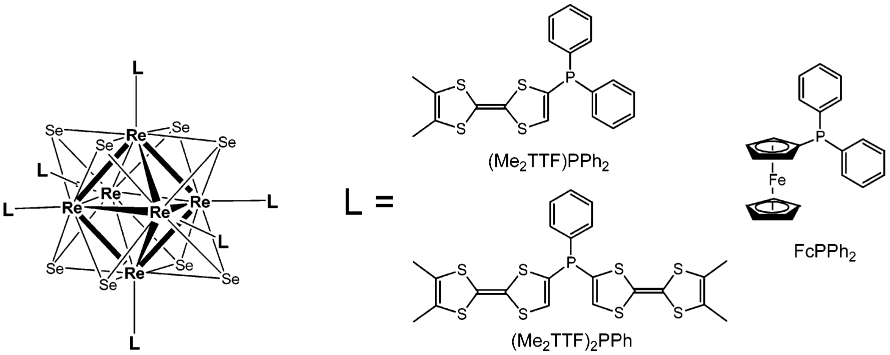
(7) Roland, B. K.; Carter, C.; Zheng, Z. *J. Am. Chem. Soc.* **2002**, *124*, 6234−6235.

(8) Wang, R.; Zheng, Z. *J. Am. Chem. Soc.* **1999**, *121*, 3549−3550.

(9) Tulsky, E. G.; Crawford, N. R. M.; Baudron, S. A.; Batail, P.; Long, J. R. *J. Am. Chem. Soc.* **2003**, *125*, 15543−15553.

10.1021/ic0486217 CCC: $30.25

Chart 1. $[Re_6Se_8L_6]^{2+}$ Cluster Core with Selenium Atoms in Inner Positions and Ligands Noted μ-L in Terminal Positions, Together with the Redox-Active Ligands Studied in This Work



utmost interest in the current search for multifunctional materials.[11] On the other hand, ferrocenes are valuable precursors for the synthesis of organometallic magnets.[12] Therefore, association of TTF or Fc derivatives onto a hexanuclear rhenium core represents a very appealing prospect to prepare compounds incorporating at least six electron donor moieties arranged in a quasi-isotropic distribution around an augmented octahedral coordination site. Since this would necessarily imply the μ_1 coordination of TTF- or Fc-based ligands at the apical sites of the rhenium cluster (Chart 1), we took advantage of the well-documented phosphine functionalization of $[Re_6Q_8]^{2+}$ (Q = S, Se) core.[13] While Fc phosphines[14] along with many examples of transition metal complexes[15] have been known for a long time, a more recent approach has consisted in the functionalization of TTFs with phosphine groups, whose chemistry has been developed to allow the creation of redox active mono- and multinuclear hybrid metal complexes where admixing metal or cluster d orbitals with the HOMO of the π-conjugated ligands may occur.[16] Hence, the synthesis of transition metal complexes[17] was described with, in one case, a radical cation salt.[18] Note that among the TTF-based complexes described so far, at the most only two TTF moieties are coordinated around the metallic center.[17,19] We report herein on the synthesis, characterization, and redox properties of three redox-active rhenium clusters (Chart 2).

Chart 2. Designation of Hybrid Cluster Salts

1	$[Re_6Se_8(MeCN)_6](SbF_6)_2$
2	$[Re_6Se_8(MePPh_2)_6](SbF_6)_2$
3	$[Re_6Se_8((Me_2TTF)PPh_2)_6](SbF_6)_2$
4	$[Re_6Se_8((Me_2TTF)_2PPh)_6](SbF_6)_2$
5	$[Re_6Se_8(FcPPh_2)_6](SbF_6)_2$

One of these species incorporates 12 TTF moieties on a single Re_6 core and therefore represents a giant leap forward in the preparation of TTF-coordinated metal complexes and extremely promising building blocks for the construction of multifunctional materials.

Experimental Section

General Methods. Standard Schlenk and vacuum-line techniques were employed for all manipulation of dioxygen- and/or moisture-sensitive compounds. Solvents were distilled from appropriate drying agents and degassed prior to use. Compound **1** was prepared by replacing $AgBF_4$ by $AgSbF_6$ in the method reported in the literature.[20] $MePPh_2$ was used as received. $(Me_2TTF)PPh_2$,[16a] $(Me_2TTF)_2PPh$,[16b] and $(Fc)PPh_2$[21] were prepared as previously described. NMR spectra were recorded on a Bruker DRX 500 spectrometer operating at 202.39 MHz for ^{31}P. Microanalyses (CHP) were performed by the "Service d'Analyse du CNRS" at Gif Sur Yvette, France. UV−vis spectra were recorded with a Perkin-Elmer Lambda 2 spectrometer.

