

Available online at www.sciencedirect.com



Inorganica Chimica Acta

Inorganica Chimica Acta 359 (2006) 4191-4196

www.elsevier.com/locate/ica

Synthesis and structural characterization of several dirhenium(III) compounds

Michael Q. Dequeant ^a, Phillip E. Fanwick ^b, Tong Ren ^{b,*}

^a Department of Chemistry, University of Miami, Coral Gables, FL 33146, USA ^b Department of Chemistry, Purdue University, 5186 Brown Laboratory, 560 Oval Drive, West Lafavette, IN 47907, USA

> Received 12 May 2006; accepted 28 June 2006 Available online 5 July 2006

Abstract

Reaction between $\text{Re}_2(\text{OAc})_4\text{Cl}_2$ and N,N'-dicyclohexylbenzamidine (HDCyBA) under molten conditions yielded $\text{Re}_2(\text{DCyBA})_2\text{Cl}_4$ (1); reaction of $[\text{Bu}_4\text{N}]_2[\text{Re}_2\text{Cl}_8]$ with N,N'-di(3-methoxyphenyl)formamidine (HDmAniF) resulted in $\text{Re}_2(\text{DMAniF})_2\text{Cl}_4$ (2); reaction of *cis*- $\text{Re}_2(\text{OAc})_2\text{Cl}_4$ with HDmAniF under reflux conditions resulted in *cis*- $\text{Re}_2(\text{OAc})_2(\text{DmAniF})_2\text{Cl}_2$ (3). Reaction between $\text{Re}_2(\text{OAc})_4\text{Cl}_2$ and $\alpha, \alpha, \alpha', \alpha'$ -tetramethyl-1,3-benzenedipropionic acid (H₂esp) under reflux conditions led to $\text{Re}_2(\text{esp})_2\text{Cl}_2$ (4). Crystallographic studies of compounds 1–4 revealed Re–Re bond lengths of 2.1679(6), 2.1804(5), 2.2468(7), and 2.2304(6) Å, respectively, which are consistent with the presence of Re–Re quadruple bond. Also reported are electrochemical properties of compounds 1–4. © 2006 Elsevier B.V. All rights reserved.

Keywords: Dirhenium(III); N,N'-Bidentate ligand; Supramolecule building block; Crystal structures

1. Introduction

Research of metallosupramolecules represents a new frontier of inorganic chemistry [1,2]. Advantages of using bimetallic building blocks have been demonstrated with the elegant work on Mo₂- and Rh₂-based supramolecules [3,4]. In comparison, dirhenium compounds have received limited attention as to their utility in supramolecular assemblies [5-11]. Previously, one-dimensional coordination polymers of interesting photophysical properties were assembled via metathesis reactions between a dirhenium synthon containing labile axial ligands, i.e. Re₂(DMBA)₄- $(NO_3)_2$ (DMBA is N,N'-dimethylbenzamidinate) [12], and various dianions [13]. In order to broaden the scope beyond 1-D assembly, building blocks containing labile equatorial ligand(s) are being sought. Described here are several dirhenium(III) compounds containing equatorial halide or acetate ligands, which may undergo substitution reaction under mild conditions.

2. Results and discussion

2.1. Preparation

Several bidentate bridging ligands were utilized in supporting the Re₂ core, and they are shown in Scheme 1. In an attempt to prepare $\text{Re}_2(\text{DCyBA})_4\text{Cl}_2$ (DCyBA = N, N'dicyclohexylbenzamidinate), an analog of the previously reported Re₂(DMBA)₄Cl₂ [12], Re₂(OAc)₄Cl₂ was reacted with 10 equiv. of HDCyBA (N,N'-dicyclohexylbenzamidine) under molten conditions. Instead of Re₂(DCyBA)₄-Cl₂, compound Re₂(DCyBA)₂Cl₄ (1) was isolated as the predominant product in a yield of 48%. Clearly, two of four equatorial Cl ligands were scavenged from another equivalent of $\text{Re}_2(\text{OAc})_4\text{Cl}_2$, which limits the theoretical yield of 1 at a maximum of 50%. Using the conditions developed for the synthesis of Re₂(DPhF)₂Cl₄ by Walton [14], compound $\text{Re}_2(\text{DmAniF})_2\text{Cl}_4$ (2) was prepared in a satisfactory yield (79%) through the reaction between [Bu₄N]₂[Re₂Cl₈] and HDmAniF (di(3-methoxyphenyl)formamidine). Reaction between cis-Re₂(OAc)₂Cl₄(H₂O)₂ and 2 equiv. of HDmAniF in the presence of Et₃N resulted

