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# Photochemical Unmasking of 1,3-Dithiol-2-ones: An Alternative Route to Heteroleptic Dithiolene Complexes from Low-Valent Molybdenum and Tungsten Precursors

Benedict J. Elvers,<sup>[a]</sup> Carola Schulzke,<sup>[a]</sup> and Christian Fischer\*<sup>[a]</sup>

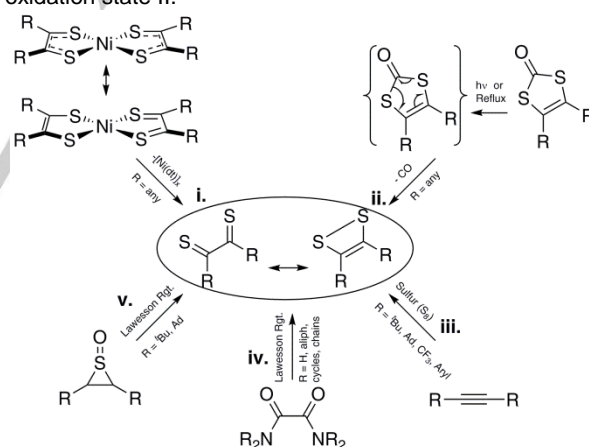
**Abstract:** Monodithiolene complexes [Mo(CO)<sub>2</sub>(dt)(dppe)] and [W(CO)<sub>2</sub>(dt)(dppe)] (dt = cyclohex-1-ene-1,2-dithiol; 5,6-dihydro-2H-pyran-3,4-dithiol and dppe = 1,2-Bis(diphenylphosphino)ethane) were synthesized by a photochemical procedure. The typical basic deprotection of the dithiolene ligand precursor was replaced by a light-induced opening of the 1,2-dithiole-2-one moiety. Advantages of this targeted approach comprise higher yields, cleaner transformations and the possibility to continuously and precisely monitor the reaction progress. The light induced pericyclic reaction of the protection group releases carbon monoxide under formation of an 1,2-dithione which is capable of oxidizing the electron rich metal precursor due to its *non-innocence* character. This procedure works well with molybdenum(0) and tungsten(0) precursors and particularly well with dithiolene ligands bearing aliphatic backbones, which are typically and notoriously difficult to handle when applying strictly chemical procedures.

## Introduction

Molybdenum and tungsten *bis*-dithiolene complexes of the type [M(CO)<sub>2</sub>(dt)<sub>2</sub>] (M = Mo, W; dt = ene-dithiolate) have been explored intensely as precursor compounds for models of several tungsten and molybdenum dependent oxidoreductases.<sup>[1]</sup> Many synthetic active site mimics have become conveniently available via non-redox substitution of the carbonyl ligands by chalcogenides (O<sup>2-</sup>, S<sup>2-</sup>, Se<sup>2-</sup>) or chalcogenates (R-O<sup>-</sup>, R-S<sup>-</sup>, R-Se<sup>-</sup>).<sup>[2]</sup> In nature molybdenum and tungsten active sites catalyse redox reactions accompanied by the transfer of an oxygen atom (i.e. formally O<sup>0</sup>) to or from substrate, which are also interesting from a synthetic point of view. The respective bio-inspired compounds can consequently also be utilized as non-biological catalysts. The redox activity of those model complexes has, in fact, already been exploited for industrially relevant reactions such as hydrogen production<sup>[3]</sup> or

reduction of CO<sub>2</sub> to formate.<sup>[4]</sup>

The synthesis of heteroleptic *mono*-dithiolene carbonyl complexes, in contrast, is a much more challenging task in coordination chemistry. This is particularly true for complexes with dithiolene ligands bearing an *aliphatic* and thus electron donating backbone and respective reports in the literature are scarce. Reactions of appropriate metal precursors [Mo(CO)<sub>3</sub>(PR<sub>3</sub>)<sub>2</sub>I<sub>2</sub>],<sup>[5]</sup> [Mo(CO)<sub>4</sub>X<sub>2</sub>] (X = Cl, Br)<sup>[6]</sup> with the alkali salts of various aromatic dithiolene ligands or those with electron pulling substituents (e.g. -CN), on the other hand, are known to yield *mono*-dithiolene complexes. Some aromatic 1,2-dithiols were even shown to react with an electron rich molybdenum precursor (e.g. [Mo(N<sub>2</sub>)<sub>2</sub>(dppe)<sub>2</sub>])<sup>[5a]</sup> by the release of one equivalent of H<sub>2</sub> resulting in a dithiolene complex with the metal in oxidation state II.



Scheme 1. Literature known pathways towards 1,2-dithiones and their tautomers: i. Nickel transfer metalation<sup>[7]</sup> ii. Chelotropic reaction of 1,3-dithiol-2-ones initiated by UV-light<sup>[8]</sup> or heat<sup>[9]</sup> iii. Sulfuration of acetylenic compounds<sup>[10]</sup> iv. Sulfuration of dioxamides<sup>[11]</sup> v. Synthesis from thiirenes-1-oxides and Lawesson's Reagent.<sup>[12]</sup>

For the selective synthesis of *mono*-dithiolene tungsten complexes with aliphatic dithiolene ligands, however, only one report is available in the literature describing the species [W(CO)<sub>4-x</sub>(PMe<sub>3</sub>)<sub>x</sub>(S<sub>2</sub>C<sub>2</sub>Me<sub>2</sub>)] (with x = 0,1,2) prepared through the nickel complex [Ni(S<sub>2</sub>C<sub>2</sub>Me<sub>2</sub>)<sub>2</sub>] as ligand donor.<sup>[13]</sup> From the nickel compound a dithione is abstracted after a net redox intramolecular disproportionation of both ligands from two radical monoanions (S<sup>-</sup>S<sup>-</sup>C<sub>2</sub>Me<sub>2</sub>) to one ene-dithiolate and one dithione/dithiete, which then coordinates to the metal precursor

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Supporting information for this article is given via a link at the end of the document.

(Fehler! Verweisquelle konnte nicht gefunden werden., i.).<sup>[14]</sup>

A general protocol for employing nickel complexes as dithione source was first established by Schrauzer<sup>[7a]</sup> (though he did not classify it as such) and later optimized by the group of Richard H. Holm (Fig 3.; i.).<sup>[7b, 7c]</sup> This strategy has become invaluable regarding the utilization and versatility of available dithiolene ligand systems. Notable disadvantages of this procedure, though, are firstly the loss of at least 50% of the used dithiolene precursor as one dithiolene necessarily remains attached to nickel (probably precipitating as a polymeric structure  $[\text{Ni}(\text{dt})_x]$ ; dt = ene-1,2-dithiolate).<sup>[7a]</sup> And, secondly, the trans-metalation reaction predominantly yields, aside the wanted *mono*-dithiolene complex  $[\text{W}(\text{CO})_4(\text{dt})]$  (in lowest yields) and the similarly useful *bis*-dithiolene complex  $[\text{M}(\text{CO})_2(\text{dt})_2]$ , the very stable, for most purposes useless, tris-dithiolene complex  $[\text{M}(\text{dt})_3]$  (M = Mo, W). In these procedures, the species which adds oxidatively to the low-valent metal precursors is actually a dithione/dithiete released from the nickel complex. Thus, an alternative and certainly feasible approach towards metal-dithiolene complexes would be the direct use of 1,2-dithiones or their valence tautomers<sup>[15]</sup>, the 1,2-dithietes. This strategy was applied successfully to Pd, Ni, Co, Ru and Fe carbonyl precursors yielding bis- and trisdithiolene complexes.<sup>[15-16]</sup> With respect to the metals of our interest (Mo, W), in one case the reaction between the easily accessible bis-(trifluoromethyl)-dithiete with hexacarbonyl molybdenum was described to yield 55% of  $[\text{Mo}(\text{S}_2\text{C}_4\text{F}_6)_3]$ .<sup>[17]</sup>

1,2-dithietes are commonly prepared by the reaction of elemental sulfur with the appropriate alkyne (Fig. 3; iii.) while not any alkyne leads to a wanted dithiete or dithione, though.<sup>[10, 16b, 18]</sup> The equilibrium between both tautomers is highly dependent on the backbone. Thus, electron-donating substituents usually stabilize dithiones ( $\text{S}_2\text{C}_2\text{R}_2$ ; R = (*p*-dimethylamino)phenyl, 1-adamantyl)<sup>[8, 19]</sup>, while electron-withdrawing substituents favor dithietes which was established for the cases  $\text{S}_2\text{C}_2(\text{CF}_3)_2$ ,  $\text{S}_2\text{C}_2(\text{CO}_2\text{Me})_2$ , and  $\text{S}_2\text{C}_2(\text{CN})_2$ .<sup>[9, 20]</sup> Both, dithiones and dithietes are, however, undoubtedly unstable unless stabilized either electronically or sterically as they constitute reactive transient intermediates.<sup>[12]</sup> Comparably stable 1,2-dithiones are available from dioxamides upon thionation with Lawesson's Reagent (Fig. 3; iv.).<sup>[11]</sup> These specific species were first tested for the oxidative addition to molybdenum by Dieck and Form followed by only two related reports more than two decades later.<sup>[21]</sup>

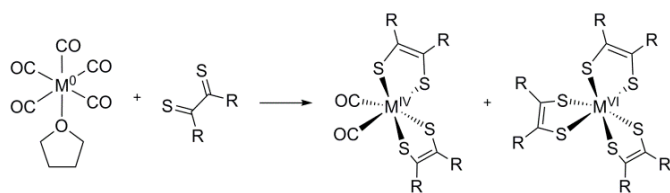
Electron donating dithiolenes which are not sterically hindered as for instance cyclic ones (e.g. cyclohex-1-ene-1,2-dithiol (cydt)<sup>[22]</sup> or 5,6-dihydro-2H-pyran-3,4-dithiol (pydt)<sup>[23]</sup>) or the well known  $\text{S}_2\text{C}_2\text{Me}_2$  (mdt)<sup>[13]</sup> are neither isolable as dithiones/dithietes nor as their unprotected alkali salts. Instead, precursors for this type of dithiolene ligand are commonly prepared in their 1,3-dithiol-2-one form. In order to coordinate such dithiolenes to metal carbonyl precursors their corresponding dithiones can be prepared *in situ* via a photochemically driven chelotropic decarbonylation (Scheme 1; ii.).<sup>[8, 24]</sup>

To synthesize the targeted heteroleptic *mono*-dithiolene carbonyl complexes of molybdenum and tungsten in this study zero valent complexes were employed, which are already coordinated by a sterically protecting diphosphane-ligand ( $[\text{M}^0(\text{CO})_4(\text{dppe})]$ ; M = Mo, W; dppe = 1,2-Bis(diphenylphosphino)ethane). To these precursors highly reactive 1,2-dithions/dithietes (obtained *in situ* by UV-light induced chelotropic decarbonylation) were oxidatively added to form carbonyl complexes of the type  $[\text{M}^{\text{II}}(\text{CO})_2(\text{dt})(\text{dppe})]$  (M = Mo, W; dt = ene-1,2-dithiol). Except for the series of tungsten *mono*-dithiolene complexes  $[\text{W}^{\text{II}}(\text{CO})_{4-x}(\text{PMe}_3)_x(\text{S}_2\text{C}_2\text{Me}_2)]$  (x = 0, 1, 2)<sup>[13]</sup> mentioned above, no further complexes of this type (notably: not one example of a respective Mo complex) are reported in the literature and their chemistry is therefore not explored very well. We here present the selective synthesis and characterisation of four novel tungsten and molybdenum *mono*-dithiolene complexes bearing two different aliphatic ligand backbones.

