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Complexing Ability of the Versatile, Redox-Active, 3-[3-(Diphenylphosphino)propylthio]-3′,4,4′-trimethyl-tetrathiafulvalene Ligand

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The synthesis of a ligand containing as an electroactive core a tetrathiafulvalene moiety, 3-[3-(diphenylphosphino)-propylthio]-3′,4,4′-trimethyl-tetrathiafulvalene, is reported. Its versatile ability to act as a bidentate or a monodentate ligand, as demonstrated by the metal carbonyl complexes obtained, is described. The novel *cis*-$Mo(CO)_4(P\text{-}TTF)_2$ **4** and *cis*-$W(CO)_4(P,S\text{-}TTF)$ **6** complexes have been characterized by X-ray diffraction analyses and cyclic voltammetry measurements. Within complex **4**, no significant influence of the two electroactive ligands on the molybdenum center was detected, whereas, in complex **6**, a weak influence of the TTF redox-active core can be observed on the redox behavior of the metal center.

Introduction

Coordination of metals by electroactive ligands containing tetrathiafulvalene (TTF) moieties has recently attracted attention due to the potential applications of these novel organic−inorganic hybrid building blocks.[1−7] Association of the TTFs to the metal can be realized through an intervening coordination function such as phosphine substituents well-known for their chelating ability toward various transition metal derivatives.[2−6] So far, the few examples of complexes with TTF-functionalized phosphine ligands described have involved the diphenylphosphino substituents (PPh_2) directly linked to the donor core.[2−6,8−10] We recently described the synthesis of phosphino ligands containing TTF where the phosphorus atom is connected to the donor core through a flexible propylthio spacer group.[11] Complexes with such ligands have not yet been described probably owing to the presence of a mixture of two isomers (*Z*/*E*) in these bis-functionalized TTFs. Herein we report the synthesis of a single-substituted ligand containing the redox-active TTF moiety together with its metal carbonyl complexes with the $Mo(CO)_4$ and $W(CO)_4$ fragments. The structural and electrochemical properties of these complexes are also presented.

Experimental Section

^1H NMR and ^{13}C NMR spectra were recorded on Bruker ARX 200 or Bruker AC 300P spectrometers. Chemical shifts are reported in parts per million referenced to TMS for ^1H NMR and ^{13}C NMR and to H_3PO_4 for ^{31}P NMR. Melting points were measured using a Kofler hot stage apparatus. Elemental analyses results were obtained from the Laboratoire Central de Microanalyse du CNRS, Lyon. Mass spectra were recorded with a ZABSpec TOF instrument by the Centre Régional de Mesures Physiques de l'Ouest, Rennes. Tetrahydrofuran was distilled from sodium−benzophenone. Methanol was distilled from calcium. Toluene was dried over sodium wire. Chromatography was performed using silica gel Merck 60 (70−260 mesh). $Mo(CO)_6$ and 1,4-diazabicyclo[2.2.2]octane (DABCO) were purchased from ACROS organics. $W(CO)_6$ was pur-

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chased from Aldrich. $M(CO)_4(NHC_5H_{10})_2$ were prepared from $M(CO)_6$ according to a published procedure.[12] Cyclic voltammetry was carried out on a 10^{-3} M solution of TTF derivatives in dichloromethane, containing 1 M NBu_4PF_6 as the supporting electrolyte. Voltammograms were recorded at 0.1 V s^{-1} at a platinum disk electrode ($A = 1$ mm^2). The potentials were measured versus a saturated calomel electrode. Single-crystal diffraction data were collected on a Kappa diffractometer equipped with a CCD detector from the Centre de Diffractométrie X, Université de Rennes 1, France.