^{*} Corresponding author. Tel.: +1 765 494 5466; fax: +1 765 494 0239. *E-mail address:* tren@purdue.edu (T. Ren).

^{0020-1693/\$ -} see front matter \odot 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.ica.2006.06.044



Scheme 1. Ligands utilized in this work.

in compound cis-Re₂(OAc)₂(DmAniF)₂Cl₂ (**3**) in good yield. Aided by an acetic acid scrubbing setup previously described [15], refluxing Re₂(OAc)₄Cl₂ with H₂esp in toluene led to compound Re₂(esp)₂Cl₂ (**4**).

2.2. Molecular structures

Molecular structures of compounds 1–4 were elucidated with single crystal diffraction studies, and they are shown in Figs. 1–4, respectively. Compound 1 crystallized in the I2/aspace group and the asymmetric unit contains one half of the molecule with an inversion center that bisects the Re– Re bond. Compound 2 crystallized in the $P2_1/c$ space group and the asymmetric unit also contains one half of the molecule with an inversion center that bisects the Re– Re bond. For compound 3, the compound crystallized in the $P2_1$ space group and the asymmetric unit contains one molecule of 3 and an ethyl acetate solvent molecule. Compound 4 crystallized in the *Pbca* space group and the asymmetric unit contains one half of the molecule with an inversion center that bisects the Re–Re bond.

As shown in Figs. 1 and 2, coordination spheres of the Re_2 core in both 1 and 2 consist of two bidentate bridging ligands in *trans* deposition, and four chloro ligands occupy-



Fig. 1. ORTEP plot of $Re_2(DCyBA)_2Cl_4$ (1) at 30% probability level. Hydrogen atoms were omitted for clarity.



Fig. 2. ORTEP plot of $Re_2(DmAniF)_2Cl_4$ (2) at 30% probability level. Hydrogen atoms were omitted for clarity.



Fig. 3. ORTEP plot of $Re_2(OAc)_2(DmAniF)_2Cl_2$ (3) at 30% probability level. Hydrogen atoms were omitted for clarity.



Fig. 4. ORTEP plot of $Re_2(esp)_2Cl_2$ (4) at 30% probability level. Hydrogen atoms were omitted for clarity.

ing the remaining equatorial sites. Similar ligand arrangements were previously reported for $Re_2[(PhN)_2CPh]_2Cl_4$ [16], $Re_2(DMBA)_2Cl_4$ [17], and $Re_2[(PhN)_2CH]_2Cl_4$ [18]. The Re–Re bond in **1** (2.1679(6) Å) and **2** (2.1804(5) Å)

Table 3

4193

are comparable to those of $\text{Re}_2(\text{DMBA})_2\text{Cl}_4$ (2.178(1) Å), $Re_{2}[(PhN)_{2}CPh]_{2}Cl_{4}$ (2.177(2) Å), and $Re_{2}[(PhN)_{2}CH]_{2}Cl_{4}$ (2.177(1) Å), and consistent with a Re–Re quadruple bond [19]. The relative short Re-Re bond distances of compounds 1 and 2 are attributed to the absence of axial chloro ligands that may donate electron density into the $\sigma(\text{Re-Re})$ orbital and destabilize the Re-Re quadruple bond (see Table 1).

