Chalcogenoacyl-bridged derivatives of the unsaturated carbyne complex $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CPh)(\mu\text{-}PCy_2)(CO)_2]$.

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Abstract

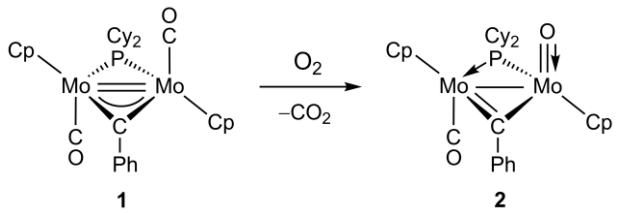
The 32-electron benzylidyne-bridged complex $[Mo_2Cp_2(\mu\text{-}CPh)(\mu\text{-}PCy_2)(CO)_2]$ reacted with elemental chalcogens E_n (E = S, Se) at 333 K to give the corresponding derivatives *trans*-$[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}C(Ph)E\}(\mu\text{-}PCy_2)(CO)_2]$, following from addition of a chalcogen atom to the Mo_2C face of the central Mo_2PC core in the parent compound, whereby a 5-electron donor, bridging chalcogenoacyl ligand was formed (Mo–Mo = 2.8662(5) Å, C–S = 1.757(5) Å in the thioacyl complex). These thermally stable products did not undergo decarbonylation under irradiation with visible-UV light, but instead rearranged into the corresponding *cis*-dicarbonyl isomers *cis*-$[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}C(Ph)E\}(\mu\text{-}PCy_2)(CO)_2]$ (Mo–Mo = 2.9208(5) Å, C–S = 1.745(5) Å in the thioacyl complex), in a process where no reaction intermediates were detected. The coordination of the chalcogenoacyl ligand in the *cis*-dicarbonyl isomers is analogous to that observed in the corresponding *trans* isomers, and involves the selective positioning of the 3-electron donor chalcogen atom *trans* to the bridging phosphanyl ligand, a structural trend common to related complexes with isoelectronic $\eta^2\text{:}\eta^2$ bridging groups such as iminoacyl, formimidoyl and diphosphenyl ligands.

Keywords: Molybdenum; Metal–metal interactions; Phosphorus ligands; Carbonyl complexes; Chalcogenoacyl ligands; Carbyne complexes.

1. Introduction

Recently we reported the preparation of the unsaturated, 32-electron benzylidyne-bridged complex $[Mo_2Cp_2(\mu\text{-CPh})(\mu\text{-PCy}_2)(CO)_2]$ (**1**) (Cp = η^5-C_5H_5). A preliminary exploration of its chemical behaviour revealed a multisite reactivity of its central Mo_2PC core, involving the participation of Mo–Mo, Mo–C and Mo–P bonds. Among other reactions, compound **1** was shown to add selenium atoms at the Mo_2C face upon reaction with grey selenium, to build a selenoacyl ligand symmetrically bridging the metal atoms in a μ-η^2:η^2 fashion [1]. In contrast, we later found that reaction of **1** with elemental oxygen instead promotes decarbonylation, to give the corresponding oxoderivative *trans*-$[Mo_2Cp_2(\mu\text{-CPh})(O)(\mu\text{-PCy}_2)(CO)]$ (**2**) (Scheme 1), a reaction taking place with retention of the overall stereochemistry of the binuclear substrate [2]. This indicates that the exact nature of the chalcogen has a critical influence on its reaction with the unsaturated complex **1**. In addition to this, we should note that the symmetrical η^2:η^2 bridging mode still is a relatively rare coordination mode on chalcogenoacyl ligands. Only a dozen compounds have been structurally characterized with S at the bridging position [3,4], but examples with O [5] and Se [1,6] at the bridging site are still much rarer. Based on the above results and considerations, we then decided to further explore the reactions of **1** with chalcogens by introducing sulphur, and also by exploring possible decarbonylation processes on the initial products formed in these reactions, in search for possible C–E bond formation/activation relationships. As it will be shown below, the unsaturated nature of complex **1** enables the addition of a single S or Se atom to its Mo_2C core under mild conditions, to yield chalcogenoacyl-bridged derivatives in a selective way, while irradiation of the latter products with visible-UV light induces a *trans* to *cis* rearrangement of these binuclear complexes without significant modification in the bridging chalcogenoacyl ligands.

