Unprecedented metal template effect on the coupling of dithiafulvene moieties

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Coordination of two dithiafulvenyldiphenylphosphines on a Mo(CO)$_4$ fragment allows a carbon–carbon bond formation upon oxidation, leading to a novel type of metallacycle substituted by a redox active vinylogous tetrathiafulvalene.

New strategies have emerged recently for creating interactions between redox active cores such as tetrathiafulvalenes (TTF) and inorganic moieties. In particular, the chemistry of hybrid building blocks where the donor molecule is linked to the metal *via* a coordination function has developed rapidly.[1–5] Along these lines, the phosphine ligand offers numerous possibilities for coordinating metals in their oxidized or reduced forms.[2–4] In continuation of our studies on dithiafulvene derivatives, and their ability to form vinylogous tetrathiafulvalenes by oxidative coupling,[6,7] we have investigated the synthesis of a new dithiafulvene functionalized by a diphenylphosphino moiety. Herein, we report the synthesis and the redox properties of this novel redox active vinylphosphine as well as its ability to coordinate the molybdenum Mo(CO)$_4$ fragment. The structural and electrochemical properties of the complex are presented together with the directing effect of the metal on the coupling reaction, upon oxidation, of the two coordinated vinylphosphines leading to a bidentate diphosphine complex with a redox active vinylogous tetrathiafulvalene backbone.

The target molecule was prepared according to the chemical pathway described in Scheme 1. Compared to methyldiphenylphosphine, it is indeed easy to generate a carbanion of methyldiphenylphosphine borane **1** which is known to react with various electrophiles.[8] Therefore, in order to prepare the vinylphosphine **4**, we treated **1** with LDA and added the 4,5-dimethyl-2-piperidin-1-yl-1,3-dithiol-2-ylium hexafluorophosphate **2** in the medium. The piperidino leaving group can simply be removed by chromatography of the reaction mixture on silica gel. Treatment of this novel phosphine borane complex **3** with DABCO[9] allows the decomplexation of the phosphine borane and affords the dithiafulvene **4** as an air stable compound easily recrystallized in MeOH.

In order to investigate the coordination chemistry of this new phosphine ligand **4** we used *cis*-Mo(CO)$_4$(piperidine)$_2$.[10] Indeed, in mild conditions both piperidino ligands can be replaced by other ligands such as phosphines in the *cis* position. Warming **4** with half
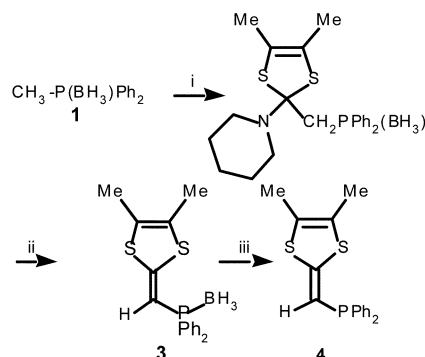
an equivalent of *cis*-Mo(CO)$_4$(piperidine)$_2$ in CH$_2$Cl$_2$ gives the complex **5** as a yellow crystalline solid. The same complex **5** can also be prepared in a one-pot procedure directly from dithiafulvene **3** by adding directly in the medium where **4** was formed the molybdenum carbonyl complex. Using this strategy, the complex **5**† was obtained in excellent yield (Scheme 2).

Two concomitant polymorphs of **5** were isolated from crystallization in MeOH (**5a** and **5b**, Fig. 1).† X-ray crystal structure analysis demonstrates that in both cases the two dithiafulvenes **4** are coordinated to the metal center *via* the phosphorus atom and that the molybdenum center is surrounded by two *cis*-coordinated ligands **4**. The two crystalline forms differ only by the relative orientation of the dithiafulvene cores.