$[Re_6Se_8(MePPh_2)_6](SbF_6)_2 \cdot 2H_2O$ ($2 \cdot 2H_2O$). A chlorobenzene solution (75 mL) containing **1** (300 mg, 0.12 mmol) and $MePPh_2$ (0.4 mL, 2.15 mmol) was heated at 130 °C with stirring under argon atmosphere for 5 days. The yellow precipitate formed was filtered

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(10) (a) Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Whangbo, M.-H. *Organic Superconductors (Including Fullerenes)*; Prentice Hall: Englewood Cliffs, NJ 07632, 1992. (b) Veciana, J.; Rovira, C.; Amabilino, D. B. *Supramolecular Engineering of Synthetic Metallic Materials*; NATO ASI Series Vol. 518; Kluwer: Dordrecht, The Netherlands, 1999. (c) *Chem. Rev.* **2004**, *104*, Special Issue on Molecular Conductors.

(11) (a) Coronado, E.; Galan-Mascaros, J. R.; Gomez-Garcia, C. J.; Laukhin V. *Nature* **2000**, *408*, 447−449. (b) Segura, J. L.; Martin, N. *Angew. Chem., Int. Ed.* **2001**, *40*, 8, 1372−1409. (c) Jeppesen, J. O.; Brœnsted Nielsen, M.; Becher, J. *Chem. Rev.* **2004**, *104*, in press.

(12) Miller, J. S. *Inorg. Chem.* **2000**, *39*, 4392−4408.

(13) (a) Willer, M. W.; Long, J. R.; McLauchlan, C. C.; Holm, R. H. *Inorg. Chem.* **1998**, *37*, 328−333. (b) Chen, Z. N.; Yoshimura, T.; Abe, M.; Sasaki, Y.; Ishisaka, S.; Kim, S.; Kitamura, H. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 1, 239−242. (c) Tulsky, E. G.; Long, J. R. *Inorg. Chem.* **2001**, *40*, 6990−7002.

(14) Sollot, G. P.; Mertwoy, H. E.; Portnoy, S.; Snead, J. L. *J. Org. Chem.* **1963**, *28*, 1090−1094.

(15) Togni, A.; Hayashi, T. *Ferrocenes*; VCH Publishers: New York, 1995.

(16) (a) Fourmigué, M.; Batail, P. *Chem. Commun.* **1991**, 1370. (b) Fourmigué, M.; Batail, P. *Bull. Soc. Chim. Fr.* **1992**, *129*, 29−36. (c) Fourmigué, M.; Huang, Y.-S. *Organometallics* **1993**, *12*, 797−802. (d) Gerson, F.; Lamprecht, A.; Fourmigué, M. *J. Chem. Soc., Perkin Trans.* **1996**, *2*, 1409−1414.

(17) (a) Fourmigué, M.; Uzelmeier, C. E.; Boubekeur, K.; Bartley, S. L.; Dunbar, K. R. *J. Organomet. Chem.* **1997**, *529*, 343−350. (b) Uzelmeier, C. E.; Bartley, S. L.; Fourmigé, M.; Rogers, R.; Grandinetti, G.; Dunbar, K. R. *Inorg. Chem.* **1998**, *37*, 6706−6713. (c) Cerrada, E.; Diaz, C.; Hurthouse, M. B.; Laguna, M.; Light, M. E. *J. Chem. Soc., Dalton Trans.* **2002**, 1104−1109. (d) Avarvari, N.; Martin, D.; Fourmigué, M. *J. Organomet. Chem.* **2002**, *643−644*, 292−300. (e) Pellon, P.; Gachot, G.; Lebris, J.; Marchin, S.; Carlier, R.; Lorcy, D. *Inorg. Chem.* **2003**, *42*, 2056−2060.

(18) Avarvari, N.; Fourmigué, M. *Chem. Commun.* **2004**, 1300−1301.

(19) (a) Iwahori, F.; Golhen, S.; Ouahab, L.; Carlier, R.; Sutter, J.-P. *Inorg. Chem.* **2001**, *40*, 6541−6542. (b) Devic, T.; Avarvari, N.; Batail, P. *Chem.—Eur. J.* **2004**, *10*, 3697−3707. (c) Liu, S.-X.; Dolder, S.; Franz, P.; Neels, A.; Stoeckli-Evans, H.; Decurtins, S. *Inorg. Chem.* **2003**, *42*, 4801−4803.

(20) Zheng, Z.; Long, J. R.; Holm, R. H. *J. Am. Chem. Soc.* **1997**, *119*, 2163−2171.

(21) Smalley, A. W. *Org. Prep. Proced.* **1978**, *10*, 195−200.