## Results and Discussion

Chandrasekaran et al. demonstrated that  $[\text{W}(\text{CO})_4(\text{S}_2\text{C}_2\text{Me}_2)]$  ( $\text{S}_2\text{C}_2\text{Me}_2$  = *cis*-1,2-dimethyl-1,2-ethylenedithiolate<sup>2-</sup> = mdt) can be obtained from a reaction of  $[\text{W}(\text{CO})_3(\text{MeCN})_3]$  with  $[\text{Ni}(\text{S}_2\text{C}_2\text{Me}_2)]$  in  $\text{CH}_2\text{Cl}_2$ .<sup>[13]</sup> Subsequent reaction of the purified (via column chromatography) *mono*-dithiolene complex  $[\text{W}(\text{CO})_4(\text{S}_2\text{C}_2\text{Me}_2)]$  with monodentate phosphane derivatives gave the targeted phosphane complexes in appreciable yields. Chandrasekaran et al. also pointed out that the comparably weaker M-CO bonds in molybdenum complexes relative to W-CO are responsible for the corresponding Mo dithiolene complex having never been observed.<sup>[13]</sup>

Here, the photochemical *in situ* generation of 1,2-dithiones was first applied to the envisioned alternative synthesis of *mono*-dithiolene complexes without a sterically protecting co-ligand aiming to obtain similar complexes as Chandrasekaran et al. (i.e.  $[\text{M}(\text{CO})_4(\text{dt})]$ , M = Mo, W). Hexa-carbonyl complexes as metal precursors were first irradiated in THF to synthesize the pre-activated, hence much more reactive (*vide supra*) solvent complexes  $[\text{M}(\text{CO})_5(\text{THF})]$  (M = Mo, W) *in situ*.<sup>[25]</sup> After the addition of cydt in equimolar amounts the solution was irradiated again for several hours resulting in a color change to violet in both cases (Mo and W). Column chromatography with  $\text{CH}_2\text{Cl}_2/n$ -hexane (1:4) in air yielded up to 20% of  $[\text{M}(\text{CO})_2(\text{cydt})_2]$  (M = Mo: **{MoCydt2}** or M = W: **{WCydt2}**) besides considerable quantities of tris-dithiolene complex running separately on the column (Scheme 2). No *mono*-dithiolene complexes ( $[\text{M}(\text{CO})_4(\text{dt})]$ ) could be obtained, which concurrently confirmed their instability under UV light.<sup>[7a]</sup>



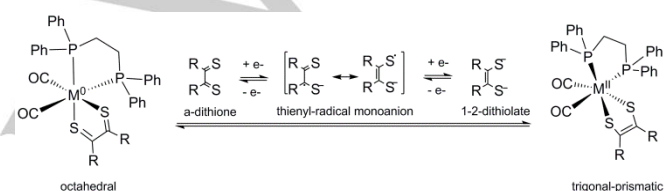
Scheme 2: Sequence for the reaction of an in situ generated 1,2-dithione with  $[M(CO)_5(THF)]$  leading only to bis- and tris-dithiolene complexes as reaction products.

Subsequently the syntheses were repeated targeting specifically the bis-dithiolene species (two equivalents of ligand precursor) but the yields could not be raised over the initial findings as of yet. Crystals of **{MoCyd<sub>2</sub>}** and **{WCyd<sub>2</sub>}** were obtained from layering a saturated benzene solution of the respective bis-dithiolene complex with methanol. With respect to yields and required radiation times this synthetic approach is much less reliable and satisfying than the one for the mono-dithiolene complexes described below. Under the given reaction conditions, most probably, the bis- and tris-dithiolene complexes are in equilibrium with each other and with available free carbon monoxide dissolved in variable quantities in solution and in the gas phase, while the tris-dithiolene complex represents the thermodynamically stable product. Thus, the photochemical approach towards the well-known *bis*-dithiolene complexes  $[M(CO)_2(cydt)_2]$  (M = Mo, W) is feasible, but leaves certainly room for being optimized further.

In order to avoid the binding of two or even three dithiolenes, the single dithiolene ligand was subsequently introduced to M(0) carbonyl complexes protected against bis- and tris-dithiolene complex formation by a bisphosphane ligand (dppe). The reasoning for utilizing bisphosphanes was: i) their capability of establishing a strong  $\pi$ -backbonding interaction with the coordinated d-electron rich metal, the strength of which depends on the substituents on the phosphorous atoms.<sup>[26]</sup> Thus their ligand strength in the spectrochemical series can be fine-tuned and may be sufficiently well beneath that of the strongest ligands, cyanides and carbonyls. ii) The chelate effect was presumed to help avoiding the unwanted substitution of dppe during the photochemical reaction, and therefore, to retain its protecting function against over-coordination by dithiolene ligands. iii) It was rationalized that this protecting ligand might be easily removable when modifying the complexes by oxidation, e.g. to reach biologically relevant enzyme models and oxidation states. A synthetic protocol for bisphosphane carbonyl complexes was already described in 1961 by Chatt and Watson.<sup>[27]</sup> The crystal structures of  $[Mo(CO)_4(dppe)]$ <sup>[28]</sup> and  $[W(CO)_4(dppe)]$ <sup>[29]</sup>, the exact compounds used as starting material for the novel photosynthetic approach reported here, were already published evidencing their proposed chemical structures.

*In situ* generated 1,2-dithiones/dithietes were found to be highly reactive, in particular as reactants in very fast homocoupling reactions, which constitutes a problem for their utilization as ligand precursors.<sup>[30]</sup> That is: the rate of the wanted reaction of the 1,2-dithione with the metal needs to be faster than the homocoupling reaction. Accordingly, the best yields were

eventually obtained when  $[M(CO)_4(dppe)]$  (M = Mo, W) was first irradiated in THF in the absence of any dithiolene precursor to form the novel mono-substituted, hence activated, THF complex  $[M(CO)_2(dppe)(THF)]$  (M = Mo: **{Mothf}** or M = W: **{Wthf}**) similar to the reactions carried out without dppe protection discussed above. The benefit of using these pre-activated complexes is that they bear one very easily replaceable rather weak ligand predestined to be exchanged (nephelauxetic effect).<sup>[25]</sup> This strategy was indeed found to accelerate the substitution reaction for at least one of the sulfur donor atoms of the *in situ* generated 1,2-dithione/dithiete. The concurrent or subsequent coordination of the second sulfur donor atom releasing one carbonyl from the metal precursor is most likely facilitated by the chelate effect, while the accompanying intramolecular oxidation of the zero valent metal centre to the oxidation state II is presumably inhibiting the back reaction (Scheme 3).



Scheme 3. Intramolecular oxidation of the central metal by the coordinated dithione yielding the ene-dithiolate complex, which is facilitated by the ligand's *non-innocence*.

After separating the mono-dithiolene complexes  $[M(CO)_2(dt)(dppe)]$  from unreacted  $[M(CO)_3(dppe)(THF)]$  and ligand homocoupling products by column chromatography with  $CH_2Cl_2/n$ -hexane (2:3) the products can readily be recrystallized from  $CH_2Cl_2/MeOH$  (62.5 % for  $[Mo(CO)_2(cydt)(dppe)]$  **{MoCyd<sub>2</sub>}**; 39.5 % for  $[W(CO)_2(cydt)(dppe)]$  **{WCyd<sub>2</sub>}**; 50.5 % for  $[Mo(CO)_2(pydt)(dppe)]$  **{MoPydt}** and 34.1 % for  $[W(CO)_2(pydt)(dppe)]$  **{WPydt}**). This novel synthetic approach, in particular when compared to literature known procedures (see above), is successful with regard to decidedly higher yields, simple, reproducible (of course) and can be easily up-scaled. The most important advantages, however, are i) the unprecedented availability of mono-dithiolene carbonyl molybdenum complexes for further modification even with aliphatic ligand systems, ii) a targeted approach towards mono-dithiolene complexes of molybdenum and tungsten avoiding the formation of large quantities of bis- and tris-dithiolenes and iii) the direct accessibility of dithiolene ligands from precursors with the most widely used protecting group (i.e. ene-dithiocarbonates).

## Structural Analysis

All compounds synthesized in course of this study were characterized by X-ray structural analysis. The structures of  $[Mo(CO)_4(dppe)]$  and  $[W(CO)_4(dppe)]$  were already published,

though, and the reported respective metrical parameters will only be discussed as far as necessary for a comparison with the new structures.<sup>[28-29]</sup>

### Ligand Precursors

The molecular structures of both protected dithiolenes used in this study (cydt, pydt) are shown in Figure 1.

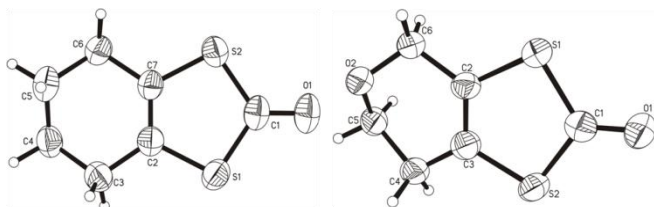


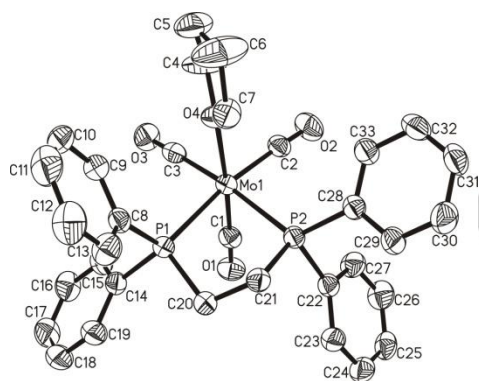
Figure 1. Molecular structure of 4,5-cyclohexano-1,3-dithiol-2-one (cydt) on the left and 5,6-dihydro-2H-pyran-3,4-dithiol-2-one (pydt) on the right. Thermal ellipsoid are shown at the 50 % probability level.