It is clear from Fig. 3 that the cis-arrangement of two acetate ligands in the precursor compound Re₂(OAc)₂Cl₄- $(H_2O)_2$ is retained in compound 3. As a paddlewheel species of mixed carboxylate and diarylformamidinate (DArF) bridging ligands, compound 3 has a Re-Re bond length of 2.2468(7) Å, which is slightly longer than those of Re_2 - $(O_2CR)_4Cl_2$ type compounds (2.224-2.240 Å) [20], and shorter than those of Re₂(DArF)₄Cl₂ compounds (2.232-2.284 Å) [21,22]. It is interesting to note that the Re-N bond length in 3 (ca. 2.05 Å) is significantly shortened from those in $\text{Re}_2(\text{DArF})_4\text{Cl}_2$ (ca. 2.10 Å) [21,22], while the Re–O bond length in 3 (ca. 2.07 Å) is elongated from that of $\text{Re}_2(\text{O}_2\text{CCMe}_3)_4\text{Cl}_2$ (2.025 Å) [23]. The bond length variations compared with the homoleptic species reflect the enhancement/weakening of bond strengths in the mixed ligand species, and are consistent with the fact that N-donor ligands have much stronger trans-influence than O-donor ligands. Structural evidences of trans-influence can also be found in Re₂(P-P)₂(O₂CR)₂Cl₂ type compounds (P–P is bidentate diphosphine) [20] (see Table 2).

Structural study of compound 4, shown in Fig. 4, confirms the "strapping" coordination mode of 'esp' ligand that was first reported for Rh₂(esp)₂(acetone)₂ [24]. The Re-Re bond length in 4 is 2.2304(6) Å, which is within the range reported for $Re_2(O_2CR)_4Cl_2$ type compounds (2.224–2.240 Å) (see Table 3).

2.3. Electrochemical properties

Redox behaviors of compounds 1-4 were probed with both cyclic and differential pulse voltammetric methods (CV and DPV) in the potential range from -2.5 to 1.5 V. Since none of the compounds exhibit redox activity in the

Table 1 Selected bond lengths (Å) and bond angles (°) for compounds 1 and 2

	Compound 1	Compound 2
Re1–Re1′	2.1679(6)	2.1804(5)
Re1–N1	2.036(6)	2.057(4)
Re1–N2	2.047(7)	2.065(5)
Re1-Cl1	2.3313(18)	2.3226(18)
Re1–Cl2	2.3323(19)	2.3208(17)
N1-Re1-N2	175.8(2)	176.72(18)
N1-Re1-Cl1	91.33(17)	87.92(15)
N1-Re1-Cl2	87.99(17)	90.92(15)
Re1'-Re1-N1	92.34(16)	91.26(13)
Re1'-Re1-N2	91.56(16)	91.95(13)
Re1'-Re1-Cl1	101.54(5)	106.26(5)
Re1'-Re1-Cl2	106.77(5)	106.74(4)

Table 2			
Selected bond	lengths (Å) and	bond angles (°)	for compound 3

Re1–Re2	2.2468(7)	Re2–Re1–N1	90.7(3)
Re1–N1	2.046(12)	Re2-Re1-N3	90.7(3)
Re1–N3	2.044(12)	Re2-Re1-O1	89.7(3)
Re1–O1	2.069(9)	Re2-Re1-O3	91.5(3)
Re1–O3	2.062(9)	Re2-Re1-Cl1	171.54(10)
Re1–Cl1	2.503(4)	Re1-Re2-N2	90.9(3)
Re2–N2	2.036(11)	Re1-Re2-N4	90.8(3)
Re2–N4	2.063(12)	Re1–Re2–O2	90.1(3)
Re2–O2	2.081(10)	Re1–Re2–O4	88.2(3)
Re2–O4	2.088(10)	Re1-Re2-Cl2	169.15(11)
Re2–Cl2	2.502(4)		

1 4010 5		
	0	
Selected bond lengths (A) and bond angles	(°) for compound A
ociected Dona ichguis i	\neg i and DOING angles	