Scheme 1



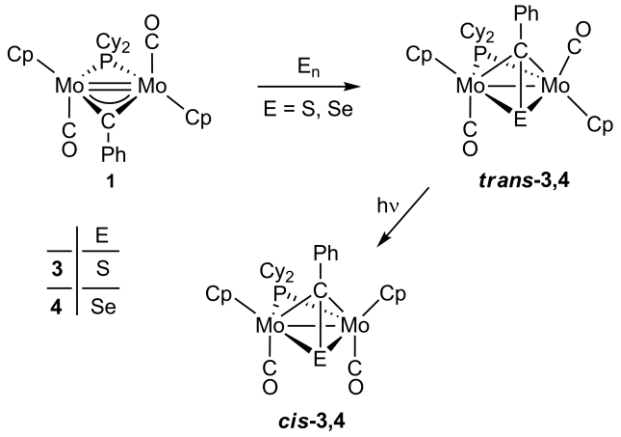
1 **2**

2. Results and Discussion

*2.1. Addition of elemental S and Se to complex **1**.*

Complex **1** reacts with S_8 or grey selenium under mild conditions (333 K in tetrahydrofuran) with eventual addition of a single atom of S or Se to its central Mo_2C core, to give the corresponding chalcogenoacyl-bridged derivatives *trans*-[Mo_2Cp_2\{μ-η^2:η^2-C(Ph)E\}(μ-PCy_2)$(CO)_2$] [E = S (***trans*-3**), Se (***trans*-4**)], with retention of the overall transoid arrangement of the MoCp(CO) fragments of the parent substrate (Scheme 2). These products hold a chalcogenoacyl ligand symmetrically bridging both metal centres in a μ-η^2:η^2 fashion, a geometry analogous to that previously found in the isoelectronic thiolato-bridged complexes [$Mo_2Cp'_2$\{μ-η^2:η^2-C(R)S\}(μ-SR´)$(CO)_2$] [3a,b]. We note that the chemical behaviour of **1** in these reactions parallels that observed previously in the reactions of heterometallic carbyne-bridged complexes of type [MFeL(μ-CR)$(CO)_x$] with elemental S and Se (M = Mo, W; L = Cp or related ligands; R = *p*-tol, Xyl; x = 5, 6) [3d,7].

Scheme 2



*2.1.1. Solid-state structure of the trans-dicarbonyl complexes **3** and **4**.*

The structure of the thioacyl complex ***trans*-3** has been determined through an X-ray analysis (Figure 1 and Table 1), and that of the selenoacyl complex ***trans*-4** was determined analogously during our preliminary investigation on the chemistry of **1** (Figure 2) [1]. Both structures are very similar to each other, and can be derived from the structure of **1** upon addition of a single chalcogen atom to the Mo_2C triangle, with displacement of the carbyne group to a position *cis* to the PCy_2 ligand (C3–Mo–P angles ca. 80^o), while the original position of the carbyne ligand (*trans* to PCy_2) is now occupied by the chalcogen atom. An structural effect of the formation of the bridging chalcogenoacyl ligand is a slight rearrangement of the transoid MoCp(CO) fragments of

these molecules, which rotate from their equivalent positions in **1** (with almost perfectly antiparallel CO ligands), so that one of the carbonyls leans slightly over the intermetallic vector (Mo–Mo–C ca. 80°), while the other points away from the dimetal site (Mo–Mo–C ca. 115°). This sort of distortion has been systematically found by us in cyclopentadienyl complexes of type $[M_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}X)(CO)_2]$ with other $\eta^2{:}\eta^2$-bound X groups such as formimidoyl [8], iminoacyl [9] or diphosphenyl ligands [10].