Both precursors crystallize in triclinic space group *P*1 with two independent (only one is shown in Figure 1) and in total four (*Z* = 4) molecules in the unit cell. They exhibit C-S bond lengths in the range of 1.741-1.759 Å and a very typical C=C bond length of 1.336(4) Å for cydt and 1.3397(2) Å for pydt, comparable to the analogous values of 1,2-dimethyl ene-dithiocarbonate (i.e. the protected mdt ligand) with 1.754 Å and 1.340 Å, respectively.<sup>[13]</sup>

### Metal Precursor Complexes

Compounds **{Mo<sub>thf</sub>}** (Fig. 2) and **{W<sub>thf</sub>}** (Fig. S1 in the SI) are the pre-activated [M(CO)<sub>3</sub>(dppe)(THF)] complexes in which one of the carbonyl ligands in [M(CO)<sub>4</sub>(dppe)] was replaced by a THF solvent molecule.

Figure 2. Molecular structure of preactivated [Mo(CO)<sub>3</sub>(dppe)(THF)] **{Mo<sub>thf</sub>}**



complex. Thermal ellipsoids are shown at the 50 % probability level. Hydrogen atoms are not shown for clarity reasons.

As expected both crystal structures are isomorphous with monoclinic space groups *P*2<sub>1</sub>/*c* and four molecules each in the respective unit cells. The geometry of both complexes is clearly octahedral with 'trans' angles of 172.22(12)° to 176.38(14)° for **{Mo<sub>thf</sub>}** and 171.9(4)° to 176.8(4)° for **{W<sub>thf</sub>}** and Bailar twist

angles between 54.9° and 60.4° for **{Mo<sub>thf</sub>}** and between 55.3° and 59.88° for **{W<sub>thf</sub>}** (see Table 1).

**Table 1.** Selected bond lengths (Å) and angles (°) for preactivated complexes **{Mo<sub>thf</sub>}** and **{W<sub>thf</sub>}** ([M(CO)<sub>3</sub>(dppe)(THF)].

	[Mo(CO) <sub>3</sub> (dppe)(THF)]	[W(CO) <sub>3</sub> (dppe)(THF)]
formula	C <sub>33</sub> H <sub>32</sub> O <sub>4</sub> P <sub>2</sub> Mo	C <sub>33</sub> H <sub>32</sub> O <sub>4</sub> P <sub>2</sub> W
M-P	2.5116(13)/ 2.5050(12)	2.493(3)/ 2.492(3)
M-CO <sub>basal</sub>	1.972(4)/ 1.970(4)	1.993(8)/ 2.004(9)
M-CO <sub>axial</sub>	1.911(4)	1.960(11)
C≡O <sub>basal</sub>	1.155(4)/ 1.166(5)	1.121(12)/ 1.128(13)
CO <sub>axial</sub>	1.178(5)	1.130(12)
M-O <sub>THF</sub>	2.310(3)	2.250(8)
C-M-C <sub>cis</sub>	89.4(6)/90.2(6)/87.5(6)	90.5(5)/90.2(5)/ 87.7(5)
P-M-P	79.77(4)	80.03(9)
Torsion angle (dppe)	56.08	55.48
Bailar twist angle (range)	54.95-60.43	55.34-59.88

The Bailar twist angle is a measure for the geometry of six-fold coordinated complexes with 60° for octahedral, 0° for trigonal prismatic and about 30° for distorted octahedral geometry.<sup>[31]</sup> This is based on the octahedral geometry being generated when the trigonal faces of a trigonal prismatic geometry are twisted against each other by 60°.

The THF molecule is coordinated in an axial position, i.e. one of the carbonyl ligands with a previously longer M-C bond length was replaced by it. This leads to a contraction of the M-C distance of the remaining axial carbonyl ligand by 0.131 Å to 1.911(4) Å **{Mo<sub>thf</sub>}** and by 0.065 Å to 1.960(11) Å **{W<sub>thf</sub>}** respectively, which is now shorter than the M-C<sub>basal</sub> distances. Notably, the M-O<sub>THF</sub> distance is shorter for tungsten **{W<sub>thf</sub>}** with 2.250(8) Å than for molybdenum **{Mo<sub>thf</sub>}** with 2.310(3) Å. These observations support the pre-activation presumption by introducing the excellent leaving group THF and suggest that the effect is slightly stronger in the case of molybdenum.

### Mono-dithiolene Complexes

The key molecules of this study, i.e. the novel mono-dithiolene bis-carbonyl dppe complexes were synthesized from the activated THF complexes. All complexes crystallize in orthorhombic space groups *P*2<sub>1</sub>2<sub>1</sub> and are essentially isomorphous with nearly identical cell parameters, no matter whether cydt or pydt as dithiolene ligand is present. Figure 3 shows the molecular structure of [Mo(CO)<sub>2</sub>(pydt)(dppe)], while

the remaining structures are depicted in the SI (Figures S3, S4, S5).

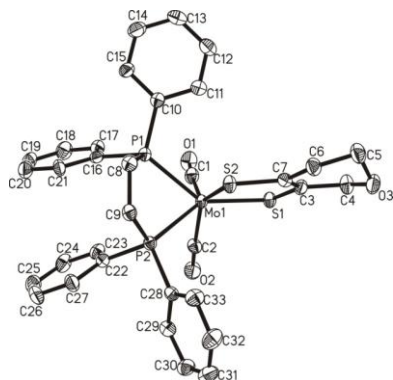


Figure 3. Molecular structure of trigonal-prismatic  $[\text{Mo}(\text{CO})_2(\text{pydt})(\text{dppe})]$  (**MoPydt**). Thermal ellipsoids are shown at the 50 % probability level. Hydrogen atoms are not shown for clarity reasons.

In course of the formation of the mono-dithiolene complexes the geometry changes from clearly octahedral to decidedly trigonal prismatic, as evidenced by the Bailar twist angle (see Table 2). This behavior was previously observed for  $[\text{W}^{\text{II}}(\text{CO})_4(\text{mdt})]$ .<sup>[13]</sup> A trigonal prismatic geometry is strongly associated with dithiolene complexes and similar structures with an  $\{\text{S}_2\text{P}_2(\text{CO})_2\}$  donor set of both, molybdenum and tungsten are predominantly in trigonal prismatic arrangements as demonstrated by several related crystal structural analyses.<sup>[5b, 13, 32]</sup>

**Table 2.** Selected bond lengths (Å) and angles (°) for mono-dithiolene complexes ( $[\text{M}(\text{CO})_2(\text{dt})(\text{dppe})]$ ).

	$[\text{Mo}(\text{CO})_2(\text{cydt})(\text{dppe})]$ <b>{MoCydt}</b>	$[\text{W}(\text{CO})_2(\text{cydt})(\text{dppe})]$ <b>{WCydt}</b>	$[\text{Mo}(\text{CO})_2(\text{pydt})(\text{dpp})]$ <b>{MoPydt}</b>	$[\text{W}(\text{CO})_2(\text{pydt})(\text{dppe})]$ <b>{WPydt}</b>
formula	$\text{C}_{33}\text{H}_{12}\text{O}_2\text{P}_2\text{S}_2\text{Mo}$	$\text{C}_{33}\text{H}_{12}\text{O}_2\text{P}_2\text{S}_2\text{W}$	$\text{C}_{33}\text{H}_{12}\text{O}_2\text{P}_2\text{S}_2\text{Mo}$	$\text{C}_{33}\text{H}_{12}\text{O}_2\text{P}_2\text{S}_2\text{W}$
M-S	2.351(3)/ 2.404(3)	2.347(3)/ 2.402(3)	2.358(6)/ 2.406(7)	2.353(3)/ 2.394(3)
C-S	1.738(12)/ 1.726(13)	1.759(14)/ 1.762(13)	1.745(6)/ 1.739(7)	1.755(13)/ 1.722(14)
C=C	1.354(17)	1.349(19)	1.341(9)	1.327(19)
M-P	2.474(3)/ 2.491(3)	2.476(3)/ 2.499(3)	2.479(7)/ 2.492(7)	2.481(3)/ 2.490(3)
M-CO	1.973(16)/ 1.965(14)	1.962(14)/ 1.996(14)	1.957(7)/ 1.983(6)	1.970(14)/ 1.981(13)
C=O	1.162(16)/ 1.145(15)	1.141(16)/ 1.172(16)	1.157(8)/ 1.143(8)	1.135(14)/ 1.149(16)
S-M-S <sup>a</sup>	81.54(10)	81.69(10)	82.01(6)	81.99(11)

C-M-C	76.7(5)	76.6(6)	77.0(3)	75.5(5)
P-M-P	72.28(10)	72.19(11)	71.932(5)	71.88(10)
Torsion angle (dppe)	7.3	7.3	6.0	5.3
Bailar twist angle	2.64	2.40	2.48	2.08

<sup>a</sup> S-M-S inner ligand angle

The averaged Bailar twist values of  $\sim 2.4^\circ$  for all mono-dithiolene complexes in this study are decidedly low, even when compared with related structurally characterized compounds where the average twist angles are very often well above  $10^\circ$ .<sup>[5b, 13, 32]</sup> The reason for this difference is most likely that in almost all related compounds mono-dentate P-donor ligands were used which tend to bind in what are rather *trans* than *cis* positions (i.e. they occupy corners on opposite trigonal faces). In case of the novel  $[\text{M}(\text{CO})_2(\text{dt})(\text{dppe})]$  the bidentate dppe can only bind in *cis* mode and the two phosphorous atoms are corners on the same trigonal face. The average M-P distances in  $[\text{M}^{\text{II}}(\text{CO})_2(\text{dt})(\text{dppe})]$  (M = Mo, W, dt = cydt, pydt) are longer compared to the mdt complex reported by the Donahue group for instance (2.471 Å) with 2.483(3) Å for **{MoCydt}** and 2.486(3) Å for **{MoPydt}** and with 2.488(3) Å and 2.486(3) Å for the respective tungsten complexes (see also Table 2).<sup>[13, 32b]</sup> Compared to the precursor complexes, the M-P bond is shortened which may account for the now trigonal-prismatic geometry and the fewer strongly and competitively  $\pi$ -backbonding carbonyl ligands.