Table 1. Crystal and Structure Refinement Data for $[Re_6Se_8(MeCN)_6](SbF_6)_2{\cdot}3MeCN$ (**1**·3MeCN), $[Re_6Se_8(MePPh_2)_6](SbF_6)_2{\cdot}2H_2O$ (**2**·2H₂O), $[Re_6Se_8((Me_2TTF)PPh_2)_6](SbF_6)_2$ (**3**), and $[Re_6Se_8(FcPPh_2)_6](SbF_6)_2{\cdot}5CH_2Cl_2$ (**5**·5CH₂Cl₂)

	1·3MeCN	**2**·2H₂O	**3**	**5**·5CH₂Cl₂
formula	$C_{34}H_{51}N_{17}F_{24}Re_{12}Se_{16}Sb_4$	$C_{78}H_{78}F_{12}O_2P_6Re_6Se_8Sb_2$	$C_{120}H_{102}F_{12}P_6S_{24}Re_6Se_8Sb_2$	$C_{138}H_{126}Cl_{10}F_{12}P_6Fe_6Re_6Se_8Sb_2$
fw	5138.68	3453.60	4719.66	4880.19
space group	*Pncb*	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z	2	1	1	1
a, Å	12.4686(12)	14.4119(19)	14.7787(16)	15.3681(17)
b, Å	17.1774(12)	14.431(2)	15.0633(18)	17.105(2)
c, Å	22.4678(16)	15.029(2)	17.740(2)	17.285(2)
α, deg		95.740(17)	89.317(15)	114.998(13)
β, deg		110.343(15)	71.736(14)	106.077(13)
γ, deg		119.293(14)	79.612(14)	103.668(14)
V, Å^3	4812.1(7)	2412.6(8)	3684.5(8)	3616.7(11)
temp, K	200	293	293	150
d_{calc}, g/cm^3	3.547	2.377	2.127	2.241
μ, mm^{-1}	22.254	11.225	7.708	8.272
θ range, deg	2.21−25.91	2.07−25.81	1.59−22.14	2.04−25.94
R_1, wR_2	0.0327, 0.0714	0.0431, 0.1010	0.0373, 0.0895	0.0325, 0.0620

off and washed with hexane. The solid was then recrystallized in a 1:1 mixture of acetone−toluene to give the product as red-orange polyhedral crystals. Yield: 350 mg (84%). Anal. Calcd for $C_{78}H_{78}F_{12}O_2P_6Re_6Se_8Sb_2$: C, 27.39; H, 2.30. Found: C, 27.71; H, 2.47. Electrospray: $m/z = 1475$ [1/2(M − 2SbF₆)]. ^{31}P NMR (CD_2Cl_2): −41 ppm. Absorption spectrum (CH_2Cl_2) [λ_{max} (ϵ_M)]: 415 nm (sh, 1345).

$[Re_6Se_8(Me_2TTFPPh_2)_6](SbF_6)_2$ (3). A chlorobenzene solution (70 mL) containing **1** (150 mg, 0.06 mmol) and $Me_2TTFPPh_2$ (177 mg, 0.43 mmol) was heated at 130 °C with stirring under argon atmosphere for 2 days. The purple precipitate formed was filtered off and washed with hexane. The solid was then dissolved in dichloromethane, and slow diffusion of diethyl ether to this solution afforded the product as dark purple polyhedral crystals. Yield: 205 mg (72%). Anal. Calcd for $C_{120}H_{102}F_{12}S_{24}P_6Re_6Se_8Sb_2$: C, 30.54; H, 2.18. Found: C, 30.19; H, 2.28. Electrospray: $m/z = 2124$ [1/2(M − 2SbF₆)]. ^{31}P NMR (CD_2Cl_2): −31 ppm. Absorption spectrum (CH_2Cl_2) [λ_{max} (ϵ_M)]: 450 nm (sh, 4496).

$[Re_6Se_8((Me_2TTF)_2PPh)_6](SbF_6)_2$ (4). A chlorobenzene solution (30 mL) containing **1** (100 mg, 0.04 mmol) and $(Me_2TTF)_2PPh$ (185 mg, 0.32 mmol) was heated at 130 °C with stirring under argon atmosphere for 3 days. After being cooled to room temperature, the solution was filtered, and then ether was added to the filtrate to form a brown precipitate. The precipitate was filtered off and washed with ether to afford the product as brown powder. Yield: 104 mg (45%). Anal. Calcd for $Re_6Se_8P_6C_{132}S_{48}H_{114}Sb_2F_{12} + 6C_4H_{10}O$: C, 30.77; H, 2.86; Found: C, 31.10; H, 2.70. Electrospray: $m/z = 2587$ [1/2(M − 2SbF₆)]. ^{31}P NMR (CD_2Cl_2): −38.5 ppm. Absorption spectrum (CH_2Cl_2) [λ_{max} (ϵ_M)]: 510 nm (6101).

$[Re_6Se_8(FcPPh_2)_6](SbF_6)_2{\cdot}5CH_2Cl_2$ (5·5CH₂Cl₂). A chlorobenzene solution (50 mL) containing **1** (200 mg, 0.08 mmol) and $FcPPh_2$ (240 mg, 0.85 mmol) was heated at 130 °C with stirring under argon atmosphere for 2 days. The orange precipitate formed was filtered off and washed with hexane. The solid was then dissolved in dichloromethane, and addition of ether to this solution afforded the product as orange powder. Yield: 300 mg (83%). Anal. Calcd for $C_{132}H_{114}F_{12}Fe_6P_6Re_6Se_8Sb_2$: C, 35.70; H, 2.59; P, 4.18. Found: C, 35.70; H, 2.65; P, 4.10. Electrospray: $m/z = 1985$ [1/2(M − 2SbF₆)]. ^{31}P NMR (CH_2Cl_2): −30 ppm. Absorption spectrum (CD_2Cl_2) [λ_{max} (ϵ_M)]: 350 nm (sh, 7400), 450 nm (3300). Single crystals suitable for X-ray study were obtained by slowly cooling a concentrated dichloromethane solution.