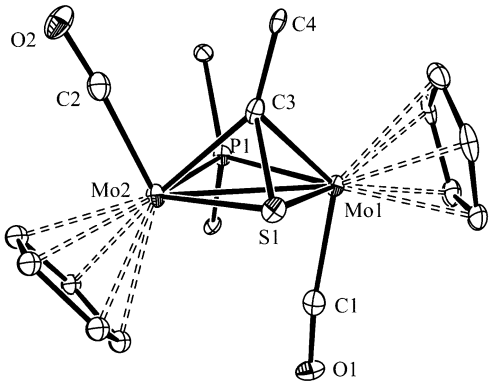


Figure 1. ORTEP diagram (30% probability) of ***trans*-3**, with Ph and Cy groups (except their C^1 atoms) omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (°) for ***trans*-3**

Mo(1)–Mo(2)	2.8662(6)	Mo(1)–P(1)–Mo(2)	71.02(4)
Mo(1)–P(1)	2.420(2)	Mo(1)–C(3)–Mo(2)	83.8(2)
Mo(2)–P(1)	2.455(1)	Mo(1)–S(1)–Mo(2)	71.73(4)
Mo(1)–C(1)	1.963(6)	Mo(2)–Mo(1)–C(1)	81.0(2)
Mo(2)–C(2)	1.933(6)	Mo(1)–Mo(2)–C(2)	115.6(2)
Mo(1)–C(3)	2.158(5)	P(1)–Mo(1)–C(1)	84.6(2)
Mo(2)–C(3)	2.135(5)	P(1)–Mo(2)–C(2)	99.4(2)
Mo(1)–S(1)	2.453(1)	P(1)–Mo(1)–C(3)	81.5(1)
Mo(2)–S(1)	2.439(2)	P(1)–Mo(2)–C(3)	81.1(1)
S(1)–C(3)	1.757(5)	C(1)–Mo(1)–C(3)	124.5(2)
		C(2)–Mo(2)–C(3)	73.1(2)

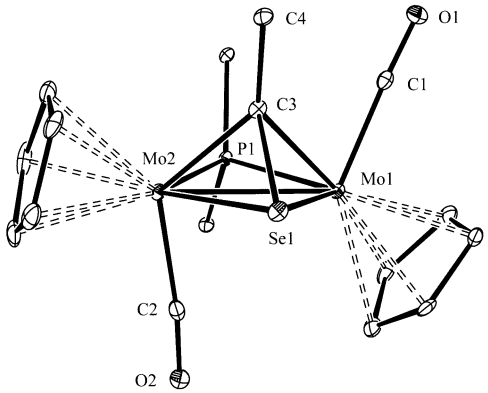


Figure 2. ORTEP diagram (30% probability) of ***trans*-4**, with Ph and Cy groups (except their C^1 atoms) omitted for clarity, taken from reference 1. Selected bond lengths (Å) and angles (°): Mo1–Mo2 = 2.8950(3), Mo1–P1 = 2.4415(6), Mo1–C1 = 1.921(2), Mo1–C3 = 2.180(2), Mo1–Se1 = 2.5611(3), Mo2–P1 = 2.4084(6), Mo2–C2 = 1.977(2), Mo2–C3 = 2.121(2), Mo2–Se1 = 2.5916(3); Se1-C3 = 1.924(2), Mo2–Mo1–C1 = 113.0(1), Mo1–Mo2–C2 = 79.5(1).