The trigonal prismatic vs. octahedral geometry of mono-dithiolene complexes of Mo and W was reported to depend, *inter alia*, on the central metal's actual redox state, which again depends on the oxidation state of the dithiolene ligand.<sup>[32b]</sup> Here, the C=C bond length of the dithiolene moiety (1.354(17) Å for **{MoCydt}**, 1.341(9) Å for **{MoPydt}**, 1.349(19) Å for **{WCydt}** and 1.237(19) Å for **{WPydt}** and the respective C-S<sub>ave</sub> distances (1.732(12) Å, 1.742(6) Å, 1.761(13) Å, 1.739(13) Å) strongly imply a fully reduced ene-1,2-dithiolate form in all cases. As the dithiolene ligand precursors cydt and pydt were *in situ* converted to their 1,2-dithione forms and reacted with metal precursors in oxidation state 0, based on the observed geometry and in accordance with the metrical parameters of the dithiolene moieties in the structures, both metals are consequently best described as being in oxidation state II. When the central metal becomes reduced to oxidation state 0 as in  $[\text{W}^0(\text{CO})_4(\text{bdt})]^{2-}$ <sup>[33]</sup> the octahedral geometry is apparently recovered, when only one dithiolene ligand is present. This noteworthy redox-controlled interconversion between trigonal prismatic and octahedral geometries was also described and explained more detailed for  $[\text{W}(\text{CO})_4(\text{mdt})]$  by the Donahue group (see also Scheme 3).<sup>[32b]</sup>

The backbone of the dppe ligand in the mono-dithiolene complexes  $[\text{M}(\text{CO})_2(\text{dt})(\text{dppe})]$  shows a rather peculiar characteristic. The plane formed by the ethylene bridge and the

two phosphane atoms in octahedral complexes bearing dppe usually exhibits torsion angles of 55.4° to 56.1° as is the case for both THF complexes for instance. Notably, all synthesized mono-dithiolene complexes, in contrast, show a torsion angle of only 7.3° in the case of cydt-complexes and of 7.3° and 5.3° for Mo and W, respectively, for pydt complexes, which essentially constitutes an in-plane arrangement. Such very low torsion angles may at least be partly enforced by the change in geometry from octahedral in the precursors to trigonal prismatic in the products. This is, however, not the case in the related aromatic complex with the benzene-dithiolene ligand  $[W^{II}(CO)_2(bdt)(dppe)]$ , which has a typical torsion angle of 56.89°.<sup>[5b]</sup> Here the dppe ligand occupies corners of opposite trigonal faces in contrast to the novel complexes  $[M(CO)_2(dt)(dppe)]$  ( $dt = cydt, pydt$ ) where dppe occupies two corners of the same trigonal face. This implies that the nature of the dithiolene has also an influence on the electronic/binding situation of the entire complex.

### Bis-dithiolene Complexes

The bis-dithiolene complexes  $[M(CO)_2(cydt)_2]$  ( $M = Mo: \{MoCydt2\}$ ,  $M = W: \{WCydt2\}$ ) as obtained by the nickel based trans-metalation synthetic procedure are literature known but their respective crystal structures have not been published before.<sup>[23, 34]</sup> We obtained these materials by the photochemical approach in as of yet unsatisfying yields but in high purity allowing the crystallization of the two complexes and their X-ray structural investigation.

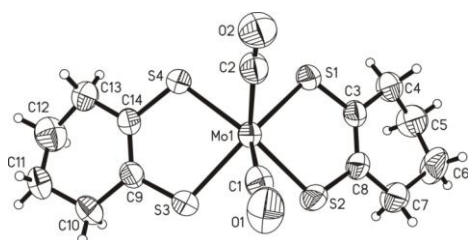


Figure 4. Molecular structure of  $[Mo(CO)_2(cydt)_2]$  **{MoCydt2}**. Thermal ellipsoids are shown at the 50 % probability level.

Again both compounds are isomorphous with triclinic space groups  $P1$  and two molecules in the unit cells each (Figures 4, S2 and Table 3).

**Table 3.** Selected bond lengths (Å) and angles (°) for bis-dithiolene complexes  $[M(CO)_2(dt)_2]$  **{MoCydt2}** and **{WCydt2}**.

formula	$C_{14}H_{16}O_2S_4Mo$	$C_{14}H_{16}O_2S_4W$
M-S	2.3576(15)/ 2.3592(16) 2.3705(18)/ 2.3630(15)	2.3607(12)/ 2.3622(14) 2.3686(15)/ 2.3601(13)
C-S	1.703(6)/ 1.715(6) 1.703(6)/ 1.707(5)	1.726(5)/ 1.720(5) 1.718(5)/ 1.721(5)

C=C	1.365(8)/ 1.366(8)	1.359(7)/ 1.360(7)
M-CO	2.019(7)/ 2.024(6)	2.026(5)/ 2.022(5)
C≡O	1.133(8)/ 1.111(7)	1.129(6)/ 1.134(6)
S-M-S <sup>a</sup>	80.99(6)/ 81.11(6)	80.99(5)/ 81.23(5)
C-M-C	83.9(3)	84.3(2)
Bailler twist angle (ave.)	0.57	0.64

<sup>a</sup> S-M-S inner ligand angle

Assigning the oxidation state of the central metals in these bis-dithiolene complexes **{MoCydt2}** and **{WCydt2}** is more ambiguous as in the case of the mono-dithiolene complexes. The  $[W(CO)_2(cydt)_2]$  complex has an average C-S<sub>ave</sub> distance of 1.721(5) Å, which is shorter by 0.02 Å and an average C=C distance of 1.359(8) Å which is longer by 0.023 Å than in the protected ligand cydt (see also Fig. 5). An even larger difference to cydt was found for the corresponding molybdenum complex **{MoCydt2}** with the C=C distance being 1.366(8) Å (hence, shorter by 0.030 Å) and the C-S<sub>ave</sub> being 1.705(6) Å (i.e. longer by 0.033 Å). This might be taken as indication that in the bis-dithiolene complexes the ligands have rather thienyl radical than ene-dithiolate character in comparison. A strictly thienyl radical oxidation state would render the metal centres divalent (i.e. OS = II and not IV) as has been previously suggested by the Donahue group.<sup>[13, 32b, 35]</sup> It is at the same time not surprising that the dithiolene ligand pushes somewhat more electron density towards a metal centre with a higher oxidation state (being d-electron deficient) and that all bonds of the *non-innocent* dithiolene ligand including the  $\pi$ -electrons are involved in this donation. The structurally determined C=C bond lengths are in fact all much closer to a double bond (ca. 1.34 Å) than to a single bond (around 1.54 Å) and still closer to a double bond than to the average of both (as in aromatics with  $\pi$ -bond delocalization).<sup>[36]</sup> In conclusion, it is reasonable to describe the bis-dithiolene complexes with metal ions in oxidation state IV and the mono-dithiolene complexes with a  $d^4$  electron count while all receive considerable electron density from the dithiolene ligands.

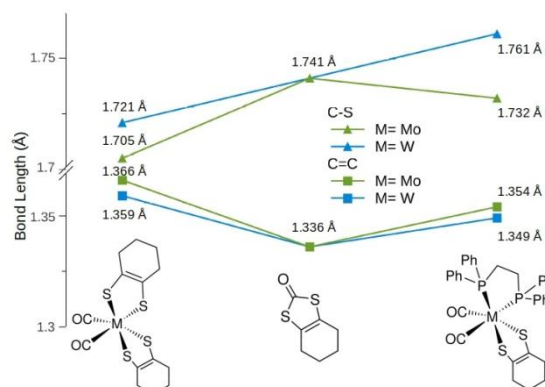


Figure 5. Ene-1,2-dithiolate or thienyl radical monoanion? C=C and C-S distances in three different environments as indicators for redox states of the cydt dithiolene ligand.

Bis-carbonyl bis-dithiolene complexes are conveniently used to synthesize oxo- or alkoxide-complexes via non-redox substitution of the remaining carbonyls.<sup>[1]</sup> Their respective suitability is supported by the very short observed C≡O distances (1.122(7) Å for {MoCyd2} and 1.132(6) Å for {WCyd2}). In free CO gas the C≡O bond length is 1.13 Å, i.e. not much different.<sup>[37]</sup> These values clearly indicate very weakly bonded CO molecules with a bond order near 3, which in complexes with a strong C-M bond would be significantly decreased. The corresponding cydt bearing mono-dithiolene complexes, in contrast, show longer C≡O bonds (range of 1.141 to 1.172 Å) and concomitantly shorter M-C bonds (range 2.019 to 2.026 Å for bis-dithiolenes; range 1.962 to 1.996 Å for mono-dithiolenes; see also Tables 2 and 3). It can therefore be expected that the carbonyl ligands in the M(II) mono-dithiolene complexes will be more difficult to replace in accordance with the d-electron counts and CO being a strong π-backbonding acceptor ligand.

### <sup>13</sup>C-NMR studies

Besides the critically important *non-innocence* of the dithiolene ligands also their σ- and π-donor properties are of interest. A comparably higher electron density at the metal in dithiolene complexes can be facilitated by electron pushing effects of dithiolenes with aliphatic backbones. In this study such electron pushing towards the coordinated metal centre was confirmed by the observed <sup>13</sup>C-NMR downfield shifts, in particular of the quaternary carbon atoms and to a lesser extent for the methylene carbon atoms (Table 4).

Table 4: Chemical shifts in the <sup>13</sup>C-NMR observed for the dithiolene moieties and the backbones of the protected and coordinated ligands.

	C=C	S-C-CH <sub>2</sub> -CH <sub>2</sub>	S-C-CH <sub>2</sub> -CH <sub>2</sub>	S-C-CH <sub>2</sub> -O
cydt	125.6	25.5	22.7	-
{MoCyd2}	153.5	36.5	25.1	-
{WCyd2}	150.7	36.1	25.2	-
{MoCyd2}	165.3	35.5	23.1	-
{WCyd2}	161.9	35.4	23.5	-
pydt	122.8/123.9	25.9	64.4	64.9
{MoPydt}	150.3	36.5	65.5	73.9
{Wpydt}	148.7	36.5	65.8	74.3

For the CO-protected cydt-ligand a chemical shift of 125.6 ppm for the C=C moiety was observed. The loss of electron density of those carbon atoms in complexes has a deshielding effect. Consequently, the signal shifted to 153.5 ppm and 150.7 ppm for mono-dithiolene complexes [M(CO)<sub>2</sub>(cydt)(dppe)] (M = Mo, W), respectively. In comparison to the CO protected cydt, <sup>13</sup>C resonances for the carbon atoms proximal to the dithiolene moiety are slightly shifted downfield from 25.5 ppm to 36.5 ppm and 36.1 ppm upon coordination to Mo and W, respectively. A downfield shift for the distal carbons is observed but even less pronounced: 22.7 ppm for the pure cydt shifted to a range of 23–26 ppm for the complexes. In a similar manner the C=C double bond in pydt complexes is shifted from ~123 ppm for the protected ligand to ~150 ppm for the mono-dithiolene complexes. The remaining methylene groups experience only small losses in electron density upon binding of the ligand to the metal centre. Both *aliphatic* dithiolene ligands are consequently confirmed not only by structural evaluation but also NMR-spectroscopically to exhibit strong donor abilities involving electron density even from the ligand's backbone.

Notably, there is a strong correlation between ligand to metal electron density transfer and the chemical shift in the carbon NMR. In contrast to X-ray diffraction analysis, <sup>13</sup>C NMR measurements are easily accessible and even more precise. Thus, <sup>13</sup>C NMR data of dithiolene ligands and their respective complexes may be evaluated systematically when discussing their non-innocent properties, in particular in the absence of crystallographic information. This observation was found to be actually rather valuable also with respect to future studies.