X-ray Structure Determination. Data collection was carried out on a Stoe-IPDS diffractometer with graphite-monochromated Mo $KL_{2,3}$ radiation ($\lambda = 0.710\,69$ Å). The data were processed with the set of programs from STOE.[22] An absorption correction was applied for all compounds using numerical procedures based on face indexing (FACEIT, STOE). Structures were solved by direct methods using SHELXS-86 and refined by the full-matrix least-squares method on F^2 using SHELXL-97.[23] Hydrogen atoms were introduced at calculated positions and not refined (riding model). Details of data collection and structure refinements are given in Table 1. In **1**, all non-hydrogen atoms were refined with anisotropic thermal parameters except atoms of free solvent molecules which were refined isotropically. One of the two free acetonitrile molecules is disordered over two positions. One of the three independent SbF_6 anions is disordered over two positions which have in common two fluorine atoms. In **2**, all non-hydrogen atoms were refined anisotropically except one carbon atom of a methyl group and six others of phenyl groups which were refined isotropically. Hydrogen atoms on the oxygen atom of the water molecule have not been introduced. In **3**, all non-hydrogen atoms were refined anisotropically. Carbon atoms of the end of TTF moieties present large ellipsoids due to disorder. Two of the six fluorine atoms of the SbF_6^- anion are disordered over two positions. In **5**, all non-hydrogen atoms were refined with anisotropic thermal parameter except five carbon atoms of cyclopentadienyl ring of the ferrocene moiety and two of the phenyl groups which were refined isotropically. One of the three dichloromethane solvent molecule is disordered on an inversion center with two chloride atoms in common.

Cyclic Voltammetry. Cyclic voltammetry studies were performed in a three-electrode cell equipped with a platinum millielectrode of 0.126 cm^2 area, an Ag/AgCl reference, and a platinum wire counter-electrode. The electrolytic media involved a 0.4 mol·L^{-1} solution of (n-Bu_4N)PF_6 in dichloromethane. All experiments have been performed at room temperature at 0.1 V·s^{-1}. For compound **3** the experiment was performed in a glovebox containing dry, oxygen-free (<1 ppm) argon, and the number of electrons processed has been calculated by using dichloronaphthoquinone as internal reference. Electrochemical experiments have been carried out with an EGG PAR 273A potentiostat with positive feedback compensation. On the basis of repetitive measurements, absolute errors on potentials have been found to be around ±5 mV.

Mass Spectrometry. Mass spectrometry analyses were performed on a JMS-700 (JEOL LTD, Akishima, Tokyo, Japan) double-focusing mass spectrometer with reversed geometry, equipped

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(22) *Stoe-IPDS Software Manual*, V2.87; STOE: Darmstadt, Germany, Dec 1997.

(23) Sheldrick, G. M. *SHELXL-97*; University of Gottingen: Gottingen, Germany, 1997.

Scheme 1. Synthesis of **3**

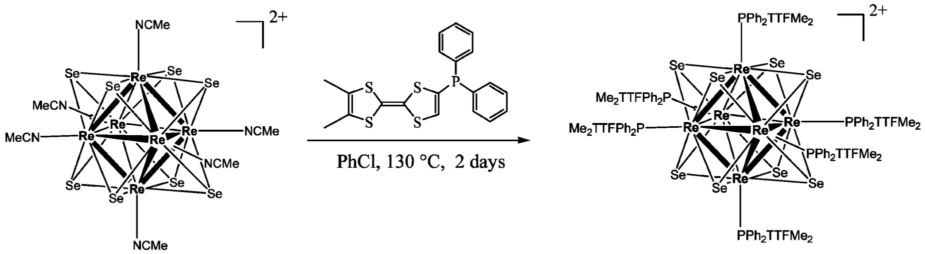


Table 2. Interatomic Distances (Å) for Clusters **1**−**3** and **5** (L = N for **1**; L = P for **2**, **3**, and **5**)

	1	**2**	**3**	**5**
Re−Re range	2.6170(6)−2.6225(7)	2.6409(8)−2.6555(13)	2.6421(9)−2.6601(9)	2.6458(7)−2.6637(6)
Re−Se range	2.514(1)−2.529(1)	2.507(2)−2.531(2)	2.494(2)−2.529(2)	2.499(1)−2.537(1)
Re−L	2.136(11)	2.487(3)	2.513(4)	2.519(2)
	2.098(10)	2.487(4)	2.496(4)	2.488(2)
	2.101(11)	2.490(4)	2.486(3)	2.494(2)

with a pneumatically assisted electrospray ionization (ESI) source. Nitrogen was used as the nebulizer gas. Positive ion mode was used with a needle voltage adjusted to obtain a ~100 nA needle current (i_{ESI}), i.e. typically ~2 kV. The desolvating plate and orifice 1 temperatures were set to 150 and 70 °C, respectively. The sample was introduced into the ESI interface via a syringe pump (PHD 2000 infusion; Harvard Apparatus, Holliston, MA) at a 30 μL·min^{-1} flow rate. A 5 kV acceleration voltage was applied. The high-resolution mass spectra (typically R = 6000 at 10% valley) were performed by electric-field scan with PEGs used as internal standard.