Re1–Re1′	2.2304(6)
Re1–O1	2.024(5)
Re1–O2	2.031(6)
Re1–O3	2.043(6)
Re1–O4	2.010(6)
Re1–Cl	2.477(3)
Re1′–Re1–O1	91.59(16)
Re1'-Re1-O2	88.98(17)
Re1'-Re1-O3	89.00(16)
Re1'-Re1-O4	91.35(17)
Re1'-Re1-Cl	171.91(7)

anodic region (0-1.5 V), DPVs in the cathodic region are shown in Fig. 5. Compound 1 undergoes a quasireversible reduction at -1.08 V (A) and an irreversible reduction at -2.19 V (**B**). The irreversibility of couple **B** is possibly due to the decomposition of compound 1 via the loss of equatorial chloro ligand(s). Voltammograms for analogous compounds Re2((PhN)2CPh)2Cl4, Re2((PhN)2CCH3)2Cl4, and Re₂((PhN)₂CH)₂Cl₄ were not recorded, and hence no



Fig. 5. Differential pulse voltammograms of compounds 1-4 recorded in THF at a scan rate of 0.0084/s.

comparison can be made. Compound 2 displays only a quasireversible reduction at -0.69 V (A). The cathodic shift of couple A in compound 1 from that of 2 is about -0.40 V, and reflects the extraordinary donor ability of N,N'-di(cyclohexyl)benzamidinate compared with diaryl-formamidinates. Compound 3 exhibits a reversible reduction at -0.87 V (A) and an irreversible reduction at -1.78 V (B). For compound 4, there is a single reversible reduction at -0.35 V, similar to that reported for other dirhenium carboxylate compounds with axial chloride ligands [25].

3. Conclusion

Several new dirhenium(III) species have been prepared and structurally characterized. Compounds 1 and 2 contain four equatorial chloro ligands that may serve as the entries for Re₂-alkynyl species. Structural studies also revealed the weakening of equatorial Re–O(OAc) bonds by the *trans*influence of DArF ligands in 3, and interesting supramolecules may be obtained by displacing these labile acetates with a strong donor ditopic linker. These aspects are being examined in our laboratory.

4. Experimental

4.1. General conditions, reagents, and instruments

Isobutyronitrile was purchased from Strem Chemicals; *m*-methoxyaniline, butylithium, and tetrafluoroboric acid were purchased from Aldrich; and all other reagents were purchased from ACROS. All solvents were purchased from VWR. Re₂(OAc)₄Cl₂ [26], N,N'-di(cyclohexyl)benzamidine (HDCyBA) [27], $\text{Re}_2(\text{OAc})_2\text{Cl}_4(\text{H}_2\text{O})_2$ [28,29], N,N'-di(3methoxyphenyl)formamidine [30], and $\alpha, \alpha, \alpha', \alpha'$ -tetramethyl-1,3-benzenedipropionic acid (H₂esp) [24] were prepared as previously described. ¹H NMR spectra were recorded on a Bruker AVANCE300 NMR spectrometer, with chemical shifts (δ) referenced to the residual solvent CDCl₃. Electronic absorption spectra in CH₂Cl₂ were obtained on either a Perkin-Elmer Lambda-900 UV-Vis-NIR spectrophotometer or a Hewlett-Packard diode array spectrometer (HP 8453). Cyclic and differential pulse voltammograms were recorded in 0.2 M n-Bu₄NPF₆ solution (THF, N₂-degassed) on a CHI620A voltammetric analyzer with a glassy carbon working electrode (diameter = 2 mm), a Pt-wire auxiliary electrode and a Ag/AgCl reference electrode. The concentration of dirhenium species is always 1.0 mM. Elemental analysis was performed by Atlantic Microlab.