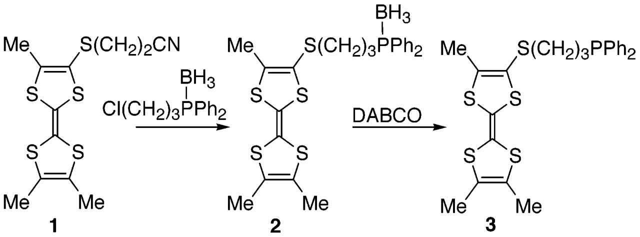
3-[3-(Boranatodiphenylphosphino)propylthio]-3′,4,4′-trimethyl-TTF 2. To a solution of cyanoethylthiotrimethyl-TTF **1** (800 mg, 2.4 mmol) in 20 mL of DMF was added under argon a solution of CsOH and H_2O (410 mg, 2.4 mmol) in 5 mL of MeOH. The mixture was allowed to stir for 30 min at rt, after which 3-chloropropyldiphenylphosphine−borane (670 mg, 2.4 mmol) was added. The mixture was stirred for 12 h, and then the solvents were evaporated. The residue was extracted with CH_2Cl_2 and washed with water. The organic layer was dried over Na_2SO_4 and evaporated. Chromatography over silica gel (4:1 CH_2Cl_2/PE) afforded **2** (692 mg, 56%) as an orange powder. Mp: 162 °C. δ_H (200 MHz; $CDCl_3$): 0.60−1.50 (m, 3H); 1.87 (m, 2H); 1.96 (s, 6H); 2.08 (s, 3H); 2.33 (m, 2H); 2.80 (t, 2H); 7.30−7.82 (m, 10H). δ_P (121 MHz; $CDCl_3$): 16.6. δ_C (75 MHz; $CDCl_3$): 13.9, 15.8, 23.7, 24.9, 38.0, 118.9, 123.2, 128.9, 129.2, 129.4, 130.0, 131.7, 132.4, 132.6, 136.2. Anal. Calcd for $C_{24}H_{28}BPS_5$: C, 55.59; H, 5.44; S, 30.91. Found: C, 55.19; H, 5.20; S, 31.08.

3-[3-(Diphenylphosphino)propylthio]-3′,4,4′-trimethyl-TTF 3. To a solution of TTF **2** (519 mg, 1 mmol) in 30 mL of dried, degassed toluene was added under argon DABCO (112 mg, 1 mmol). The mixture was stirred for about 4 h at 50 °C. The reaction was followed by TLC. The solution was filtrated through a silica gel column with degassed toluene. Toluene was evaporated with a vacuum pump to afford TTF **3** (394 mg, 78%) as an orange powder. Mp: 93 °C. δ_H (200 MHz; $CDCl_3$): 1.72 (m, 2H); 1.94 (s, 6H); 2.03 (s, 3H); 2.12 (m, 2H); 2.80 (t, 2H); 7.30−7.55 (m, 10H). δ_P (121 MHz; $CDCl_3$): −16.4. δ_C (75 MHz; $CDCl_3$) 13.8, 15.4, 26.2, 26.9, 37.1, 106.0, 110.2, 119.0, 122.8, 128.5, 128.6, 132.6, 132.8, 135.2, 138.3.

***cis*-Mo(CO)$_4$(P-TTF)$_2$ 4.** To a solution of the TTF **2** (519 mg, 1 mmol) in 10 mL of dried, degassed toluene was added under argon DABCO (112 mg, 1 mmol). The mixture was stirred for 4 h at 50 °C, after which the $Mo(CO)_4(NHC_5H_{10})_2$ (0.5 mmol, 188 mg) in 10 mL of degassed CH_2Cl_2 was added and stirring was continued for 15 min. Solvent was removed, and the residue was extracted with CH_2Cl_2 and washed with water. Chromatography over silica gel (4:1 CH_2Cl_2/PE) afforded the complex **4** (243 mg, 20%) as an orange powder. δ_H (200 MHz; $CDCl_3$): 1.37 (m, 4H); 1.91 (s, 12H); 1.96 (s, 6H); 1.98 (m, 4H); 2.47 (t, 4H); 7.25−7.40 (m, 20H). δ_P (121 MHz; $CDCl_3$): 26.6. Found: $M^{+\bullet}$, 1217.9453. HRMS: calcd for $C_{52}H_{50}MoO_4P_2S_{10}$ 1217.9446, found 1217.9453. Anal. Calcd for $C_{52}H_{50}MoO_4P_2S_{10}$: C, 51.3; H, 4.14; S, 24.88; P, 5.08. Found: C, 51.7; H, 4.37; S, 24.84; P, 4.92.