## Conclusions

In summary, the light induced chelotropic reaction of dithiolene ligand precursors of the very common dithiocarbonate type is introduced as an elegant method to coordinate dithiolene ligands to conveniently available metal precursors. The *in situ* prepared 1,2-dithiones/dithietes are very reactive and need to be trapped very quickly. The use of zero valent metal precursors of molybdenum and tungsten, already bearing a strong  $\pi$ -backbonded ligand like dppe and a THF-molecule as excellent leaving group, was found to be beneficial as these complexes show almost no side reaction and yield mono-dithiolene complexes in high quantity. This method, in particular for molybdenum facilitates the synthesis of mono-dithiolene carbonyl complexes as precursors for further CO substitution reactions and eventually the generation of models for humane/eukaryotic molybdenum enzymes. The previously reported chemistry in this context has so far been restricted to aromatic ligand systems or mnt for molybdenum and has also been developed only minimally further in case of tungsten. The presented method can be expected to open up this field allowing the use of more sophisticated and, in particular, aliphatic ligand systems in large varieties, which is currently under exploration. The use of  $[M(CO)_5(THF)]$  ( $M = Mo, W$ ) as precursor molecules, in contrast, leads to the well known bis-dithiolene complexes of the type  $[M(CO)_2(dt)_2]$ .

All complexes described here as well as their ligand precursors could be structurally characterized by X-ray diffraction. Based on the observed metrical parameters together with  $^{13}C$ -NMR data the relative electronic properties/structures could be evaluated. In all complexes the dithiolene ligands serve as rather effective donors of electron density toward the metal centre. This effect was observed to be larger in the formally tetravalent bis-dithiolene than in the divalent mono-dithiolene complexes.

## Experimental Section

### Synthesis of Compounds

The syntheses of all complexes were carried out in a dry argon atmosphere using dry degassed solvents. Acetonitrile and dichloromethane were freshly distilled from molecular sieves, THF was distilled from sodium/benzophenone and methanol was dried over magnesium turnings and freshly distilled prior to use.  $Mo(CO)_6$ ,  $W(CO)_6$  and 1,2-bis(diphenylphosphino)ethane (dppe) were purchased from Strem Chemicals, Inc. The metal halide lamps HPA1200 and HPM13 used for the photoreactions were purchased from Dr. Fischer Company and were used without any filters (for emission spectra of each lamp type see SI). Generated CO gas was monitored by a normal pressure device for the automatic registration of gas consumption or generation.<sup>[38]</sup>

### X-ray Structure Determination

Crystals of cydt, pydt,  $\{Mothf\}$ ,  $\{Wthf\}$ ,  $\{MoCyd2\}$ ,  $\{WCyd2\}$ ,  $\{MoCyd1\}$ ,  $\{WCyd1\}$ ,  $\{MoPydt\}$  and  $\{WPydt\}$  were mounted on a glass fiber in inert paraffin oil. Data were recorded at 170 K on a STOE-IPDS 2 T diffractometer with graphite-monochromated  $Mo-K\alpha$ -radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structures were solved by direct methods (SHELXS-2013 or SHELXT-2016) and refined by full-matrix least-squares techniques using the WingX GUI<sup>[39]</sup> All non-hydrogen-atoms were refined

with anisotropic displacement parameters. All hydrogen atoms were refined isotropically at calculated positions using a riding model with their  $U_{iso}$  values constrained to  $1.2 U_{eq}$  of their pivot atoms.

In  $\{Wthf\}$  SIMU constraints were used for the three CO ligands. In heavy metal carbonyl complexes the CO ligands tend to form unusual ellipsoids. This behaviour was countered by applying the constraint. In  $\{MoCyd2\}$  half a dichloromethane per complex formula is co-crystallized. The specific occupancy percentage was established using the SQUEEZE/PLATON routine for an electron count but the solvent was not removed from the refinement. All non-hydrogen atoms of this partially occupied solvent molecule were treated with DELU and SIMU constraints. In  $\{WCyd2\}$  again half a dichloromethane per complex formula is co-crystallized. Here it was so badly disordered, however, that it was omitted from the refinement using the SQUEEZE/PLATON<sup>[40]</sup> procedure, which yielded 84 electrons and a total void volume of  $333 \text{ \AA}^3$  per unit cell. In  $\{MoCyd2\}$  and  $\{WCyd2\}$  the outer carbon atoms of the cyclohexene rings are disordered over two positions each. This disorder was modelled and the respective atoms constrained (SIMU/DELU/SADI for  $\{MoCyd2\}$  and SIMU/DELU for  $\{WCyd2\}$ ). Selected crystal and refinement data are summarized in Tables S1 and S2 (SI).

CCDC 1823625-1823631, 1894461-1894463 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### Other Physical Methods

UV-vis spectra were obtained at ambient temperature with a Shimadzu UV-3600 spectrophotometer, while IR spectra were recorded in THF between NaCl or KBr windows (layer thickness 0.04 mm) under argon with an FT-IR spectrometer Shimadzu IRAffinity-1. Elemental analyses (C, H, N, and S) were carried out with an Elementar Vario MICRO elemental analyzer.  $^1H$ ,  $^{13}C$ ,  $^{31}P$  NMR spectra were recorded on a Bruker Avance II 300 spectrometer (300, 75 and 121.5 MHz, respectively). Chemical shifts ( $\delta$ ) are given in parts per million (ppm) using solvent signals as reference ( $CDCl_3$   $^1H$ :  $\delta = 7.24$  ppm;  $^{13}C$ :  $\delta = 77.0$  ppm;  $C_4D_8O$   $^1H$ :  $\delta = 1.72$  ppm;  $^{13}C$ :  $\delta = 25.2$  ppm) relative to external tetramethylsilane ( $\delta = 0$  ppm).

### Synthesis of 4,5-Cyclohexano-1,3-dithiol-2-one (cydt)

This ligand precursor was prepared by modification of known procedures.<sup>[22-23, 41]</sup> Bromination of cyclohexanone (9 g; 91.7 mmol, 1 eq.) was carried out in 40°C warm water with elemental bromine (5.2 ml; 99.9 mmol, 1.09 eq.) and a catalytic amount of HBr as a starter for the autocatalytic reaction. The intermediate product was isolated after typical workup with water and brine and used without further purification. The entire product was then reacted with potassium isopropyl xanthate (17.58 g; 0.1 mol, 1.1 eq.) in a 50:50 mixture of acetone and ethanol overnight yielding O-isopropyl-S-(2-cyclohexanonyl) dithiocarbonate in ~98 % yield. The following ring closing step to yield the final product worked best with sulfuric acid added to a solution of the xanthate in ether/dichloromethane overnight. The entire product mixture was then poured onto crushed ice (ca. 400 ml) and extracted with diethylether. Subsequent vacuum distillation in a Kugelrohr Apparatus gave colourless crystals of pure cydt suitable for X-ray analysis. Yield: 96.8 % (15.3 g, 89 mmol).

$^1H$  NMR (300 MHz,  $CDCl_3$ , 25°C):  $\delta = 1.88$  (m, 4H,  $2^*CH_2$ ), 2.44 (ddd,  $J_1 = 6.2$  Hz,  $J_2 = 3.8$  Hz,  $J_3 = 2.5$  Hz, 4H,  $2^*CH_2$ ) ppm.  $^{13}C$  NMR (75.5 MHz,  $CDCl_3$ , 25°C):  $\delta = 22.7$  ( $CH_2$ ), 25.5 ( $CH_2-C-S$ ), 125.6 ( $C_{quat.-S}$ ); 192.5 ( $C=O$ ) ppm. UV-vis:  $\epsilon$  in THF ( $M^{-1}cm^{-1}$ ) = 3218 (217 nm); 3191 (238 nm);

2538 (275 nm). IR (NaCl, 0.04 mm, in THF<sub>abs.</sub>, c = 0.2 M):  $\nu = 1334 \text{ cm}^{-1}$  (C=C),  $1603 \text{ cm}^{-1}$ ,  $1630 \text{ cm}^{-1}$ ,  $1673 \text{ cm}^{-1}$  and  $1740 \text{ cm}^{-1}$ .

#### Synthesis of 6,7-Dihydro-4H-1,3-dithiol[4,5-c]pyran-2-one (pydt)

The synthesis of pydt was performed by the same method as for cydt but tetrahydro-4H-pyran-4-one (12.0 g; 0.12 mol, 1 eq.) was used instead of cyclohexanone. Vacuum sublimation gave colourless crystals of pure pydt suitable for X-ray analysis. Yield: 69.3 % (14.51 g, 83.2 mmol).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25°C):  $\delta = 2.59$  (tt,  $J_1 = 5.4 \text{ Hz}$ ,  $J_2 = 2.2 \text{ Hz}$ , 2H,  $\text{CH}_2$ ), 4.04 (t,  $J_1 = 5.4 \text{ Hz}$ , 2H,  $\text{CH}_2$ ), 4.42 (t,  $J_1 = 2.2 \text{ Hz}$ , 2H,  $\text{CH}_2$ ) ppm.  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ , 25°C):  $\delta = 25.9$  ( $\text{CH}_2$ ), 64.4 (O- $\text{CH}_2$ ), 64.9 (O- $\text{CH}_2$ -C-S), 122.8 ( $\text{C}_{\text{quart.}}$ -S), 123.9 ( $\text{C}_{\text{quart.}}$ -S), 191.1 (C=O) ppm.

UV-vis:  $\epsilon$  in acetonitrile ( $\text{M}^{-1} \text{ cm}^{-1}$ ) = 3121 (217 nm), 3531 (240 nm), 5969 (275 nm). IR (KBr):  $\nu = 1330 \text{ cm}^{-1}$  (C=C),  $1633 \text{ cm}^{-1}$ ,  $2872 \text{ cm}^{-1}$  and  $2970 \text{ cm}^{-1}$ .

#### Synthesis of $[\text{Mo}(\text{CO})_4(\text{dppe})]$

$[\text{Mo}(\text{CO})_4(\text{dppe})]$  was prepared with small modifications to a procedure reported by Chatt and Watson.<sup>[27]</sup>  $[\text{Mo}(\text{CO})_6]$  (2.75 g, 10.4 mmol, 1 eq.) and dppe (4.16 g, 10.4 mmol, 1 eq.) were filled into a pressure reaction vessel and sealed *in vacuo*. After heating for 2 h at 150°C and 15 h at 170°C the white solid was dissolved and recrystallized in acetone yielding the product  $[\text{Mo}(\text{CO})_4(\text{dppe})]$  as clear platelets. Yield: 67.2 % (4.24 g, 7 mmol).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25°C):  $\delta = 2.53$  (m,  $J_1 = 1.78 \text{ Hz}$ , 4H,  $2^*\text{CH}_2$ ), 7.33 (m, 12H,  $\text{CH}_{\text{arom}}$ ), 7.57 (m, 8H,  $\text{CH}_{\text{arom}}$ ) ppm.  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ , 25°C):  $\delta = 28.1$  (m,  $\text{CH}_2$ ), 128.6 (m); 129.8 (s), 131.45 (m), 136.5 (m,  $J_1 = 34.5 \text{ Hz}$ ), 209.3 (br t,  $J_1 = 8.6 \text{ Hz}$ ,  $\text{C}_{\text{arom., quart.}}$ ); 217.2 (m, CO) ppm.  $^{31}\text{P}$  NMR (121.5 MHz,  $\text{CDCl}_3$ , 25°C):  $\delta = 55.95$  (s) ppm.  $^{95}\text{Mo}$  NMR (19.6 MHz,  $\text{CDCl}_3$ , 25°C):  $\delta = -1777$  (t,  $J = 133.7 \text{ Hz}$ ) ppm. UV-vis:  $\epsilon$  in THF ( $\text{M}^{-1} \text{ cm}^{-1}$ ) = 2648 (343 nm). IR (NaCl; 0.04 mm; in dry THF), c = 0.038 M):  $\nu = 1300 \text{ cm}^{-1}$  -  $1700 \text{ cm}^{-1}$ ,  $1886 \text{ cm}^{-1}$ ,  $1914 \text{ cm}^{-1}$ ,  $2021 \text{ cm}^{-1}$ . Calcd for  $\text{C}_{30}\text{H}_{24}\text{O}_4\text{P}_2\text{Mo}$ : C: 59.42; H: 3.99. Found: C: 59.66; H: 3.99.