4.2. Synthesis of $Re_2(DCyBA)_2Cl_4$ (1)

 $Re_2(OAc)_4Cl_2$ (0.100 g, 0.147 mmol) and N,N'-dicyclohexylbenzamidine (0.418 g, 1.47 mmol) were heated at 210 °C for 48 h under argon. Upon cooling, the reaction mixture was washed with 20 mL of CH₃OH in order to remove excess ligand and by-products. The solid residue collected was dissolved in CH₂Cl₂ and filtered. The filtrate was concentrated to ca. 2 mL and layered with 30 mL of hexanes. Re₂(DCyBA)₄Cl₂ was collected as dark red needle crystals (0.076 g, 48%). MS-FAB (*m/e*, based on ¹⁸⁶Re): 1045 [(Re₂(DCyBA)₂Cl₃)⁺]. ¹H NMR: 7.52 (m), 3.79 (m), 2.01 (d), 1.52 (m), 1.38 (m), 0.93 (t), 0.79 (m). *Anal.* Calc. for C₃₈H₅₄N₄Cl₄Re₂: C, 42.10, H, 5.04, N, 5.18. Found: C, 42.26, H, 5.23, N, 4.91%. Electrochemical data (CV), $E_{1/2}(A)$, -1.08 V (ΔE_p , 0.058 V; *i*_{backward}/*i*_{forward}, 0.57); $E_{pa}(B)$, -2.15 V. Vis–NIR, λ_{max}/nm (ε/M^{-1} cm⁻¹): 418 (11620) and 558 (2250).

4.3. Synthesis of $Re_2(DmAniF)_2Cl_4(2)$

[Bu₄N]₂[Re₂Cl₈] (0.200 g, 0.175 mmol) and *N,N'*-di-(3-methoxyphenyl)formamidine (0.134 g, 0.523 mmol) were heated under argon atmosphere at 150 °C for 36 h. The resultant solid was extracted with 25 mL of dichloromethane. The solid residue was dissolved in THF and re-crystallized from hexanes/THF to provide the desired product. The dichloromethane filtrate was rotovapped, and the resultant solid was washed with hot ethanol and re-crystallized from Et₂O/THF to afford an additional crop of the product. Yield: 0.14 g (79%). *Anal.* Calc. for C₃₁H₃₂N₄Cl₆Re₂: C, 33.55, H, 2.91, N, 5.05. Found: C, 33.57, H, 2.88, N, 5.18%. Electrochemical data (CV), $E_{1/2}(A)$, -0.69 V (ΔE_p , 0.069 V; $i_{backward}/i_{forward}$, 0.59). Vis–NIR, λ_{max}/nm ($\varepsilon/$ M⁻¹ cm⁻¹): 430 (11500) and 584 (3640).

4.4. Synthesis of $Re_2(OAc)_2(DmAniF)_2Cl_2(3)$

Re₂(OAc)₂Cl₄(H₂O)₂ (0.100 g, 0.150 mmol), N,N'-di-(3-methoxyphenyl)formamidine (0.076 g, 0.300 mmol), and 0.75 mL of NEt₃ were mixed in 30 mL of THF and refluxed under argon for 24 h. After the removal of insoluble materials via filtration, solvents were removed on a rotovap. The resultant residue was dissolved in dichloromethane and filtered, and the solvent was removed subsequently from the filtrate. The same procedure was repeated with methanol and ethyl acetate, and the ethyl acetate solution was reduced to 5 mL, layered with hexanes to afford powdery product. Yield: 0.12 g (75%). Orange block crystals were obtained through the slow evaporation of an ethyl acetate solution. MS-FAB (m/e, based on ¹⁸⁶Re): 1037 [(Re₂(DmA $niF_{2}(OAc_{2}Cl)^{+}$]. ¹H NMR: 8.65 (s), 7.19 (t), 6.86 (d), 6.80 (d), 6.75 (s), 3.66 (s), 3.24 (s). Anal. Calc. for C₃₄H₄₆N₄O₄-Cl₂Re₂: C, 35.14, H, 3.99, N, 4.82. Found: C, 34.92, H, 3.65, N, 5.13%. Electrochemical data (CV), $E_{1/2}(\mathbf{A})$, -0.87 V $(\Delta E_{\rm p}, 0.107 \text{ V}; i_{\rm backward}/i_{\rm forward}, 0.64); E_{\rm pa}(\mathbf{B}), -1.78 \text{ V}.$ Vis–NIR, $\lambda_{\rm max}/{\rm nm} (\varepsilon/{\rm M}^{-1} \text{ cm}^{-1})$: 414 (5650).