***cis*-W(CO)$_4$(NHC$_5$H$_{10}$)(P-TTF) 5.** To a solution of TTF **2** (519 mg, 1 mmol) in 10 mL of dried, degassed toluene was added under argon DABCO (112 mg, 1 mmol). The mixture was stirred for 4 h at 50 °C, after which the $W(CO)_4(NHC_5H_{10})_2$ (464 mg, 1 mmol) in 10 mL of degassed CH_2Cl_2 was added. Stirring was continued for 15 min, and the solvent was evaporated. The residue was extracted with CH_2Cl_2 and washed with water. The organic layer was dried over Na_2SO_4, and evaporation of the solvent gave the complex **5** as an orange powder. δ_H (200 MHz; $CDCl_3$): 1.58 (m, 4H); 1.70 (m, 2H); 1.88 (m, 2H); 1.96 (s, 6H); 2.03 (s, 3H); 2.12 (m, 2H); 2.68 (m, 4H); 2.78 (m, 2H); 2.86 (br, 1H); 7.18−7.63 (m, 10H). δ_P (121 MHz; $CDCl_3$): 22.0. HRMS: calcd for $C_{33}H_{36}NO_4PS_5W$ 885.0487, found 885.0491.

Scheme 1



***cis*-W(CO)$_4$(P,S-TTF) 6.** To a solution of TTF **2** (519 mg, 1 mmol) in 10 mL of dried, degassed toluene was added DABCO (112 mg, 1 mmol) under argon. The mixture was stirred for 4 h at 50 °C, after which the $W(CO)_4(NHC_5H_{10})_2$ (464 mg, 1 mmol) in 10 mL of degassed CH_2Cl_2 was added. The reaction mixture was stirred for 15 min, and the solvent was removed under reduced pressure. The residue was extracted with CH_2Cl_2, washed with water, and dried over Na_2SO_4. The residue was chromatographed over silica gel (4:1 CH_2Cl_2/PE) and afforded the complex **6** (648 mg, 81%) as an orange powder. Mp: 180 °C. δ_H (200 MHz; $CDCl_3$): 1.92 (s, 6H); 2.05 (m, 2H); 2.16 (s, 3H); 2.56 (m, 2H); 3.22 (m, 2H); 7.20−7.60 (m, 10H). δ_P (121 MHz; $CDCl_3$): 2.4. δ_C (75 MHz; $CDCl_3$): 13.8, 15.3, 23.1, 29.9, 43.3, 104.0, 113.9, 122.7, 122.9, 128.6, 130.1, 132.1, 134.9, 135.8, 136.3, 202.4. HRMS: calcd for $C_{28}H_{25}O_4PS_5W$, 799.9604, found, 799.9598.

Results and Discussion

The new ligand was prepared from the preformed TTF derivative **1** according to the chemical pathway described in Scheme 1.[13] This was realized in order to avoid the presence of two TTF isomers (*Z*/*E*) as it was the case in our previously published phosphino ligands containing tetrathiafulvalene (TTF).[11] The cyanoethyl thiolate protecting group, an efficient building block for the preparation of a wide range of TTF derivatives,[14] was cleaved with cesium hydroxide and reacted with 3-chloropropyldiphenylphosphine−borane leading to TTF **2** in good yield. As the other phosphine−borane complexes, TTF **2** is stable and can be handled under atmospheric conditions without any particular conditions.[15,16] Decomplexation of phosphine borane can be realized using a soft method, which does not interact with the TTF core, such as treatment with DABCO under inert atmosphere to afford TTF **3** in good yields.[17]