The C3–Mo lengths involving the chalcogenoacyl ligands of compounds ***trans*-3** and ***trans*-4** expectedly display single-bond values of ca. 2.15 Å (cf. 2.11(1) Å for the bridging carbonyl in complex $[Mo_2Cp_2(\mu\text{-CPh})(\mu\text{-PCy}_2)(\mu\text{-CO})]$) [11]. The same applies to the respective S–Mo (ca. 2.44 Å) and Se–Mo (2.58 Å) lengths, which also are consistent with the formulation of single bonds in each case, their differences being entirely attributable to the distinct covalent radii of the chalcogen atoms involved (0.15 Å larger for Se) [12]. These Mo–E lengths are in turn comparable to those measured in related chalcogenoacyl-bridged complexes involving Mo atoms, such as the dimolybdenum complexes $[Mo_2Cp'_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-C(R)S}\}(\mu\text{-SR}')(CO)_2]$ (ca. 2.45 Å) [3a,b], and the heterometallic complexes $[MoFeCp\{\mu\text{-}\eta^2\text{:}\eta^2\text{-C(}p\text{-Tol)S}\}(CO)_5]$ [2.441(1) Å] [3d], and $[MoRh\{\mu\text{-}\eta^2\text{:}\eta^2\text{-C(}C_2SiMe_3\text{)Se}\}Cl(CO)_2\{HB(pzMe_2)_3\}(PPh_3)]$ [2.5617(2) Å] [6]. Incidentally, we note that the MoRh complex, along with compound ***trans*-4**, still seem to be the only selenoacyl-bridged complexes structurally characterized so far. The C–E values of the chalcogenoacyl ligands in our complexes also approach the corresponding single-bond figures; for instance, the C–S length of 1.757(5) Å in ***trans*-3** is close to the reference single-bond figure of 1.78 Å for a (sp^2)C–S bond [12], and is significantly longer than the reference double-bond length of 1.62 Å [13]. As a result of this $\eta^2\text{:}\eta^2$ coordination mode, the chalcogenoacyl ligands in complexes ***trans*-3** and ***trans*-4** act as 5-electron donor groups to the dimetal centre, therefore single metal–metal bonds have to be formulated for these 34-electron complexes, according to the 18-electron rule, which is consistent with the intermetallic lengths of 2.8662(6) Å and 2.8950(3) Å measured respectively for these molecules, which are figures similar, for instance, to the Mo–Mo length determined in the electron-precise cluster $[WMo_2Cp_2(\mu_3\text{-CH})(\mu\text{-PCy}_2)(CO)_7]$ [2.9283(3) Å] [14].

*2.1.2. Solution structure of trans-dicarbonyl complexes **3** and **4**.*

Spectroscopic data in solution for complexes ***trans*-3** and ***trans*-4** (Table 2) are very similar to each other and fully consistent with the respective structures found in the solid-state. Their *trans*-dicarbonyl arrangement is deduced from the corresponding IR spectra, which display in each case two C–O stretching bands with the pattern (weak and strong, in order of decreasing frequencies) characteristic of transoid $M_2(CO)_2$ oscillators with carbonyl ligands defining angles close to 180º (ca. 145º in the crystal) [15].

The $^{31}P\{^1H\}$ NMR spectra of these complexes display resonances at 133.8 and 124.3 ppm respectively. These chemical shifts are comparable to that measured for the isoelectronic propenylylidene-bridged complex $[Mo_2Cp_2\{\mu\text{-}\kappa^2\text{:}\eta^3\text{-CPhCHC(CO}_2\text{Me)}\}(\mu\text{-PCy}_2)(CO)_2]$ (140.3 ppm) [1], although considerably lower than the shifts usually found in related electron-precise dimolybdenum complexes holding

single-donor-atom bridging ligands, such as the tricarbonyl complex [Mo_2Cp_2(μ-COMe)(μ-PCy_2)$(CO)_3$] (δ_P = 219.7 ppm) [16], or the tetracarbonyl complex [Mo_2Cp_2(μ-H)(μ-PCy_2)$(CO)_4$] (δ_P = 218.8 ppm) [17]. Obviously, the number of donor atoms at the bridging position has a significant effect on the shielding of the P atom in these binuclear species, irrespective of the overall electron count of the complex, or other factors.

Table 2. Selected IR and NMR data for new compounds

Compound	ν(CO)[a]	δ(P)[b]	δ(μ-C) [J_{CP}][b]
trans-[Mo_2Cp_2\{μ-η^2:η^2-C(Ph)S\}(μ-PCy_2)$(CO)_2$] (***trans*-3**)	1886 (sh), 1873 (vs)	133.8[c]	99.9 [26][c]
cis-[Mo_2Cp_2\{μ-η^2:η^2-C(Ph)S\}(μ-PCy_2)$(CO)_2$] (***cis*-3**)	1934 (vs), 1887 (w)[d]	157.7	87.0 [22][c]
trans-[Mo_2Cp_2\{μ-η^2:η^2-C(Ph)Se\}(μ-PCy_2)$(CO)_2$] (***trans*-4**)	1889 (sh), 1872 (vs)	124.3	89.6
cis-[Mo_2Cp_2\{μ-η^2:η^2-C(Ph)Se\}(μ-PCy_2)$(CO)_2$] (***cis*-4**)	1934 (vs), 1887 (w)[d]	152.8	