4.5. Synthesis of $Re_2(esp)_2Cl_2$ (4)

 $Re_2(OAc)_4Cl_2$ (0.100 g, 0.147 mmol) and $\alpha, \alpha, \alpha', \alpha'$ -tetramethyl-1,3-benzenedipropionic acid (0.082 g, 0.294 mmol) were placed in a 50 mL Schlenck flask fitted with soxhlet M.Q. Dequeant et al. | Inorganica Chimica Acta 359 (2006) 4191-4196

Table 4 Crystal data and structure refinement of compounds 1–4

Compound	1	2	3 · EtOAc	4
Chemical formula	C ₃₈ H ₅₄ Cl ₄ N ₄ Re ₂	C ₃₀ H ₃₀ Cl ₄ N ₄ O ₄ Re ₂	C ₃₈ H ₄₄ Cl ₂ N ₄ O ₁₀ Re ₂	C ₃₂ H ₄₀ Cl _{1.66} O _{9.36} Re _{2.34}
Formula weight	1081.05	1024.78	1160.07	1068.90
Space group	I2/a	$P2_1/c$	$P2_1$	Pbca
a (Å)	16.4360(13)	11.3030(7)	11.0678(5)	16.9838(5)
b (Å)	13.0541(9)	15.6769(10)	15.8044(8)	12.0023(3)
c (Å)	19.0354(13)	9.7168(6)	12.0515(6)	17.3998(5)
β (°)	98.332(2)	112.2370(10)	90.4660(10)	90
$V(Å^3)$	4041.1(5)	1593.72(17)	2107.98(18)	3546.86(17)
Z	4	2	2	4
$T(^{\circ}\mathrm{C})$	27	27	27	-123
λ (Mo K α) (Å)	0.71073	0.71073	0.71073	0.71073
$\rho_{\rm calc} ({\rm g/cm^3})$	1.777	2.135	1.828	2.002
$\mu (\text{mm}^{-1})$	6.282	7.967	5.923	8.257
R	0.039	0.030	0.044	0.053
wR_2	0.064	0.063	0.095	0.106

extraction apparatus and put under argon. To this was added 30 mL of distilled toluene and the thimble of the soxhlet apparatus was filled with K₂CO₃. The solution was refluxed in a sand bath for 5 days with frequent changes of K₂CO₃ pad. On cooling to ambient temperature, crude product was collected via filtration. The crude product was redissolved in dichloromethane, and slow evaporation of dichloromethane solution afforded pure **4** as red plate crystals. Yield: 0.10 g (70%). MS-FAB (*m/e*, based on ¹⁸⁶Re): 961 [(Re₂(esp)₂Cl)⁺]. ¹H NMR: 7.08 (d), 6.79 (s), 3.19 (s), 1.57 (s). *Anal.* Calc. for C₃₂H₄₂O₉ClRe₂: C, 39.27, H, 4.33. Found: C, 39.27, H, 4.42%. Electrochemical data (CV), $E_{1/2}(A)$, -0.35 V (ΔE_p , 0.089 V; *i*_{backward}/*i*_{forward}, 0.88) Vis–NIR, λ_{max}/nm (ε/M^{-1} cm⁻¹): 399 (310) and 498 (352).