In order to form metal carbonyl complexes with this ligand, we realized the synthesis of *cis*-$M(CO)_4L_2$ derivatives (M = Mo, W) according to the procedure described by Darensbourg et al.[12] Indeed the use of these disubstituted metal derivatives with L = piperidine allows the facile

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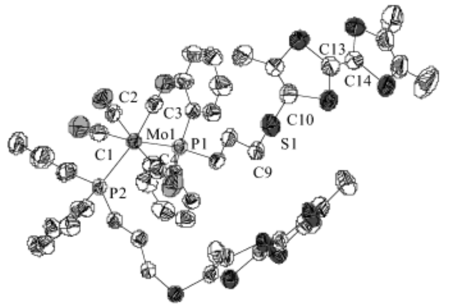
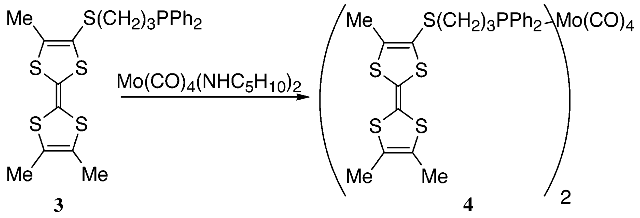


Figure 1. ORTEP view of complex **4** showing the atom labeling (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths: Mo1−C3 1.982(5), Mo1−C1 1.983(5), Mo1−C4 2.020(5), Mo1−C2 2.046(5), Mo1−P2 2.5472(12), Mo1−P1 2.5535(11), C13−C14 1.345(8), S1−C10 1.771(6), S1−C9 1.829(5).

Scheme 2



replacement of the two labile piperidino ligands by another ligand such as the diphenylphosphinopropylthio TTF **3**.

Then, to a solution of TTF **3** in CH_2Cl_2 was added 1 equiv of *cis*-$Mo(CO)_4$(piperidine)$_2$, and the mixture was warmed. After 15 min, analysis of the medium by ^1H NMR and ^{31}P NMR reveals that the two piperidine ligands have been replaced by two phosphino TTF **3** (Scheme 2). Chromatographic separation of the reaction mixture on silica gel affords the complex **4** as an orange crystalline solid. X-ray crystal structure analysis demonstrates that two TTF **3** are indeed coordinated to the metal center via the phosphorus atom (P-TTF) and the molybdenum center is surrounded by two cis-coordinated ligand **3** (Figure 1). Phosphorus−molybdenum bond lengths are in the usual range (Mo−P1, 2.5472(12) Å; Mo−P2, 2.5535(11) Å) with a P1−Mo−P2 interligand angle of 100.26(4)°. One singlet is observed on the ^{31}P NMR spectra of **4**, *cis*-$Mo(CO)_4$(P-TTF **3**)$_2$, at (δ 26.6 ppm) indicating equivalent phosphorus environments.