[a] Recorded in THF solution, data in cm^{-1}.
[b] Recorded at room temperature in CD_2Cl_2 solution at 121.48 (^{31}P) and 100.61 MHz (^{13}C), unless otherwise stated; δ in ppm relative to external 85% aqueous H_3PO_4 and internal tetramethylsilane, respectively, with C-P coupling constants [J_{CP}] in Hz.
[c] Recorded at 233 K.
[d] Recorded in CH_2Cl_2 solution, data in cm^{-1}.

Complexes ***trans*-3** and ***trans*-4** exhibit in the corresponding $^{13}C\{^1H\}$ NMR spectra quite shielded resonances for the carbon atom of the chalcogenoacyl ligand (99.9 and 89.6 ppm respectively). The thioacyl resonance in turn displays a large P-C coupling of 26 Hz, which is consistent with the acute P–Mo–C angles of ca. 80° found in the crystal; unfortunately, no coupling was observed for the selenoacyl resonance, due to broadness. In any case, we note that the above low chemical shifts seem to be characteristic of the μ-η^2:η^2 coordination mode of chalcogenoacyl ligands (cf. 95.6 and 106.0 ppm for the heterometallic complexes [WFeCp\{μ-η^2:η^2-C(*p*-Tol)S\}$(CO)_5$] [3d], and [MoFe\{μ-η^2:η^2-C(*p*-Tol)S\}$(CO)_5$\{$HB(pz)_3$\}] [7a], respectively). Other resonances in both the ^1H and the $^{13}C\{^1H\}$ NMR spectra of these complexes are as expected and deserve no further comments.

*2.2. Formation and structural characterization of cis-dicarbonyl complexes **3** and **4**.*

Irradiation of tetrahydrofuran solutions of compounds ***trans*-3** and ***trans*-4** with visible-UV light for 25 min gives selectively the corresponding *cis*-dicarbonyl isomers ***cis*-3** and ***cis*-4** (Scheme 2), with no intermediates being detected when monitoring the above rearrangements by IR spectroscopy.

The structure of the thioacyl complex ***cis*-3** has been determined through an X-ray diffraction analysis (Figure 3 and Table 3). This structure can be derived from that of the corresponding isomer ***trans*-3** after a 180° rotation in one of the MoCp(CO) fragments so as to reach a cisoid conformation, with carbonyl ligands almost perfectly parallel to each other (Mo–Mo–C angles ca. 89 and 91°). However, the central Mo_2CSP

core of the molecule is little perturbed by this rearrangement, with only very modest changes in the corresponding interatomic lengths, just some lengthening in the Mo–S bonds [2.47 vs. 2.45 Å], but some shortening in the Mo–P bonds. The intermetallic length is enlarged to a more significant extent [2.9208(6) vs. 2.866(2) Å], which can be interpreted as a way to alleviate the increased steric repulsions between the different hydrocarbon groups implied by the *cis* arrangement of terminal ligands in this molecule.

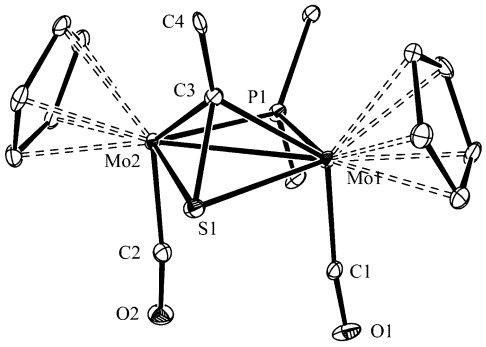


Figure 3. ORTEP diagram (30% probability) of ***cis*-3**, with Ph and Cy groups (except their C^1 atoms) omitted for clarity. Only one of the two independent molecules present in the unit cell is shown.