The redox behavior of **3**, **4** and **5** was investigated by cyclic voltammetry in dichloromethane. For **3** and **4**, only one irreversible oxidation wave is observed, assigned to the oxidation of the dithiafulvene core into the cation radical ($E_{pa} = 1.07$ V for **3** and $E_{pa} = 0.73$ V *vs.* SCE for **4**). While for **5** the oxidation of the dithiafulvene core occurs at $E_{pa}^1 = 0.60$ V *vs.* SCE followed by a second irreversible oxidation wave at higher potential ($E_{pa}^2 = 1.35$ V *vs.* SCE) corresponding to the oxidation of the metallic center. The 340 mV potential anodic shift for **3** when compared to **4** indicates the electron withdrawing effect of the borane complexation. Contrariwise, the oxidation peak potential for **5** (*e.g.* 0.60 V) is at a lower potential than the ligand itself (*e.g.* 0.73 V), indicating an electron donating effect of the molybdenum redox center on the dithiafulvene. This is a surprising feature as usually the complexation of the Mo(CO)$_4$ fragment to a redox active phosphine, such as
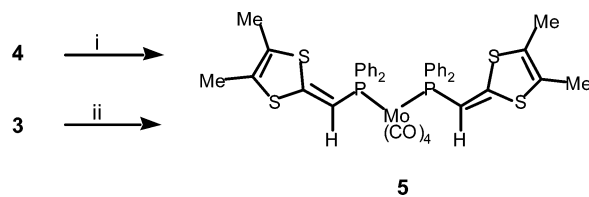
Scheme 2 *Reagents and conditions*: i) *cis*-Mo(CO)$_4$(piperidine)$_2$ (0.5 equiv.), CH$_2$Cl$_2$; ii) DABCO, toluene, 50 °C, 4 h, *cis*-Mo(CO)$_4$(piperidine)$_2$ (0.5 equiv.).
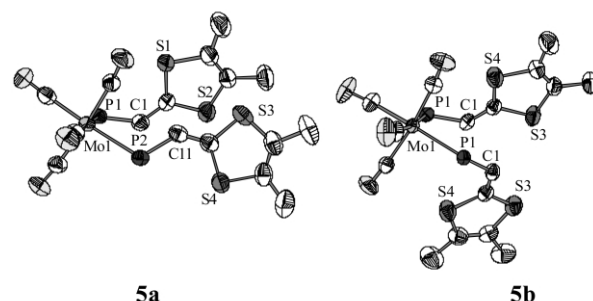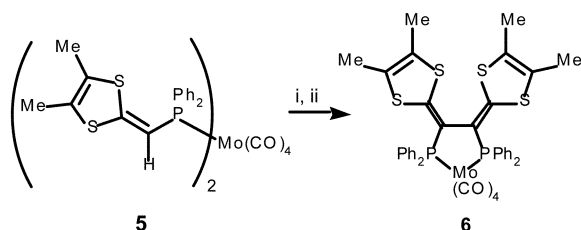
Fig. 1 Molecular structures of **5a** and **5b** (thermal ellipsoids set at 50% probability, H atoms and phenyl rings omitted for clarity). Selected bond lengths [Å] and angles [°] for **5a**: Mo1–P1 2.5543 (12), Mo1–P2 2.5456 (11), P1–C1 1.795 (4), C1–C2 1.343 (5), P2–C11 1.798 (4), C11–C12 1.338 (6), P1–Mo–P2 91.65 (4), for **5b**: Mo–P1 2.5756 (7), P1–C1 1.809 (3), C1–C2 1.328 (4), P1–Mo–P1 99.08 (3).

Scheme 1 *Reagents and conditions*: i) LDA, THF, −80 °C, **2**; ii) chromatography on silica gel column; iii) DABCO, 4 h, toluene, 50 °C.

TTF[2b] or metallocene,[11] induces a positive shift of about 200 mV.