Contrariwise following the same experimental procedure using the tungsten analogue, *cis*-$W(CO)_4$(piperidine)$_2$, analysis of the medium by ^1H NMR reveals that only one piperidino ligand has been replaced by the phosphino TTF **3** affording the complex **5**, *cis*-$W(CO)_4$(piperidine)(P-TTF **3**) (Scheme 3). This was confirmed by mass spectrometry. Even when adding an excess of TTF **3** in the medium the result remains unchanged. Actually it was already reported that substitution of the second piperidino ligand needed more rigorous conditions than in the corresponding molybdenum species.[12] After chromatography of the crude product on silica gel column an orange crystalline air stable solid was obtained. The crystal structure of this complex reveals that the phosphorus and sulfur atoms (P,S-TTF) of the same ligand **3** are, this time, coordinated to the metal affording the complex **6**, *cis*-$W(CO)_4$(P,S-TTF **3**). Interestingly, the silica gel is acid enough for displacing the remaining piperidino labile ligand and replacing it by the thio ether function of the already coordinated, via the phosphorus atom, TTF **3** inducing the formation of a six-membered metallocyclic ring. The ORTEP of **6** is given in Figure 2. Within this complex **6** the W−P and S−W distances (W−P, 2.4959(12) Å; S−W, 2.5500(15) Å) are in the usual range with an interligand angle of S−W−P 84.79(4)°. The ^{31}P NMR spectra reveal a singlet at (δ 2.4 ppm) at lower field than the signal observed for the phosphorus atom of TTF **3** itself (δ −16.4 ppm). It is worth noting that the synthesis of complexes **4** and **6** can be realized in a one-pot procedure directly from TTF **2**, by performing the borane decomplexation and the addition of *cis*-$M(CO)_4$(piperidine)$_2$ directly in the medium where the TTF **3** was formed affording **4** in low yield (20%) and **6** in good yield (81%).

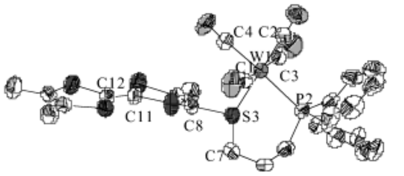
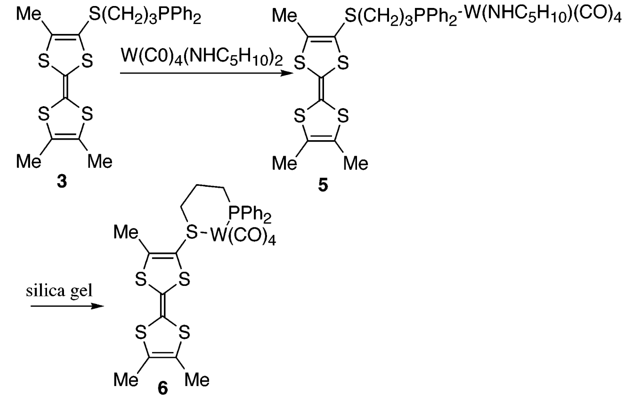


Figure 2. ORTEP view of complex **6** showing the atom labeling (50% probability ellipsoids). Hydrogen atoms are omitted for clarity. Selected bond lengths: W1−C2 1.940(6), W1−C4 1.995(5), W1−C1 2.002(6), W1−C3 2.011(6), W1−P2 2.4959(12), W1−S3 2.5500(15), C11−C12 1.343(7), S3−C8 1.764(4), S3−C7 1.823(5).

Scheme 3



Even if the mode of coordination is different, the solid state packing of these two complexes (i.e., **4** and **6**) reveals alternate layers of organic and inorganic entities with a distinct organization of the neutral TTF moieties. Within the molybdenum complex **4** the two TTFs of the complex are perpendicular to each other, and each TTF of two neighboring complexes is orthogonal with the shortest S···S contact being equal to 3.6 Å (Figure 3). Contrariwise with the tungsten complex the organic parts form segregated stacks with a crisscross overlap of one dithiole ring of the TTFs, while the inorganic part forms also segregated stacks, the shortest S···S contact between two TTFs being equal to 3.7 Å (Figure 4).