Table 3. Selected bond lengths (Å) and angles (°) for ***cis*-3**

Mo(1)–Mo(2)	2.9208(6)	Mo(1)–P(1)–Mo(2)	74.13(4)
Mo(1)–P(1)	2.429(1)	Mo(1)–C(3)–Mo(2)	86.0(2)
Mo(2)–P(1)	2.417(1)	Mo(1)–S(1)–Mo(2)	72.51(4)
Mo(1)–C(1)	1.986(6)	Mo(2)–Mo(1)–C(1)	91.2(1)
Mo(2)–C(2)	1.994(6)	Mo(1)–Mo(2)–C(2)	88.9(1)
Mo(1)–C(3)	2.153(5)	P(1)–Mo(1)–C(1)	85.4(1)
Mo(2)–C(3)	2.130(5)	P(1)–Mo(2)–C(2)	85.7(2)
Mo(1)–S(1)	2.472(1)	P(1)–Mo(1)–C(3)	87.4(1)
Mo(2)–S(1)	2.468(1)	P(1)–Mo(2)–C(3)	88.2(1)
S(1)–C(3)	1.745(5)	C(1)–Mo(1)–C(3)	128.8(2)
		C(2)–Mo(2)–C(3)	126.1(2)

Spectroscopic data in solution for ***cis*-3** and ***cis*-4** (Table 2 and Experimental section) indicate that these complexes share the same structure, in turn consistent with the solid-state structure of the former. In the first place, their IR spectra display in each case two C–O stretching bands with the pattern (strong and weak, in order of decreasing frequencies) characteristic of $M_2(CO)_2$ oscillators with almost parallel CO ligands [15]. On the other hand, their ^{31}P NMR spectra display resonances at 157.7 and 152.8 ppm, some 25 ppm more deshielded than those of the corresponding transoid isomers, which is a common trend observed when comparing related pairs of isomers in complexes of the type $[M_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}Y)(CO)_2]$ (Y = 3-electron donor ligand) and related species [2,17]. The retention of the $\mu\text{-}\eta^2\text{:}\eta^2$ coordination mode of the chalcogenoacyl ligands in solution is indicated by the low chemical shift of the thioacyl ^{13}C NMR resonance in ***cis*-3** (89.6 ppm), while the overall C_s symmetry implied by the cisoid conformation of terminal ligands in these complexes is reflected in the observation of single ^{13}C or ^{1}H NMR resonances for the pairs of equivalent CO and Cp ligands.

2.3. Structural preferences in complexes bearing 5-electron donor μ-η^2:η^2 ligands.

As discussed above, and irrespective of the cisoid or transoid conformation of their terminal ligands, the bridging chalcogenoacyl ligands in complexes **3** and **4** are arranged so that the chalcogen atom is placed near the Mo_2P plane, therefore *trans* to the bridging PCy_2 ligand, whereas the CPh group is displaced to a position *cis* to it. In a formal sense, for these 5-electron donor ligands we can view the chalcogen atom as providing the dimetal centre with 3 electrons, while the CR group accounts for 2 electrons (***A*** in Chart 1). Interestingly, the same sort of spatial and electronic arrangement has been found previously in related cyclopentadienyl complexes of type $[M_2Cp_2(\mu\text{-}PR_2)(\mu\text{-}X)(CO)_2]$ when X is a related η^2:η^2-bound 5-electron donor such as a formimidoyl [8] or iminoacyl ligand (***B*** in Chart 1) [9], or a diphosphenyl ligand (***C*** in Chart 1) [10]. In all these complexes, the 3-electron donor part of the ligand (E, NR, PR) is placed specifically *trans* to the PCy_2 group, while the 2-electron donor part is placed *cis* to it. Such a geometric preference must have an electronic origin since, for instance, one might anticipate, on steric grounds alone, that the chalcogenoacyl ligand would rather prefer a conformation with the CR and E sites exchanged. In line with this, we note that the recently reported structure of the thiolate complex *trans*-$[Mo_2Cp_2(\mu\text{-}PS)\{\mu\text{-}S(p\text{-}Tol)\}(CO)_2]$ [19], bearing a η^2:η^2-bound thiophosphinylidyne (PS) ligand, which is isoelectronic with the 5-electron donors under discussion and obviously devoid of any steric preference, is specifically coordinated with its 3-electron donor part (the S atom) *trans* to the bridging thiolate ligand (***D*** in Chart 1). More work, however, will be needed to establish the generality and intimate origin of the above geometric preference.