#### Synthesis of $[\text{W}(\text{CO})_4(\text{dppe})]$

The same method was applied as for  $[\text{Mo}(\text{CO})_4(\text{dppe})]$ : dppe (2.46 g, 6.19 mmol, 1 eq.) and  $[\text{W}(\text{CO})_6]$  (2.18 g, 6.19 mmol, 1 eq.) gave a pale yellow solid which was dissolved and recrystallized in a mixture of acetone and methanol (1:1). Yield: 84.7 % (3.64 g, 5.24 mmol). The analytical data presented here are consistent with those reported.<sup>[29]</sup>

$^1\text{H}$  NMR (300 MHz,  $\text{CHCl}_3$ , 25°C):  $\delta = 2.60$  (m, 4H,  $2^*\text{CH}_2$ ), 7.36 (m, 12H,  $\text{CH}_{\text{arom}}$ ), 7.56 (m, 8H,  $\text{CH}_{\text{arom}}$ ) ppm.  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CHCl}_3$ , 25°C):  $\delta = 29.5$  ( $\text{CH}_2$ ), 30.1 ( $\text{CH}_2$ ), 128.7, 128.8, 130.0, 131.7, 135.9, 136.4, 135.9, 136.4, 201.3 ( $\text{C}_{\text{arom., quart.}}$ ), 207.9 (CO), 208.0 (CO), 208.3 (CO), 208.4 (CO) ppm.  $^{31}\text{P}$  NMR (121.5 MHz,  $\text{CHCl}_3$ , 25°C):  $\delta = 41.23$  (s, Sat.<sub>183W</sub>:  $J = 214.62 \text{ Hz}$ ) ppm. UV-vis:  $\epsilon$  ( $\text{M}^{-1} \text{ cm}^{-1}$ ) = 2160 (337 nm). IR (NaCl, 0.04 mm, in dry THF, c = 0.072 M):  $\nu = 1300 \text{ cm}^{-1}$ - $1700 \text{ cm}^{-1}$ ,  $1880 \text{ cm}^{-1}$ ,  $1904 \text{ cm}^{-1}$ ,  $2016 \text{ cm}^{-1}$ . Calcd for  $\text{C}_{30}\text{H}_{24}\text{O}_4\text{P}_2\text{W}$ : C: 51.90; H: 3.48. Found: C: 51.91; H: 3.30.

#### Synthesis of $[\text{Mo}(\text{CO})_3(\text{dppe})(\text{THF})]$ {Mothf}

A tempered reaction vessel at 20°C was charged with  $[\text{Mo}(\text{CO})_4(\text{dppe})]$  (338.1 mg, 0.56 mmol) and the atmosphere was replaced by argon. The solid was dissolved in 10 ml dry THF and irradiated over a period of 120 minutes while an argon stream was passed over the solvent. The yellow solution was transferred into a Schlenk vessel and the amount of solvent was reduced at low pressure. Diffusion of dry *n*-hexane into the solution

yielded yellow prismatic crystals. Remaining insignificant impurities of  $[\text{Mo}(\text{CO})_4(\text{dppe})]$  were detected only in the  $^{31}\text{P}$ -NMR.

$^1\text{H}$  NMR (300 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta = 1.77$  (m, 4H,  $2^*\text{CH}_2$ ), 2.68 (m,  $4\text{H}_{\text{dppe}}$ ,  $2^*\text{CH}_2$ ), 3.61 (m, 4H,  $2^*\text{CH}_2$ ), 7.21 bis 7.37 (m, 12H,  $\text{CH}_{\text{arom}}$ ), 7.62 bis 7.82 (m, 8H,  $\text{CH}_{\text{arom}}$ ) ppm.  $^{31}\text{P}$  NMR (121.5 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  (ppm) = 51.66 (s) ppm.  $^{135}\text{DEPT}$  NMR (75.5 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta = 26.1$  (neg.,  $\text{CH}_2$ ), 27.1 (neg.,  $\text{CH}_2$ ), 67.9 (neg.,  $\text{CH}_2$ ), 126.6 (pos., CH), 129.1 (pos., CH), 129.7 (pos., CH), 132.4 (pos., CH), 133.0 (pos., CH), 133.2 (pos., CH) ppm.

#### Synthesis of $[\text{W}(\text{CO})_3(\text{dppe})(\text{THF})]$ {Wthf}

The synthesis of the tungsten solvent complex was performed as described above for  $[\text{Mo}(\text{CO})_3(\text{dppe})(\text{THF})]$ , with  $[\text{W}(\text{CO})_4(\text{dppe})]$  (519.2 mg, 0.75 mmol) yielding yellow prismatic crystals.

$^1\text{H}$  NMR (300 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta = 1.77$  (m, 4H,  $2^*\text{CH}_2$ ), 2.72 (m,  $4\text{H}_{\text{dppe}}$ ,  $2^*\text{CH}_2$ ), 3.61 (m, 4H,  $2^*\text{CH}_2$ ), 7.21 bis 7.37 (m, 12H,  $\text{CH}_{\text{arom}}$ ), 7.64-7.82 (m, 8H,  $\text{CH}_{\text{arom}}$ ) ppm.  $^{31}\text{P}$  NMR (121.5 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta = 50.05$  (s, Satellite (Sat.))<sub>183W</sub>:  $J = 231.87 \text{ Hz}$ ) ppm. Calcd for  $\text{C}_{33}\text{H}_{32}\text{O}_4\text{P}_2\text{W}$ : C: 53.68; H: 4.37. Found: C: 53.91; H: 4.45.

#### Synthesis of $[\text{Mo}(\text{CO})_2(\text{cydt})_2]$ {MoCyd2t}

A tempered reaction vessel at 20°C was charged with  $[\text{Mo}(\text{CO})_6]$  (430 mg, 1.63 mmol, eq.) and the atmosphere was replaced with pure nitrogen. The solid was dissolved in dry THF and irradiated for 30 minutes. To the now yellow solution, cydt (227.2 mg, 1.32 mmol, 0.81 eq.) dissolved in dry THF was added. Irradiation proceeded for several hours yielding a brownish solution. The solvent was removed *in vacuo*. Column chromatography was performed using dichloromethane and *n*-hexane (1:4) as eluent yielding a violet band  $[\text{Mo}(\text{CO})_2(\text{cydt})_2]$  as the desired product. The solvent was removed *in vacuo*, the solid dissolved in a minimal amount of benzene and the product crystallized by slow diffusion of methanol into the solution.

This compound, although not characterized crystallographically before, was first described by Sugimoto *et al.*<sup>[23]</sup> In addition to the analytical data provided there we recorded proton and carbon NMR data.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25°C):  $\delta = 1.85$  (m, 4H,  $2^*\text{CH}_2$ ), 3.25 (m, 4H,  $2^*\text{CH}_2$ ) ppm.  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ , 25°C):  $\delta = 23.1$  ( $\text{CH}_2$ ), 35.5 ( $\text{CH}_2$ ), 165.3 ( $\text{C}_{\text{quart., C-S}}$ ) ppm.

#### Synthesis of $[\text{W}(\text{CO})_2(\text{cydt})_2]$ {WCyd2t}

The synthesis of this compound was carried out following the same procedure as described for  $[\text{Mo}(\text{CO})_2(\text{cydt})_2]$ . This compound, although not characterized crystallographically before, was first described by the Sugimoto group.<sup>[34, 42]</sup> In addition to analytical data provided there we recorded proton and carbon NMR data.

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , 25°C):  $\delta = 1.80$  (m, 4H,  $2^*\text{CH}_2$ ), 3.19 (m, 4H,  $2^*\text{CH}_2$ ) ppm.  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{CDCl}_3$ , 25°C):  $\delta = 23.5$  ( $\text{CH}_2$ ), 35.4 ( $\text{CH}_2$ ), 161.9 ( $\text{C}_{\text{quart., C-S}}$ ), 191.1 (CO) ppm.  $^{135}\text{DEPT}$  NMR (75.5 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta = 23.5$  (neg.,  $\text{CH}_2$ ), 35.4 (neg.,  $\text{CH}_2$ ) ppm.

#### Synthesis of $[\text{Mo}(\text{CO})_2(\text{cydt})(\text{dppe})]$ {MoCyd2t}

A tempered reaction vessel at 20°C was charged with  $[\text{Mo}(\text{CO})_4(\text{dppe})]$  (509.4 mg, 0.83 mmol, 1 eq.) and the atmosphere was replaced with argon. The solid was dissolved in 10 ml dry THF and irradiated for around 30 minutes yielding a yellow solution. A solution of cydt (198 mg, 1.15 mmol, 1.38 eq.) in 5 ml dry THF was added and irradiated for several hours. The dark red solution was transferred into a Schlenk flask

and adsorbed on silica gel *in vacuo*. Column chromatography was performed using silica packed as a slurry and  $\text{CH}_2\text{Cl}_2$  and *n*-hexane (2:3) for elution. The desired product was eluted as a red-brownish band and the solvent was removed *in vacuo*. Yield: 62.5 % (362 mg, 0.52 mmol). The brownish solid was dissolved in a minimal amount of dry THF and crystallization was achieved after diffusion of dry methanol into the solution yielding brownish-red prismatic needles.