The effect of ligand environment, especially of the TTF core, on the redox properties of the bound metal ion was studied by cyclic voltammetry. For that purpose we prepared the metal carbonyl complexes $Mo(CO)_4(PPh_3)_2$ and $W(CO)_4(PPh_3)_2$. Furthermore, to analyze more precisely the influence

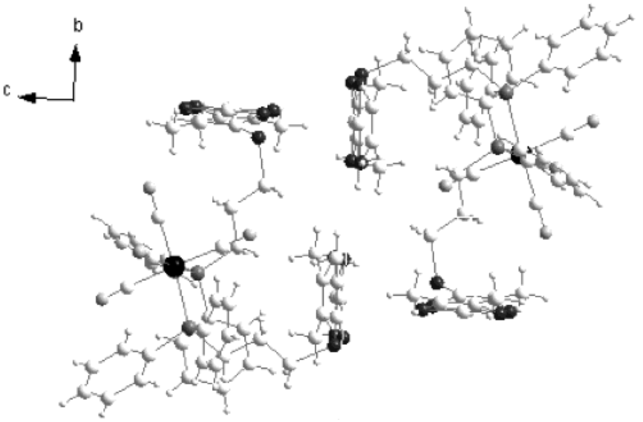


Figure 3. Crystal structure of complex **4** projection viewed along the *a* axis.

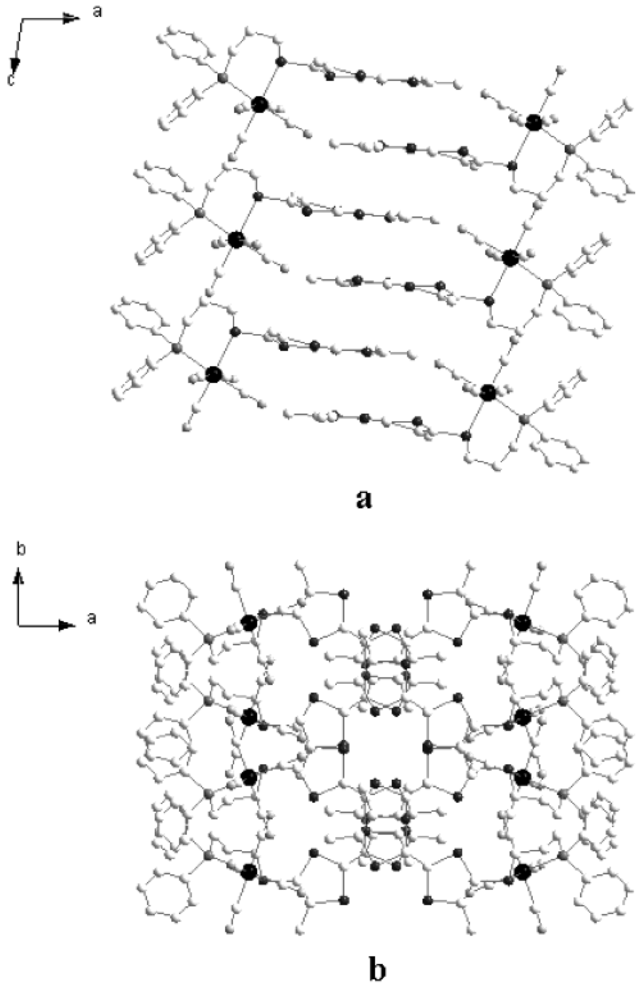


Figure 4. Crystal structure of complex **6**: (a) projection onto the *ac* plane showing the segregated stacks of organic and inorganic entities; (b) projection onto the *ab* plane showing the crisscross overlap of the dithiole moieties.

Scheme 4

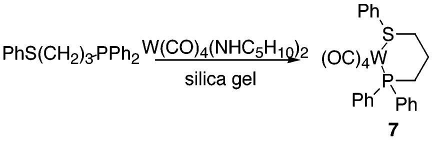


Table 1. Oxidation Peak Potentials in V vs SCE in CH_2Cl_2, Pt Working Electrode, NBu_4PF_6