Results and Discussion

Synthesis and Crystal Structures. Chalco-halogenated octahedral rhenium clusters based on the Re_6 core are prepared by high-temperature solid-state reactions.[1] In molecular forms, some of these clusters are soluble in organic solvents, thus allowing their coordination chemistry by substituting the apical halogen atoms by various ligands. A common synthetic strategy has been the substitution of halogen atoms by solvent molecules, and the solvated cluster core $[Re_6Se_8(MeCN)_6]^{2+}$ with six labile acetonitrile molecules in apical positions has been regarded as a giant octahedral center with six available coordination sites. Here, we used $[Re_6Se_8(MeCN)_6](SbF_6)_2$ (**1**), instead of $[Re_6Se_8(MeCN)_6](BF_4)_2$,[20] as a precursor to the title compounds.

Reaction of **1** with $(Me_2TTF)PPh_2$ in chlorobenzene at 130 °C for 2 days, monitored by ^{31}P NMR, affords the corresponding hexasubstituted cluster **3** in good yield (Scheme 1). The complete replacement of MeCN by the phosphine was definitely assessed by X-ray diffraction analysis. Suitable single crystals were obtained by layering diethyl ether upon concentrated dichloromethane solution of **3** at room temperature.

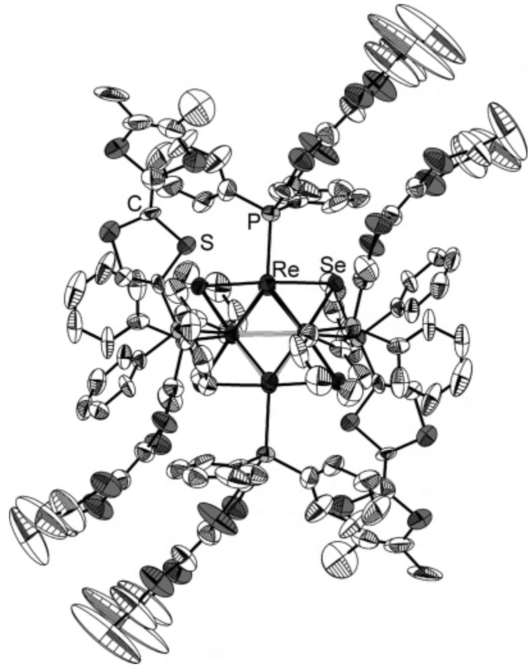
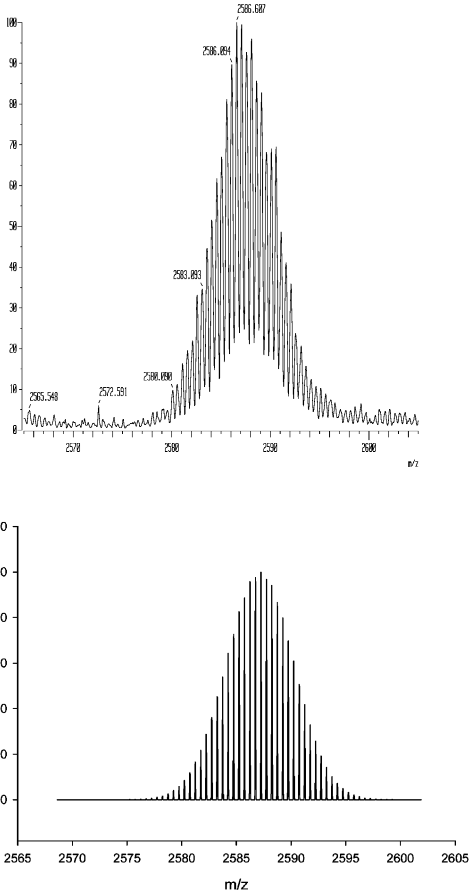


Figure 1. Molecular structure of the $[Re_6S_8(Me_2TTFPPh_2)_6]^{2+}$ hybrid cluster in **3**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are at the 50% probability level.

