Inorganica Chimica Acta 425 (2015) 233–238

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: www.elsevier.com/locate/ica

Redox-active TTF carboxylate as an axial bridging ligand for dirhenium metal–metal bonded complexes

Bradley W. Smucker [a,*], John Bacsa [b], Jitendra K. Bera [c], Eric W. Reinheimer [d,1]

[a] Department of Chemistry, Austin College, Sherman, TX 75092, USA
[b] Department of Chemistry, Emory University, Atlanta, GA 30322, USA
[c] Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India
[d] Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, TX 77842, USA

ARTICLE INFO

Article history:
Received 24 July 2014
Received in revised form 1 October 2014
Accepted 4 October 2014
Available online 14 October 2014

Keywords:
Tetrathiafulvalene monocarboxylate
Dirhenium compounds
Redox properties
X-ray crystal structures

ABSTRACT

Tetrathiafulvalene monocarboxylate, $[TTFCO_2]^-$, was used as a carboxylate bridging ligand for three new dirhenium complexes. The acetate ligands of *cis*-$Re_2(dppm)_2Cl_2(OAc)_2$, *trans*-$Re_2(dppm)_2Cl_4(OAc)$, and *cis*-$Re_2Cl_4(OAc)_2$ are displaced by $TTFCO_2H$ to form *cis*-$Re_2(dppm)_2Cl_2(TTFCO_2)_2$ (**1**), *trans*-$Re_2(dppm)_2Cl_4(TTFCO_2)$ (**2**), and *cis*-$Re_2Cl_4(TTFCO_2)_2$ (**3**), respectively. Depending on their respective solubility, the complexes were characterized via single crystal X-ray diffraction as well as electrochemical and spectroscopic properties.

1. Introduction

The coordination of functionalized redox-active tetrathiafulvalene (TTF) moieties to metal complexes has attracted significant attention over the past two decades because of the interesting electronic [1], magnetic [2], photophysical [3], and chemical [4] properties engendered by the TTF radical. Coordination of TTF-containing ligands to transition metal centers is typically achieved by functionalizing TTF with nitrogen (pyridyl, dipyridyl, terpyridyl, pyrazine, amido and imino groups) or phosphorus (phosphino and chelating diphosphino ligands of tertiary phosphines) containing substituents [5]. Other groups such as oxazolyl, imidazolyl, acetylacetonate (acac) and Schiff-Base groups have also been coupled to TTF cores and incorporated into metal complexes [6].

In sharp contrast to the situation with mononuclear transition metal species, coordination of redox-active ligands, such as TTF, to metal–metal bonded compounds has received limited attention. The diversity of the structural and electronic properties of metal–metal bonded compounds and the variety of ligand types that are tolerated makes them attractive candidates for reactions with redox switchable ligands [7]. Examples of redox-active ligands that have been used to span dimetal units are TEMPO [8] (2,2,6,6-tetramethylpyridinyl-1-oxy), TCNE [9] (tetracyanoethylene), TCNQ [10] (7,7,8,8-tetracyanoquinodimethane) and DMDCNQI [11] (2,5-dimethyl-N,N′-dicyanoquinonediimine). With one exception, these acceptor ligands bind to the axial positions of the M–M core [12].

One example in which the TTF molecule has been coordinated directly to a metal–metal bonded species is the work of Matsubayashi et al. who reported axial coordination of TTF to $Rh_2(O_2CCH_3)_4$ through the sulfur atom in 1988 [13]. More interesting, however, is coordination through equatorial sites which results in stronger electronic communication between the metal centers and redox-active ligands. Work in this vein has concentrated primarily on incorporating pendant redox-active ferrocene units attached to mono- and di-carboxylate anions into di-molybdenum, -tungsten and -rhenium complexes [14].

Tetrathiafulvalene derivatives with carboxylic acid substituents have been used to prepare coordination complexes of transition [15] and rare-earth metals [16]. The mono-substituted $TTFCO_2H$ molecule is readily synthesized by a variety of methods and is a common precursor in organic reactions of functionalized TTF derivatives [17]. Recently there have been reports of TTF mono- and tetra-substituted carboxylate molecules being employed for various anionic and supramolecular applications [18,19]. Of specific relevance to the current study is the report that $TTFCO_2H$ reacts with the dirhodium paddlewheel complex $Rh_2(Bu^tCO_2)_4$ to form the $TTFCO_2$-bridged complexes $[Rh_2(Bu^tCO_2)_3(TTFCO_2)$

---

[*] Corresponding author. Tel.:+1 903 813 2217.
E-mail address: bsmucker@austincollege.edu (B.W. Smucker).