	E_{pa}^1/E_{pc}^1	E_{pa}^2/E_{pc}^2	$\Delta E(E_{pa}^2 - E_{pa}^1)$, mV
$Mo(CO)_4(PPh_3)_2$	0.85/0.76		
$W(CO)_4(PPh_3)_2$	0.74[a]		
7	0. 84[a]		
TTF **2**	0.35/0.29	0.82/0.76	470
TTF **3**	0.35/0.29	0.79/0.73	440
$Mo(CO)_4(PTTF)_2$ **4**	0.36/0.30	0.87/0.76	510
$W(CO)_4$(P,S TTF) **6**	0.38/0.31	0.88/0.73	500

[a] Irreversible process.

of the TTF core in complex **6** we also prepared complex **7** from an analogue P,S bidentate ligand, the diphenyl[3-(phenylthio)propyl]phospine ($Ph_2P(CH_2)_3SPh$). Following the experimental procedure we used for synthesizing complex **6**, we reproduced the original P,S-metallocycle ring formation with $W(CO)_4(piperidine)_2$ and obtained **7** (Scheme 4). Oxidation peak potentials of the complexes **4** and **6** are collected in Table 1 together with the data of TTF **2** and **3** as well as $Mo(CO)_4(PPh_3)_2$, $W(CO)_4(PPh_3)_2$, and **7** for comparison. Complexes $Mo(CO)_4(PPh_3)_2$, $W(CO)_4(PPh_3)_2$, and **7** exhibit one oxidation wave which is not fully reversible in the case of the molybdenum complex and irreversible for the tungsten complexes. The lack of reversibility of this oxidation step is essentially due to the loss of carbonyl ligands occurring during the process.

Concerning the complex *cis*-$Mo(CO)_4(P\text{-}TTF)_2$ **4** two oxidation waves are observed. The first reversible oxidation step corresponds to the oxidation of the two TTFs in its radical cations while the second oxidation process is due to the concomitant oxidation of TTF radical cations into the dications and the oxidation of the molybdenum center. However, this process is not fully reversible due to the loss of carbonyl ligands. The reduction wave observed at $E_{pc}^2 = 0.76$ V is essentially due to the reduction of the TTF dications into its radical cations. According to the value of the second oxidation peak potential ($E_{pa}^2 = 0.87$ V) and to the oxidation of $Mo(CO)_4(PPh_3)_2$ ($E_{pa} = 0.85$ V), no significant influence of the TTF core on the molybdenum center can be detected. Similarly the redox behavior of the TTF core, within this complex, is not influenced by the presence of the molybdenum center.

The analysis of the redox behavior of $W(CO)_4$(P,S-TTF) **6** indicates also two oxidation processes involving first the reversible oxidation of the TTF and then the second oxidation of the TTF together with the metal center. The first oxidation step is a monoelectronic transfer, and an anodic shift of 30 mV is observed, compared with TTF **2**, indicating that weak interactions might occur between the TTF redox center and the metal one. Considering the values of the oxidation potential of **7** ($E_{pa} = 0.84$ V) and the second oxidation peak potential of **6** ($E_{pa}^2 = 0.88$ V), an anodic shift of 40 mV is observed for oxidation of the metal center. This confirms that weak interactions occur between the TTF redox center and the metal one either through space or through bond interactions. This result differs from what was observed for **4** where the TTF was coordinated through the phosphorus atom and a spacer involving four atoms (between the PPh_2 and the TTF moieties), while in **6** the coordination through the sulfur atom brings closer the TTF to the metal center.

In summary we have prepared a new redox-active ligand containing two binding sites through a phosphorus and sulfur atoms. Depending on the metal used for the formation of metal carbonyl complexes with this novel ligand, it acts either as a monodentate (P) ligand or as a bidentate (P,S) ligand. A weak influence of the TTF redox-active core on the redox behavior of the metal center can be observed in the case of the P,S coordination which brings nearer the TTF to the metal. It will be of interest to study the chemical or electrochemical oxidation of these complexes and to analyze the influence of the organometallic fragments toward the organization of the TTF radical cation moieties in the solid state.

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Supporting Information Available: X-ray crystallographic files in CIF format for complexes **4** and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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