On the basis of our preceding studies concerning the oxidative coupling of dithiafulvene derivatives which proceeds through a radical cation–radical cation mechanism,[6,7] we examined the electrochemical oxidation of **3**, **4** and **5** through macroscale electrolyses. No product resulting from a carbon–carbon bond formation upon electrochemical oxidation was observed. Next, we tried the chemical oxidation of **3–5** with an oxidizing agent, tris(4-bromophenyl)aminium hexachloroantimonate, which has proved recently to be an efficient reactant for the synthesis of vinylogous TTF starting from dithiafulvenes.[12] The derivatives **3** and **4** do not undergo intermolecular coupling upon oxidation, but instead we mainly isolated the corresponding phosphine oxide. Treatment of **5** with two equivalents of $(BrC_6H_4)_3NSbCl_6$ followed by a reduction with $Na_2S_2O_4$ leads, after chromatography on a silica gel column, to the metallacycle **6** resulting from an intramolecular carbon–carbon bond formation upon oxidation (Scheme 3).

The X-ray molecular structure of **6** is shown in Fig. 2.† The five-membered ring is not planar and adopts a half chair conformation due to the steric interactions generated by the two dithiole rings. The shortest S…S contact between the two dithiole rings is 3.12 Å and the acute dihedral angle between the two dithiole rings (C2–C1–C11–C12) amounts to 47.8(5)°. The redox behavior of **6** was investigated by cyclic voltammetry. One reversible bielectronic wave at $E_{pa} = 0.48$ V *vs.* SCE corresponding to the reversible oxidation of the vinylogous TTF core into the dication is observed at a lower potential than the dithiafulvene core in **5**. An irreversible oxidation wave attributable to the oxidation of the metallic center occurs at $E_{pa} = 1.25$ V *vs.* SCE.

It is worth noting that in the absence of a metal template no reaction was observed upon oxidation of the dithiafulvenyl ligand **4** or **3**, either chemically or electrochemically. The coordination of the dithiafulvenyl phosphine **4** brings closer the two radical cation moieties, thanks to the *cis* position of the two ligands on the

molybdenum center: in both isomers **5a** and **5b**, the distances between the carbon atoms involved in the formation of the metallacycle do not exceed 3.3 Å. Therefore, upon oxidation, an intramolecular coupling occurs leading to an unprecedented bidentate diphosphine complex with a vinylogous tetrathiafulvalene backbone.

In conclusion, we have presented here a unique example of carbon–carbon bond formation between two original vinylphosphine ligands in the coordination sphere of the $Mo(CO)_4$ fragment. Current work is devoted to studying the chelating ability of this redox active phosphine ligand towards low and, even more interesting, high oxidation state transition metal derivatives and the formation of new metallacycles upon oxidation.

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Scheme 3 *Reagents and conditions*: i) 2 equiv. of $(BrC_6H_4)_3NSbCl_6$, CH$_2$Cl$_2$, reflux, 1 h; ii) Na$_2$S$_2$O$_4$, CH$_2$Cl$_2$, reflux, 1 h.
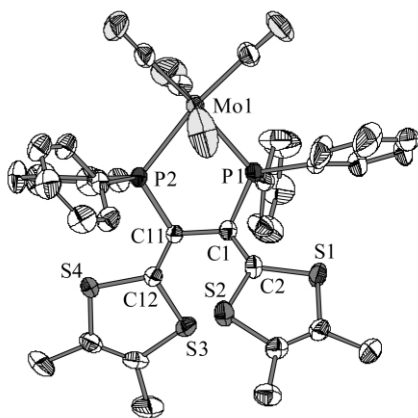

Fig. 2 Molecular structure of **6** (thermal ellipsoids set at 50% probability, H atoms omitted for clarity). Selected bond lengths [Å] and angles [°]: Mo1–P1 2.5084 (10), Mo1–P2 2.4865 (9), P1–C1 1.829 (4), P2–C11 1.839 (3), C1–C2 1.371 (5), C1–C11 1.478 (4), C11–C12 1.375 (5), P1–Mo1–P2 79.12 (3), Mo1–P1–C1 107.71 (11), P1–C1–C11 113.0 (2), Mo1–P2–C11 109.97 (11), P2–C11–C1 116.9 (2).