$^1\text{H}$  NMR (300 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  = 1.73 (s, 4H, 2\* $\text{CH}_2$ ), 2.51 (m, 4H, 2\* $\text{CH}_2$ ), 2.87 (s (br), 4H, 2\* $\text{CH}_2$ ), 6.99 (m, 4H, 4  $\text{CH}_{\text{arom}}$ ), 7.02 to 7.53 (m, 16H,  $\text{CH}_{\text{arom}}$ ).  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  = 25.0 (s,  $\text{CH}_2$ ), 28.6 (t,  $J^1$  = 21.5 Hz,  $\text{CH}_2$ ), 36.3 (s,  $\text{CH}_2$ ), 128.8 (dt,  $J^1$  = 5.0 Hz,  $J^2$  = 34.7 Hz, CH), 130.6 (d,  $J^1$  = 33.0 Hz, CH), 133.5 (dt,  $J^1$  = 16.9 Hz,  $J^2$  = 5.0 Hz, CH), 136.4 (m,  $\text{C}_{\text{quart., arom.}}$ ), 138.3 (m,  $\text{C}_{\text{quart., arom.}}$ ), 153.3 (t,  $J^1$  = 2.2 Hz,  $\text{C}_{\text{quart., C-S}}$ ), 243.2 (d, CO,  $J$  = 14.7 Hz) ppm.  $^{31}\text{P}$  NMR (121.5 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  = 82.80 (s) ppm.  $^{135}\text{DEPT}$  NMR (75.5 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  = 25.0 (neg.,  $\text{CH}_2$ ), 28.8 (neg.,  $\text{CH}_2$ ), 36.5 (neg.,  $\text{CH}_2$ ), 128.8 (pos., CH), 130.6 (pos., CH), 133.5 (pos., CH) ppm. HH-COSY NMR (300 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  = 1.71 und 2.87 (2  $\text{CH}_2$ ,  $\text{cydt}$  with  $\text{CH}_2$ ,  $\text{cydt}$ ) ppm. HSQC-DEPT NMR (300 and 75.5 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  = 1.73 ( $^1\text{H}$ , 2  $\text{CH}_2$ ,  $\text{cydt}$ ) and 25.0 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,  $\text{cydt}$ ), 2.51 ( $^1\text{H}$ , 2  $\text{CH}_2$ ) and 28.8 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,  $\text{dppe}$ ), 2.87 ( $^1\text{H}$ ,  $\text{CH}_2$ ,  $\text{cydt}$ ) and 36.5 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ), 7.02-7.53 ( $^1\text{H}$ ,  $\text{CH}_{\text{arom.}}$ ) and 128.8-138.4 ( $^{13}\text{C}$ ,  $\text{CH}_{\text{arom.}}$ ) ppm. HMBC NMR (300 and 75.5 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  = 1.73 ( $^1\text{H}$ ,  $\text{CH}_2$ ,  $\text{cydt}$ ) and 25.0 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ), 2.87 ( $^1\text{H}$ ,  $\text{CH}_2$ ,  $\text{cydt}$ ) and 25.0 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ), 1.73 ( $^1\text{H}$ ,  $\text{CH}_2$ ,  $\text{cydt}$ ) and 153.9 ( $^{13}\text{C}$ , C-S), 2.87 ( $^1\text{H}$ ,  $\text{CH}_2$ ,  $\text{cydt}$ ) and 153.9 ( $^{13}\text{C}$ , C-S), 7.02-7.53 ( $^1\text{H}$ ,  $\text{CH}_{\text{arom.}}$ ) and 128.8-138.4 ( $^{13}\text{C}$ ,  $\text{CH}_{\text{arom.}}$ ) ppm. Rf-value (silica gel): 0.28 (*n*-hexane/ $\text{CH}_2\text{Cl}_2$ : 3/2). UV-vis:  $\epsilon$  in THF ( $\text{M}^{-1}\text{cm}^{-1}$ ) = 6818 (321 nm), 5201 (432 nm). IR (NaCl, 0.04 mm, in THF):  $\nu$  = 0.035 M:  $\nu$  = 1300-1700  $\text{cm}^{-1}$ , 1874  $\text{cm}^{-1}$ , 1938  $\text{cm}^{-1}$ , 1949  $\text{cm}^{-1}$ . IR (KBr):  $\nu$  = 1433  $\text{cm}^{-1}$ , 1861  $\text{cm}^{-1}$ , 1935  $\text{cm}^{-1}$ . Calcd for  $\text{C}_{34}\text{H}_{32}\text{O}_2\text{P}_2\text{S}_2\text{Mo}$ : C: 58.79; H: 4.64; S: 9.23. Found: C: 58.34; H: 4.78; S: 9.25.

#### Synthesis of $[\text{W}(\text{CO})_2(\text{cydt})(\text{dppe})]$ $\{\text{WCydt}\}$

The synthesis followed the procedure described for  $[\text{Mo}(\text{CO})_2(\text{cydt})(\text{dppe})]$ ;  $[\text{W}(\text{CO})_4(\text{dppe})]$  (900 mg, 1.3 mmol, 1 eq.) and  $\text{cydt}$  (307.3 mg, 1.78 mmol, 1.37 eq.) were used. The product crystallized as dark red prismatic blocks. Yield: 50.5 % (513.4 mg, 0.656 mmol).

$^1\text{H}$  NMR (300 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  = 1.68 (m, 4H, 2  $\text{CH}_2$ ), 2.59 (s, 4H), 2.79 (m, 4H, 2\* $\text{CH}_2$ ), 7.04 (m, 4H,  $\text{CH}_{\text{arom.}}$ ), 7.23 (m, 6H,  $\text{CH}_{\text{arom.}}$ ), 7.40 (m, 10H,  $\text{CH}_{\text{arom.}}$ ) ppm.  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  = 25.2 (s,  $\text{CH}_2$ ), 29.8 (m,  $\text{CH}_2$ ), 36.2 (s,  $\text{CH}_2$ ), 128.8 (dt,  $J^1$  = 31.4 Hz,  $J^2$  = 5.0 Hz, CH), 130.7 (d,  $J^1$  = 30.3 Hz, CH), 133.7 (dt,  $J^1$  = 18.7 Hz,  $J^2$  = 5.0 Hz, CH), 136.0 (m,  $\text{C}_{\text{quart.}}$ ), 138.7 (m,  $\text{C}_{\text{quart.}}$ ), 150.7 (t,  $J^1$  = 2.5 Hz,  $\text{C}_{\text{quart.}}$ ), 235.7 (m, CO) ppm.  $^{31}\text{P}$  NMR (121.5 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  = 61.96 (s, Sat.<sub>183W</sub>:  $J$  = 187.07 Hz) ppm.  $^{135}\text{DEPT}$  NMR (75.5 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  = 25.2 (neg.,  $\text{CH}_2$ ), 29.8 (neg.,  $\text{CH}_2$ ), 36.2 (neg.,  $\text{CH}_2$ ), 128.8 (pos., CH), 130.7 (pos., CH), 133.7 (pos., CH). HH-COSY NMR (300 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  = 1.68 and 2.79 (2  $\text{CH}_2$ ,  $\text{cydt}$  with  $\text{CH}_2$ ,  $\text{cydt}$ ) ppm. HSQC NMR (300 and 75.5 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  = 1.68 ( $^1\text{H}$ , 2  $\text{CH}_2$ ,  $\text{cydt}$ ) and 25.2 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,  $\text{cydt}$ ), 2.59 ( $^1\text{H}$ , 2  $\text{CH}_2$ ) and 29.8 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,  $\text{dppe}$ ), 2.79 ( $^1\text{H}$ ,  $\text{CH}_2$ ,  $\text{cydt}$ ) and 36.1 ( $\text{C}_4\text{D}_8\text{O}$   $^{13}\text{C}$ ,  $\text{CH}_2$ ), 7.04-7.40 ( $^1\text{H}$ ,  $\text{CH}_{\text{arom.}}$ ) and 128.6-138.7 ( $^{13}\text{C}$ ,  $\text{CH}_{\text{arom.}}$ ) ppm. HMBC NMR (300 and 75.5 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  = 1.68 ( $^1\text{H}$ ,  $\text{CH}_2$ ,  $\text{cydt}$ ) and 25.2 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ), 2.79 ( $^1\text{H}$ ,  $\text{CH}_2$ ,  $\text{cydt}$ ) and 25.2 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ), 1.68 ( $^1\text{H}$ ,  $\text{CH}_2$ ,  $\text{cydt}$ ) and 150.7 ( $^{13}\text{C}$ , C-S), 2.79 ( $^1\text{H}$ ,  $\text{CH}_2$ ,  $\text{cydt}$ ) and 150.7 ( $^{13}\text{C}$ , C-S) ppm. Rf-value (silica gel): 0.24 (*n*-hexane/ $\text{CH}_2\text{Cl}_2$ : 3:2). UV-vis:  $\epsilon$  in THF ( $\text{M}^{-1}\text{cm}^{-1}$ ) = 3530 (387 nm), 2785 (467 nm). IR (NaCl, 0.04 mm, in dry THF,  $c$  = 0.033 M):  $\nu$  = 1300-1700  $\text{cm}^{-1}$ , 1865  $\text{cm}^{-1}$ , 1931  $\text{cm}^{-1}$ , 1942  $\text{cm}^{-1}$ . IR (KBr):  $\nu$  = 1433  $\text{cm}^{-1}$ , 1854  $\text{cm}^{-1}$ , 1923  $\text{cm}^{-1}$ . Calcd for  $\text{C}_{34}\text{H}_{32}\text{O}_2\text{P}_2\text{S}_2\text{W}$ : C: 52.19; H: 4.19; S: 8.19. Found: C: 52.12; H: 4.00; S: 7.91.

#### Synthesis of $[\text{Mo}(\text{CO})_2(\text{dppe})(\text{pydt})]$ $\{\text{MoPydt}\}$

$[\text{Mo}(\text{CO})_2(\text{dppe})(\text{pydt})]$  was prepared as described for the analogous compound  $[\text{Mo}(\text{CO})_2(\text{cydt})(\text{dppe})]$  with  $\text{pydt}$  (205.4 mg, 1.18 mmol, 1.1 eq.) ligand instead of  $\text{cydt}$ . Yield: 52.4 % (391.4 mg, 0.562 mmol).