$[Re_6Se_8(Me_2TTFPPh_2)_6](SbF_6)_2$ (**3**) crystallizes in space group $P\bar{1}$, with half a cluster on an inversion center and an anion in a general position. The molecular structure of the dication is depicted Figure 1. The structural characteristics of the $[Re_6Se_8]^{2+}$ core are those classically observed for 24-electron rhenium clusters (Table 2). The six rhenium atoms form a nearly regular octahedron with mean Re−Re distances of 2.652(6) Å. The three independent $Me_2TTFPPh_2$ ligands show classical geometry for TTF moieties. They are not flat but present a chair conformation as often encountered within neutral TTF. Some disorder is observed for terminal methyl groups. As shown in Figure 1, the distribution of the six TTF units around the octahedral $[Re_6Se_8]^{2+}$ core is not isotropic. Instead, segregation occurs where two subgroups of three TTF moieties circumvent an equatorial zone occupied by all 12 phenyls groups. It is likely that this partition of the cluster coordination sphere results from favorable S···S and phenyl van der Waals embraces. Indeed, some short intramolecular contacts (<4 Å) between sulfur atoms of the TTF moieties are observed (S···S: 3.94(1), 3.72(2), 3.97(2), 3.95(2) Å) as well as between sulfur atoms of the TTF moieties and selenium atoms of the cluster core (Se···S: 3.11(2), 3.41(2), 3.29(2) Å). There are also several inter-



a)

b)

Figure 2. High- resolution (R = 6000) ESI mass spectrum (a) and theoretical isotopic distribution (b) of the doubly charged species $[Re_6Se_8((Me_2TTF)_2PPh)_6]^{2+}$ ($C_{132}H_{114}P_6S_{48}Re_6Se_8$).

molecular contacts between TTF moieties (S···S: 3.59(2), 3.94(3) Å). Compound **3** represents an unprecedented example of a TTF-containing metal cluster and also the first complex supporting more than two TTF moieties.

Furthermore, an hybrid cluster supporting 12 TTF units has been prepared by following the same procedure, now engaging $(Me_2TTF)_2PPh$. NMR and mass spectrometry analyses are in agreement with hexasubstitution of the cluster core and the formula $[Re_6Se_8((Me_2TTF)_2PPh)_6](SbF_6)_2$. The mass spectrum corresponds to the theoretical isotopic distribution calculated for the dicationic species $[Re_6Se_8((Me_2TTF)_2PPh)_6]^{2+}$ (Figure 2), thus demonstrating unambiguously the formation of cluster **4**.[24] Despite numerous attempts, no single crystals could be obtained for this compound.

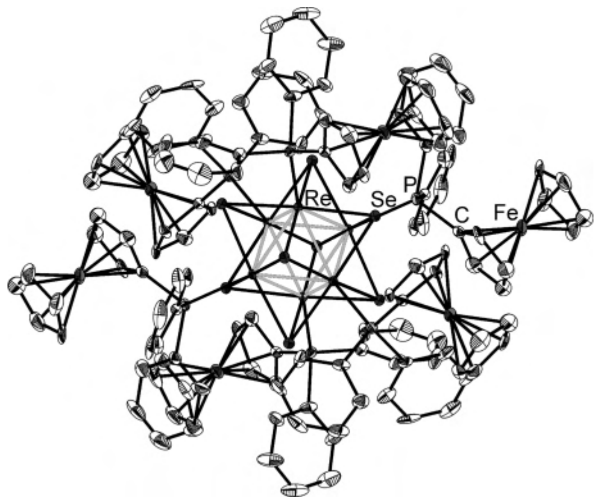


Figure 3. Molecular structure of the $[Re_6S_8(FcPPh_2)_6]^{2+}$ in **5**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are at the 50% probability level.

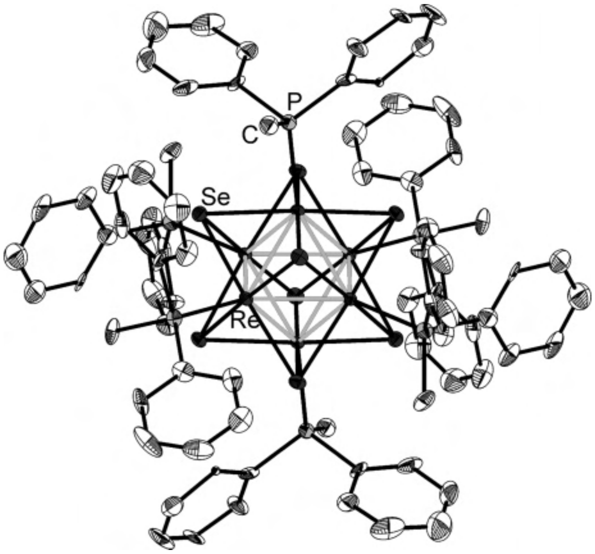


Figure 4. Molecular structure of the $[Re_6S_8(MePPh_2)_6]^{2+}$ cluster in **2**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are at the 50% probability level.