4.6. Structure determination

Compounds 1–3. Single crystals were obtained as previously stated. X-ray intensity data were measured at 300 K on a Bruker SMART1000 CCD-based X-ray diffractometer system using Mo K α ($\lambda = 0.71073$ Å). Crystals used for data collection were cemented to a quartz fiber with epoxy glue. Data were measured using omega scans of 0.3° per frame for 10 s for 1 and 2, and 40 s for 3, so that a hemisphere (1271 frames) was collected. The frames were integrated with the Bruker SAINT[®] software package [31] using a narrow-frame integration algorithm, which also corrects for the Lorentz and polarization effects. Absorption corrections were applied using SADABS.

Structures were solved and refined using the Bruker SHELXTL[©] (Version 5.1) software package [32] in space groups of I2/a (1), $P2_1/c$ (2), and $P2_1$ (3). Positions of all non-hydrogen atoms were revealed by direct method. All non-hydrogen atoms are anisotropic and the hydrogen atoms were put in calculated positions and riding mode. Each structure was refined to convergence by least squares method on F^2 , SHELXL-93, incorporated in SHELXTLPC V 5.03. Crystallographic data are given in Table 4.

Compound 4. X-ray intensity data were collected at 150(1) K on a Nonius Kappa CCD-based X-ray diffractometer. The frames were integrated with the DENZO-SMN [33] and Lorentz and polarization corrections were applied to the data. Absorption corrections were applied using SCALE-PACK [33] and a secondary extinction correction was applied [34]. The structure of compound 4 was solved and refined using the structure solution program PATTY in DIRDIF-99 [35] in the space group of *Pbca*. The non-hydrogen atoms were located in succeeding difference Fourier syntheses. During the course of structural analysis, the axial chloro ligand (Cl1) was found to be disordered with a ReO₄ anion, a phenomenon observed and rationalized previously [36-38]. The disordered Cl/ReO₄ was refined to convergence with the occupancy constraint at the occupancy ratio of 85/15 for Cl/ReO₄. All non-hydrogen atoms are anisotropic and the hydrogen atoms were put in calculated positions and riding mode. The structure was refined to convergence by least squares method on F^2 using SHELXL-97 [35]. Crystallographic data are also given in Table 4.

5. Supplementary materials

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 604647, 604648, 604649 and 604913 for compounds 1–4, respectively. Copies of this information may be obtained free of charge from the director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK.

Acknowledgements

We thank the generous support from the National Science Foundation (CHE 0242623 to T.R.) and Purdue University.

References

- [1] S. Leininger, B. Olenyuk, P.J. Stang, Chem. Rev. 100 (2000) 853.
- [2] M. Fujita, Acc. Chem. Res. 32 (1999) 53.

- [3] F.A. Cotton, C. Lin, C.A. Murillo, Acc. Chem. Res. 34 (2001) 759.
- [4] F.A. Cotton, C. Lin, C.A. Murillo, Proc. Natl. Acad. Sci. USA 99 (2002) 4810.
- [5] J.K. Bera, P. Angaridis, F.A. Cotton, M.A. Petrukhina, P.E. Fanwick, R.A. Walton, J. Am. Chem. Soc. 123 (2001) 1515.
- [6] J.K. Bera, R. Clerac, P.E. Fanwick, R.A. Walton, J. Chem. Soc., Dalton Trans. (2002) 2168.
- [7] J.K. Bera, J. Bacsa, B.W. Smucker, K.R. Dunbar, Eur. J. Inorg. Chem. (2004) 368.
- [8] K.J. Nelson, R.W. McGaff, D.R. Powell, Inorg. Chim. Acta 304 (2000) 130.
- [9] S.-M. Kuang, P.E. Fanwick, R.A. Walton, Inorg. Chem. 39 (2000) 2968.
- [10] S.-M. Kuang, P.E. Fanwick, R.A. Walton, Inorg. Chem. 41 (2002) 1036.
- [11] S.L. Bartley, M.J. Bazile, R. Clerac, H.H. Zhao, O.Y. Xiang, K.R. Dunbar, J. Chem. Soc., Dalton Trans. (2003) 2937.
- [12] M.Q. Dequeant, P.M. Bradley, G. Xu, D.L. Lutterman, C. Turro, T. Ren, Inorg. Chem. 43 (2004) 7887.
- [13] M.Q. Dequeant, R. McGuire Jr., D.R. McMillin, T. Ren, Inorg. Chem. 44 (2005) 6521.
- [14] N.D. Reddy, P.E. Fanwick, R.A. Walton, Inorg. Chim. Acta 319 (2001) 224.
- [15] G. Zou, J.C. Alvarez, T. Ren, J. Organomet. Chem. 596 (2000) 152.
- [16] F.A. Cotton, L.W. Shive, Inorg. Chem. 14 (1975) 2027.
- [17] F.A. Cotton, W.H. Ilsley, W. Kaim, Inorg. Chem. 19 (1980) 2360.
- [18] F.A. Cotton, L.M. Daniels, S.C. Haefner, Inorg. Chim. Acta 285 (1999) 149.
- [19] F.A. Cotton, C.A. Murillo, R.A. Walton (Eds.), Multiple Bonds between Metal Atoms, third ed., Springer Science and Business Media, Inc., New York, 2005.
- [20] R.A. Walton, in: F.A. Cotton, C.A. Murillo, R.A. Walton (Eds.), Multiple Bonds between Metal Atoms, third ed., Springer Science and Business Media, Inc., New York, 2005.