$^1\text{H}$  NMR (300 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  = 2.55 (m, 4H, 2\* $\text{CH}_2$ ), 2.87 (t, 2H,  $\text{CH}_2$ ), 3.73 (t, 2H,  $\text{CH}_2$ ), 4.66 (s, 2H,  $\text{CH}_2$ ), 7.00 (m, 4H, 4  $\text{CH}_{\text{arom.}}$ ), 7.20-7.31 (m, 6H,  $\text{CH}_{\text{arom.}}$ ), 7.36-7.43 (m, 6H,  $\text{CH}_{\text{arom.}}$ ); 7.46 bis 7.52 (m, 4H,  $\text{CH}_{\text{arom.}}$ ) ppm.  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  = 28.6 (m,  $\text{CH}_2$ ), 36.5 (s,  $\text{CH}_2$ ), 65.5 (s,  $\text{CH}_2$ ), 73.9 (s,  $\text{CH}_2$ ), 128.9 (dt, 2\*2 CH,  $J^1$  = 32.1 Hz,  $J^2$  = 5.2 Hz), 130.8 (d, 2\*2 CH,  $J^1$  = 31.4 Hz), 133.4 (dt, 2\*2 CH,  $J^1$  = 15.3 Hz,  $J^2$  = 5.0 Hz), 136.2 (m,  $\text{C}_{\text{quart.}}$ ), 138.0 (m,  $\text{C}_{\text{quart.}}$ ), 150.3 (s,  $\text{C}_{\text{quart., C-S}}$ ), 150.4 (s,  $\text{C}_{\text{quart., C-S}}$ ), 242.8 (d, CO,  $J$  = 15.3 Hz) ppm.  $^{31}\text{P}$  NMR (121.5 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  = 82.97 (s) ppm.  $^{135}\text{DEPT}$  NMR (75.5 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  = 28.6 (neg.,  $\text{CH}_2$ ), 36.5 (neg.,  $\text{CH}_2$ ), 65.5 (neg.,  $\text{CH}_2$ ), 73.9 (neg.,  $\text{CH}_2$ ), 128.7 (pos., CH), 129.1 (pos., CH), 130.5 (pos., CH), 130.9 (pos., CH), 133.3 (pos., CH) ppm. HH-COSY NMR (300 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  = 2.87 and 3.73 (2  $\text{CH}_2$ ,  $\text{pydt}$  with  $\text{CH}_2$ ,  $\text{pydt}$ ), 2.87 and 4.66 (2  $\text{CH}_2$ ,  $\text{pydt}$  with  $\text{CH}_2$ ,  $\text{pydt}$ ) ppm. HSQC NMR (300 and 75.5 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  = 2.55 ( $^1\text{H}$ , 2  $\text{CH}_2$ ,  $\text{pydt}$ ) and 28.6 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,  $\text{pydt}$ ), 2.87 ( $^1\text{H}$ , 2  $\text{CH}_2$ ) and 36.5 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ,  $\text{dppe}$ ), 3.73 ( $^1\text{H}$ ,  $\text{CH}_2$ ,  $\text{pydt}$ ) and 65.5 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ), 4.66 ( $^1\text{H}$ ,  $\text{CH}_2$ ,  $\text{pydt}$ ) and 73.9 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ), 6.97-7.52 ( $^1\text{H}$ ,  $\text{CH}_{\text{arom.}}$ ) and 128.7-138.0 ( $^{13}\text{C}$ ,  $\text{CH}_{\text{arom.}}$ ) ppm. HMBC NMR (300 and 75.5 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  = 2.87 ( $^1\text{H}$ ,  $\text{CH}_2$ ,  $\text{pydt}$ ) and 65.5 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ); 2.87 ( $^1\text{H}$ ,  $\text{CH}_2$ ,  $\text{pydt}$ ) and 150.3 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ); 3.73 ( $^1\text{H}$ ,  $\text{CH}_2$ ,  $\text{pydt}$ ) and 73.9 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ); 3.73 ( $^1\text{H}$ ,  $\text{CH}_2$ ,  $\text{pydt}$ ) and 73.9 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ); 3.73 ( $^1\text{H}$ ,  $\text{CH}_2$ ,  $\text{pydt}$ ) and 150.3 ( $^{13}\text{C}$ , C-S); 4.66 ( $^1\text{H}$ ,  $\text{CH}_2$ ,  $\text{pydt}$ ) and 150.3 ( $^{13}\text{C}$ , C-S); 6.97-7.52 ( $^1\text{H}$ ,  $\text{CH}_{\text{arom.}}$ ) and 128.9-133.4 ( $^{13}\text{C}$ ,  $\text{CH}_{\text{arom.}}$ ). Rf-value (silica gel): 0.55 (*n*-hexane/ $\text{CH}_2\text{Cl}_2$ : 3.5/1.5). UV-vis:  $\epsilon$  in acetonitrile ( $\text{M}^{-1}\text{cm}^{-1}$ ) = 4281 (425 nm). IR (KBr):  $\nu$  = 1431  $\text{cm}^{-1}$ , 1863  $\text{cm}^{-1}$ , 1929  $\text{cm}^{-1}$ . Calcd for  $\text{C}_{33}\text{H}_{30}\text{O}_3\text{P}_2\text{S}_2\text{Mo}$ : C: 56.90; H: 4.34; S: 9.20. Found: C: 56.85; H: 4.78; S: 9.25.

#### Synthesis of $[\text{W}(\text{CO})_2(\text{dppe})(\text{pydt})]$ $\{\text{WPydt}\}$

$[\text{W}(\text{CO})_2(\text{dppe})(\text{pydt})]$  was prepared as described for the analogous compound  $[\text{W}(\text{CO})_2(\text{cydt})(\text{dppe})]$  with  $\text{pydt}$  ligand (144 mg, 0.827 mmol, 1.1 eq.) instead of  $\text{cydt}$ . Yield: 34.1 % (198.5 mg, 0.253 mmol).

$^1\text{H}$  NMR (300 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  = 2.62 (m, 4H, 2\* $\text{CH}_2$ ); 2.81 (t, 2H,  $\text{CH}_2$ ), 3.70 (t, 2H,  $\text{CH}_2$ ), 4.62 (s, 2H,  $\text{CH}_2$ ), 7.05 (m, 4H, 4  $\text{CH}_{\text{arom.}}$ ), 7.20-7.31 (m, 6H,  $\text{CH}_{\text{arom.}}$ ), 7.34-7.47 (m, 10H,  $\text{CH}_{\text{arom.}}$ ) ppm.  $^{13}\text{C}$  NMR (75.5 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  = 29.8 (m,  $\text{CH}_2$ ), 36.5 (s,  $\text{CH}_2$ ), 65.8 (s,  $\text{CH}_2$ ), 74.3 (s,  $\text{CH}_2$ ), 128.9 (dt, 2\*2 CH,  $J^1$  = 28.5 Hz,  $J^2$  = 5.0 Hz), 130.8 (d, 2\*2 CH,  $J^1$  = 28.5 Hz), 133.7 (dt, 2\*2 CH,  $J^1$  = 17.1 Hz,  $J^2$  = 5.0 Hz), 135.8 (d,  $\text{C}_{\text{quart.}}$ ,  $J^1$  = 48 Hz), 138.5 (d,  $\text{C}_{\text{quart.}}$ ,  $J^1$  = 48 Hz), 148.6 (s,  $\text{C}_{\text{quart., C-S}}$ ), 148.7 (s,  $\text{C}_{\text{quart., C-S}}$ ), 234.6 (m, CO) ppm.  $^{31}\text{P}$  NMR (121.5 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  = 59.94 (s, Sat.<sub>183W</sub>:  $J$  = 184 Hz) ppm.  $^{135}\text{DEPT}$  NMR (75.5 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  = 29.8 (neg.,  $\text{CH}_2$ ), 36.5 (neg.,  $\text{CH}_2$ ), 65.8 (neg.,  $\text{CH}_2$ ), 74.3 (neg.,  $\text{CH}_2$ ), 128.7 (pos., CH), 129.1 (pos., CH), 130.6 (pos., CH), 131.0 (pos., CH), 133.6 (pos., CH), 133.8 (pos., CH). HH-COSY NMR (300 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  = 2.81 (2  $\text{CH}_2$ ,  $\text{pydt}$  and 3.70  $\text{CH}_2$ ,  $\text{pydt}$ ), 2.81 (2  $\text{CH}_2$ ,  $\text{pydt}$  and 4.62  $\text{CH}_2$ ,  $\text{pydt}$ ) ppm. HSQC-DEPT NMR (300 and 75.5 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  = 2.62 ( $^1\text{H}$ , 2  $\text{CH}_2$ ,  $\text{dppe}$ ) and 29.8 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ), 2.81 ( $^1\text{H}$ , 2  $\text{CH}_2$ ) and 36.5 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ), 3.70 ( $^1\text{H}$ ,  $\text{CH}_2$ ,  $\text{pydt}$ ) and 65.8 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ), 4.62 ( $^1\text{H}$ , 2  $\text{CH}_2$ ,  $\text{pydt}$ ) and 74.3 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ), 7.05-7.47 ( $^1\text{H}$ ,  $\text{CH}_{\text{arom.}}$ ) and 128.7-138.5 ( $^{13}\text{C}$ ,  $\text{CH}_{\text{arom.}}$ ) ppm. HMBC NMR (300 and 75.5 MHz,  $\text{C}_4\text{D}_8\text{O}$ , 25°C):  $\delta$  = 2.81 ( $^1\text{H}$ ,  $\text{CH}_2$ ,  $\text{pydt}$ ) and 148.7 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ), 3.70 ( $^1\text{H}$ ,  $\text{CH}_2$ ,  $\text{pydt}$ ) and 74.3 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ), 3.70 ( $^1\text{H}$ ,  $\text{CH}_2$ ,  $\text{pydt}$ ) and 148.7 ( $^{13}\text{C}$ , C-S), 4.62 ( $^1\text{H}$ ,  $\text{CH}_2$ ,  $\text{pydt}$ ) and 65.8 ( $^{13}\text{C}$ ,  $\text{CH}_2$ ), 4.62 ( $^1\text{H}$ ,  $\text{CH}_2$ ,  $\text{pydt}$ ) and 148.6 ( $^{13}\text{C}$ , C-S), 7.05-7.47 ( $^1\text{H}$ ,  $\text{CH}_{\text{arom.}}$ ) and 128.7-138.5 ( $^{13}\text{C}$ ,  $\text{CH}_{\text{arom.}}$ ) ppm. Rf-value (silica gel): 0.57 (*n*-hexane/ $\text{CH}_2\text{Cl}_2$ : 4/1). UV-vis:  $\epsilon$  in acetonitrile ( $\text{M}^{-1}\text{cm}^{-1}$ ) = 7975 (296 nm), 4775 (388 nm), 1083 (500 nm). IR (KBr):  $\nu$  = 1433  $\text{cm}^{-1}$ , 1852  $\text{cm}^{-1}$ , 1921  $\text{cm}^{-1}$ . Calcd for  $\text{C}_{33}\text{H}_{30}\text{O}_3\text{P}_2\text{S}_2\text{W}$ : C: 50.52; H: 3.85; S: 8.17. Found: C: 50.71; H: 3.74; S: 8.16.

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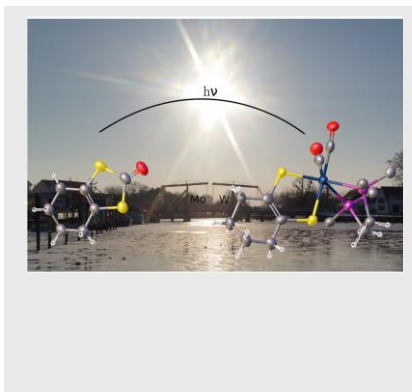
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**Keywords:** dithiolene • molybdenum • tungsten • chelotropic elimination • mono-dithiolene complexes

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## FULL PAPER

Light Induced Ring Opening of 1,3-Dithiol-2-ones is bridging the gap between dithiocarbonates and mono-dithiolene complexes of Molybdenum and Tungsten.

**Coordination Chemistry**

*Benedict J. Elvers, Carola Schulzke, and Christian Fischer\**

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**Photochemical Unmasking of 1,3-Dithiol-2-ones: An Alternative Route to Heteroleptic Dithiolene Complexes from Low-Valent Molybdenum and Tungsten Precursors**