Similarly, reaction of **1** with diphenylferrocenylphosphine ($FcPPh_2$) yields $[Re_6Se_8(FcPPh_2)_6](SbF_6)_2$ (**5**) in good yields. Suitable single crystals for X-ray study were obtained by slow cooling of a concentrated dichloromethane solution. **5** crystallizes in the space group $P\bar{1}$, and the chemical formula derived from the single-crystal X-ray diffraction study is $[Re_6Se_8(FcPPh_2)_6](SbF_6)_2 \cdot 5CH_2Cl_2$ (Figure 3). Bond lengths and angles within the $[Re_6Se_8]^{2+}$ core are similar to other clusters described above (Table 2). The ferrocene moieties (Fe−Cp distances: 1.651(4), 1.661(4), 1.639(4), 1.653(4), 1.649(4), 1.655(4) Å) present a geometry similar to that reported for the uncoordinated ligand.[25]

Finally, as a reference for electrochemical studies, the $[Re_6Se_8(MePPh_2)_6]^{2+}$ cluster incorporating the nonelectroactive $MePPh_2$ ligand has been prepared in an analogous manner, using a large excess of $MePPh_2$. The compound $[Re_6Se_8(MePPh_2)_6](SbF_6)_2$ (**2**) has been obtained in good yield and crystallized by slow evaporation of acetone from an acetone/toluene solution. The molecular structure of $[Re_6Se_8(MePPh_2)_6]^{2+}$ is reported in Figure 4. The $[Re_6Se_8]^{2+}$ core presents the same structural characteristics as previously observed (Table 2). In the case of **2**, only the oxidation of the cluster core to a 23 e^- species is expected to occur.

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(24) Complete mass spectrometry results and a discussion about gas-phase reactivity of clusters **1**−**4** are found in the following: Rondeau, D.; Perruchas, S.; Avarvari, N.; Vékey, K.; Batail, P. *J. Mass Spectrom*. **2005**, *40*, 60−65.

(25) Adeleke, J. A.; Liu, L.-K. *Acta Crystallogr. C* **1993**, *C49*, 680−682.

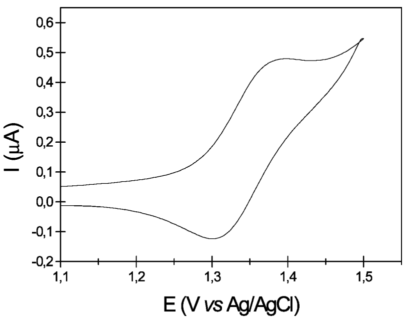

Figure 5. Cyclic voltammogram of **2** in dichloromethane.

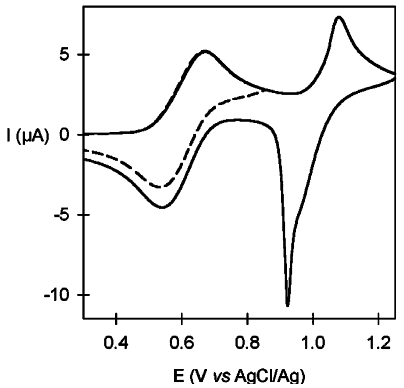

Figure 6. Cyclic voltammogram of **3** in dichloromethane.

Table 3. Redox Potentials (Free Ligand in Parentheses) and Corresponding Couple Involved for **2**−**5**

compd	$E_{1/2}$ (V) vs Ag/AgCl in CH_2Cl_2	redox couple involved
2	1.35	$[Re_6Se_8(MePPh_2)_6]^{2+/3+}$
3	0.58 (0.33)	$[Re_6Se_8(Me_2TTFPPh_2)_6]^{2+/8+}$
	1.05 (0.71)	$[Re_6Se_8(Me_2TTFPPh_2)_6]^{8+/14+}$
4	0.60 (0.38−0.49)	$[Re_6Se_8((Me_2TTF)_2PPh)_6]^{2+/14+}$
	1.02 (0.90)	$[Re_6Se_8((Me_2TTF)_2PPh)_6]^{14+/26+}$
5	0.80 (0.63)	$[Re_6Se_8(FcPPh_2)_6]^{2+/8+}$
	1.62	$[Re_6Se_8(FcPPh_2)_6]^{8+/9+}$

Electrochemical Study. The redox properties of the clusters have been studied by cyclic voltammetry (Table 3). The reference compound **2** exhibits a reversible process centered at $E_{1/2} = 1.35$ V corresponding to the oxidation of the cluster core involving the couple $[Re^{III}{}_6Se_8(MePPh_2)_6]^{2+}$/$[Re^{III}{}_5Re^{IV}{}_6Se_8(MePPh_2)_6]^{\bullet 3+}$ (Figure 5). The oxidation potential value is in agreement with those already reported in the literature for such rhenium clusters hexasubstituted by phosphine ligands. For example, for $PPh_2(CH_2)_nPPh_2O$ ($n = 2-5$) or $PPh_2(CH_2)_6PPh_2$, $E_{1/2}$ values are ranging from 1.08 to 1.17 V, and $E_{1/2} = 1.14$ V for PEt_3.[13c]

The cyclic voltammogram of **3** performed in semi-infinite diffusion conditions in dichloromethane (Figure 6) exhibits two oxidation waves corresponding to the generation of the radical cation ($TTF^{\bullet +}$) and the dication (TTF^{2+}) at $E_{1/2} = 0.58$ V and $E_{1/2} = 1.05$ V, respectively (free ligand: 0.33 and 0.71 V), involving the couples $[Re_6Se_8(Me_2TTFPPh_2)_6]^{2+/8+}$ and then $[Re_6Se_8(Me_2TTFPPh_2)_6]^{8+/14+}$.