- [21] F.A. Cotton, T. Ren, J. Am. Chem. Soc. 114 (1992) 2495.
- [22] J.L. Eglin, C. Lin, T. Ren, L. Smith, R.J. Staples, D.O. Wipf, Eur. J. Inorg. Chem. (1999) 2095.
- [23] D.M. Collins, F.A. Cotton, L.D. Gage, Inorg. Chem. 18 (1979) 1712.
- [24] C.G. Espino, K.W. Fiori, M. Kim, J. Du Bois, J. Am. Chem. Soc. 126 (2004) 15378.
- [25] V. Srinivasan, R.A. Walton, Inorg. Chem. 19 (1980) 1635.
- [26] F.A. Cotton, N.F. Curtis, B.F.G. Johnson, W.R. Robinson, Inorg. Chem. 4 (1965) 326.
- [27] A. Littke, N. Sleiman, C. Bensimon, D.S. Richeson, G.P.A. Yap, S.J. Brown, Organometallics 17 (1998) 446.
- [28] F.A. Cotton, C. Oldham, R.A. Walton, Inorg. Chem. 6 (1967) 214.
- [29] A.R. Chakravarty, F.A. Cotton, A.R. Cutler, R.A. Walton, Inorg. Chem. 25 (1986) 3619.
- [30] C. Lin, J.D. Protasiewicz, E.T. Smith, T. Ren, Inorg. Chem. 35 (1996) 6422.
- [31] SAINT V 6.035 Software for the CCD Detector System, Bruker-AXS Inc., 1999.
- [32] (a) SHELXTL 5.03 (WINDOW-NT Version): Program library for Structure Solution and Molecular Graphics, Bruker-AXS Inc., 1998;
 (b) G.M. Sheldrick, SHELXS-90: Program for the Solution of Crystal Structures, University of Göttingen, Göttingen, Germany, 1990;
 (c) G.M. Sheldrick, SHELXL-93: Program for the Refinement of Crystal Structures, University of Göttingen, Göttingen, Germany, 1993.
- [33] Z. Otwinowski, W. Minor, Methods Enzymol. 276 (1997) 307.
- [34] SHELXL-97, 1997.
- [35] The DIRDIF-99 Program System, 1999.
- [36] J.K. Bera, P.E. Fanwick, R.A. Walton, Inorg. Chem. 40 (2001) 2914.
- [37] K.E. Meyer, P.E. Fanwick, R.A. Walton, Inorg. Chem. 31 (1992) 4486
- [38] A.L. Ondracek, W. Wu, P.E. Fanwick, R.A. Walton, Inorg. Chem. 35 (1996) 5249.