[1] Current address: Rigaku Americas Corporation, The Woodlands, TX 77381, USA.

http://dx.doi.org/10.1016/j.ica.2014.10.002
0020-1693/

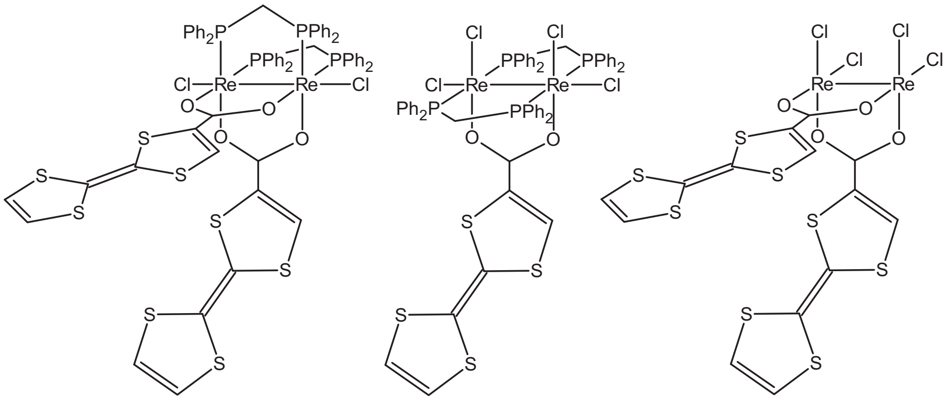

Fig. 1. Schematic representations of *cis*-$Re_2Cl_2(dppm)_2(TTFCO_2)_2$ (left), *trans*-$Re_2Cl_4(dppm)_2(TTFCO_2)$ (middle), and *cis*-$Re_2Cl_4(TTFCO_2)_2$ (right).

$(NEt_3)_2$], *cis*-[$Rh_2(Bu^tCO_2)_2(TTFCO_2)_2(NEt_3)_2$] and *trans*-[$Rh_2(Bu^tCO_2)_2(TTFCO_2)_2(NEt_3)_2$]. These are the first instances of metal–metal bonded complexes with a TTF containing molecule bound in equatorial positions to the M–M core [20]. Ouahab and coworkers have further used [$TTFCO_2$]$^-$ as a ligand in a binuclear gadolinium(III) complex [16] or as an anion in a binuclear copper(II) complex [21].

Herein we report the use of [$TTFCO_2$]$^-$ as a bridging ligand for a series of multiply-bonded dirhenium complexes. The coordination of the carboxylate form of $TTFCO_2H$ to dirhenium compounds *cis*-$Re_2Cl_2(dppm)_2(TTFCO_2)_2$ (**1**), *trans*-$Re_2Cl_4(dppm)_2(TTFCO_2)$ (**2**), and *cis*-$Re_2Cl_4(TTFCO_2)_2$ (**3**) (Fig. 1) as well as their respective structural and electrochemical and spectroscopic properties, depending on their respective solubilities, were investigated.

2. Experimental

All operations were performed under a nitrogen atmosphere using standard Schlenk-line techniques unless otherwise indicated. Solvents were distilled prior to use from the appropriate drying agents. The dinuclear starting materials *cis*-$Re_2Cl_2(dppm)_2(O_2CCH_3)_2$ [22], *trans*-$Re_2Cl_4(dppm)_2(O_2CCH_3)$ [23], and *cis*-$Re_2Cl_4(O_2CCH_3)_2$ [24], were synthesized from their respective literature preparations.

2.1. Physical measurements

IR spectra were measured as Nujol mulls between CsI plates on a Nicolet 740 FT-IR spectrometer. UV–Vis spectra were measured in HPLC grade CH_2Cl_2 on a Shimadzu UV-1601pc spectrophotometer. The cyclic voltammetric studies were performed on a CH Instruments Electrochemical Analyzer in dichloromethane containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate ([TBA][PF_6], recrystallized from ethanol) as the supporting electrolyte with a scan rate of 100 mV/s. The working electrode was a BAS Pt disk electrode, the reference electrode was Ag/AgCl, and the counter electrode was a Pt wire. The Cp_2Fe/Cp_2Fe^+ couple occurs at +0.48 V versus Ag/AgCl under the same experimental conditions.