The first wave is a classical reversible process. The weak broadening of this oxidation wave is not significant to conclude to sizable intramolecular or intermolecular interactions between TTF moieties. The second wave presents a strong adsorption phenomenon, probably due to the insolubility of the $[Re_6Se_8(Me_2TTFPPh_2)_6]^{14+}$ species in CH_2Cl_2. This adsorption phenomenon has also been observed in mixtures of CH_2Cl_2/MeCN. Thin layer cyclic voltammetry (TLCV) revealed that the first oxidation wave corresponds to six one-electron processes. The second wave is likely to be a similar process, but the adsorption phenomenon occurring in the return scan did not allow an accurate measure of the number of electrons expected to be exchanged in this oxidation step.

Compound **4** exhibits two quasi reversible processes centered at $E_{1/2} = 0.60$ and 1.02 V (Supporting Information) both corresponding to the oxidation of the six ligands $(Me_2TTF)_2PPh$ into radical cations and then dications, very likely involving $[Re_6Se_8((Me_2TTF)_2PPh)_6]^{2+/14+}$ and $[Re_6Se_8((Me_2TTF)_2PPh)_6]^{14+/26+}$ couples, respectively (free ligand: 0.38−0.49 and 0.90 V). Accurate electron counts could not be carried out because both waves present an adsorption phenomenon due to the precipitation of highly charged oxidized species on the electrode.

The first oxidation step (250 mV for **3** and 275 mV for **4)** occurs at higher potential values compared to the corresponding free ligands. Similar anodic shifts have already been reported for other phosphino-TTF complexes[17d] and can be attributed to a decrease of the electronic density on the TTF moieties upon coordination. Unlike the hybrid cluster **2**, no cluster core oxidation is observed for **3** and **4**, indicating that further one-electron oxidations of the already highly positively charged species, $[Re_6Se_8(Me_2TTFPPh_2)_6]^{14+}$ and $[Re_6Se_8((Me_2TTF)_2PPh)_6]^{26+}$, occur at higher potentials.

Compound **5** exhibits two quasi reversible processes with $E_{1/2} = 0.80$ V and $E_{1/2} = 1.62$ V (Supporting Information). Very likely, the first one corresponds to the oxidation of the six ligands $Cp_2Fe^{II}PPh_2$ into $Cp_2Fe^{III}PPh_2{}^+$ (free ligand, 0.63 V; ferrocene, 0.49 V) and the second one to the cluster core oxidation. Then couples involved are $[Re_6Se_8(FcPPh_2)_6]^{2+/8+}$ and $[Re_6Se_8(FcPPh_2)_6]^{8+/9+}$. The oxidation potential involving the couple $[Re_6Se_8(FcPPh_2)_6]^{8+}$/$[Re_6Se_8(FcPPh_2)_6]^{9+}$, i.e., oxidation of the cluster core, presents an anodic shift of 270 mV compare to the reference compound **2**, again a manifestation of a charge effect due to the presence of six ferrocenium cations on the cluster. For the oxidation of ferrocene into ferrocenium the anodic shift amounts to 170 mV when compared to the free $FcPPh_2$. In complexes such as $(FcPPh_2)ReCO_4Cl$ and $(FcPPh_2)_2ReCO_3Cl$ the reported anodic shifts were about 50 mV.[26] Note also that a ferrocene-containing molybdenum octahedral cluster, formulated as $Na_2[Mo_6Cl_8(FcCOO)_6]$, has been reported.[27]

To summarize, complexes **3**−**5** deliver up to 12, 24, and 6 electrons, respectively, at accessible potentials, which make them valuable electron donors for electrocrystallization experiments aiming at obtaining new molecular materials.

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(26) Miller, T. M.; Ahmed, K. J.; Wrighton, M. S. *Inorg. Chem.* **1989**, *28*, 2347−2355.

(27) Prokopuk, N.; Shriver, D. F. *Inorg. Chem.* **1997**, *36*, 5609−5613.

Summary and Outlook

The synthesis and characterization of redox-active, TTF−phosphine and Fc−phosphine complexes based on an hexanuclear rhenium chalcogenide cluster core reported herein deliver three-dimensional π-donor hybrid molecules showing concomitant 6 e^- (for **3** and **5**) or 12 e^- (for **4**) loss. Current work in our laboratory focuses on isolation of the corresponding radical cation species by the electrocrystallization technique or by chemical oxidation.

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Supporting Information Available: X-ray crystallographic files (CIF) and other characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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