2.2. Syntheses[2]

2.2.1. cis-$Re_2Cl_2(dppm)_2(TTFCO_2)_2$, 1

A 100 mL Schlenk flask was charged with *cis*-$Re_2Cl_2(dppm)_2(O_2CCH_3)_2$ (101.7 mg, 0.076 mmol), $TTFCO_2H$ (41.2 mg, 0.167 mmol), 40 mL of EtOH, and a boiling stick. The resulting orange heterogeneous solution was refluxed for 12 h. The resulting red precipitate was isolated, by filtration, from the red/orange solution, and washed with EtOH, CH_2Cl_2 and Et_2O to give 103.9 mg (78% yield). IR (CsI-Nujol): 1564 (w), 1545 (m), 1537 (m), 1261 (m), 1092 (m), 1024 (m), 794 (m), 786 (m), 767 (m), 750 (w), 738 (m), 735 (m), 697 (w), 688 (w), 678 (w), 527 (m), 517 (m), 508 (m), 491 (m), 476 (w), 464 (w), 415 (w), 403 (w) and 230 (w) cm^{-1}.

2.2.2. trans-$Re_2Cl_4(dppm)_2(TTFCO_2)$, 2

A 15 mL CH_2Cl_2 dark yellow solution containing *trans*-$Re_2Cl_4(dppm)_2(O_2CCH_3)$ (33.4 mg, 0.025 mmol) was combined with 15 mL of a brown/orange methanol solution containing $TTFCO_2H$ (8.1 mg, 0.032 mmol) to make a red solution in a 50 mL Schlenk flask. After stirring 12 h, the solution was partially condensed to ~5 mL and a red solid was precipitated by the addition of 20 mL of Et_2O and washed with 2 × 20 mL of Et_2O to give 8 mg (21%) of a red product. IR (CsI-Nujol): 1618 (w), 1572 (w), 1533 (w), 1197 (w), 1150 (w), 1092 (m), 1031 (w), 1000 (w), 845 (w), 773 (m), 737 (m), 688 (m), 518 (m), 504 (m), 479 (w), 422 (w) and 325 (w) cm^{-1}. UV–Vis (CH_2Cl_2) λ_{max}, nm ($\varepsilon = M^{-1}\,cm^{-1}$): 319 ($8.0 \times 10^3$), 422 ($2.8 \times 10^3$), and 495 ($2.5 \times 10^3$).

2.2.3. cis-$Re_2Cl_4(TTFCO_2)_2$, 3

A 100 mL Schlenk flask was charged with *cis*-$Re_2Cl_4(O_2CCH_3)_2$ (32.8 mg, 0.049 mmol), $TTFCO_2H$ (28.6 mg, 0.115 mmol), 40 mL of EtOH, and a boiling stick to make an orange-red solution. The solution was refluxed for 12 h giving a wine-red solution. The solution was filtered and the solvent removed *in vacuo*. The red–purple solid was re-dissolved in a minimal amount of EtOH and combined with a mixture of toluene and hexanes (40 mL each) and filtered to give 46.4 mg (94% yield) of a purple powder. IR (CsI-Nujol): 1565 (m), 1545 (m), 1537 (m), 1161 (w), 1092 (w), 794 (w), 784 (m), 767 (m), 750 (w), 734 (m), 697 (m), 689 (m), 677 (w), 527 (w), 517 (m), 508 (w), 491 (m), 475 (w), 465 (w), and 415 (w) cm^{-1}. UV-Vis (CH_2Cl_2) λ_{max}, nm ($\varepsilon = M^{-1}\,cm^{-1}$): 250 ($1.7 \times 10^5$), 288 ($2.3 \times 10^5$), 314 ($2.2 \times 10^5$), 460 ($2.5 \times 10^4$), 510 ($3.1 \times 10^4$) and 570 ($2.1 \times 10^4$).

2.3. X-ray crystallographic data collection and structural solutions

For compounds **1** and **2**, the data were collected on a Bruker-AXS SMART 1000 CCD diffractometer at 110 ± 2 K with graphite monochromated Mo Kα ($\lambda\alpha = 0.71073$ Å) radiation and were corrected for Lorentz and polarization effects. Frame integration, Lorentz–polarization corrections, and final cell parameter calculations

---

[2] Compounds were synthesized and characterized in 2002 and were no longer available for further analysis at the time of writing.