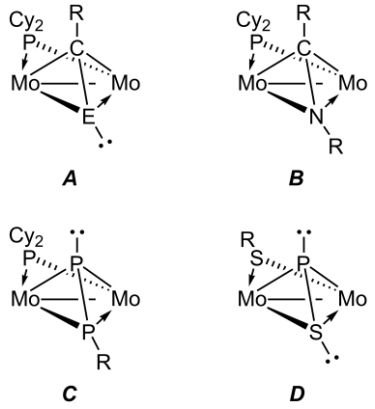


Chart 1. The specific spatial arrangement and electron contributions of 5-electron donor μ-η^2:η^2 ligands found in different dimolybdenum cyclopentadienyl complexes (E = S, Se).

3. Conclusions

Compound **1** displays a multisite reactivity at the Mo_2PC core allowing a chalcogen atom (S or Se) to be added at the Mo_2C face to give the corresponding derivatives *trans*-$[Mo_2Cp_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}C(Ph)E\}(\mu\text{-}PCy_2)(CO)_2]$ featuring a 5-electron donor bridging

chalcogenoacyl ligand, with retention of the transoid stereochemistry of the binuclear substrate. These products undergo photochemically-induced rearrangement into the corresponding *cis*-dicarbonyl isomers, with little perturbation of the bridging chalcogenoacyl ligand. Moreover, irrespective of the transoid or cisoid conformation of the terminal ligands in these substrates, the bridging chalcogenoacyl ligand is specifically coordinated so that its 3-electron donor group (the chalcogen atom) is positioned *trans* to the bridging PCy_2 ligand, whereas the CPh group is placed *cis* to it. This geometric preference is common to other related 5-electron donor μ-η^2:η^2-bound ligands, such as formimidoyl, iminoacyl, diphosphenyl and even thiophosphinylidyne ligands, and likely has an electronic origin.

4. Experimental

All reactions and manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were purified according to literature procedures [20], and distilled under nitrogen prior to use. Petroleum ether refers to that fraction distilling in the range 338-343 K. Complex $[Mo_2Cp_2(\mu\text{-CPh})(\mu\text{-}PCy_2)(CO)_2]$ (**1**) (Cp = η^5-C_5H_5) was prepared as described previously [11]. All other reagents were obtained from the usual commercial suppliers and used as received. Photochemical experiments were performed using jacketed Schlenk tubes, cooled by tap water (ca. 288 K). A 400 w mercury lamp placed ca. 1 cm away from the Schlenk tube was used for all experiments. Chromatographic separations were carried out using jacketed columns cooled by tap water (ca. 288 K). Commercial aluminium oxide (activity I, 70-290 mesh) was degassed under vacuum prior to use. The later was mixed under nitrogen with the appropriate amount of water to reach the activity desired. IR stretching frequencies of CO ligands were measured in solution using CaF_2 windows, are referred to as ν(CO) and are given in cm^{-1}. Nuclear magnetic resonance (NMR) spectra were routinely recorded at 300.13 (^{1}H), 121.48 (^{31}P{^{1}H}) and 100.61 MHz (^{13}C{^{1}H}) at room temperature in CD_2Cl_2 solutions unless otherwise stated. Chemical shifts (δ) are given in ppm, relative to internal tetramethylsilane (^{1}H and ^{13}C), or external 85% aqueous H_3PO_4 solutions (^{31}P). Coupling constants (J) are given in hertz.

*4.1. Preparation of trans-[$Mo_2Cp_2\{\mu$-η^2:η^2-C(Ph)S$\}(\mu$-$PCy_2)(CO)_2$] (**trans-3**).*

Solid S_8 (0.005 g, 0.020 mmol) was added to a tetrahydrofuran solution (10 mL) of compound **1** (0.050 g, 0.075 mmol), and the mixture was stirred at 333 K for 2 h to give an orange solution. The solvent was then removed under vacuum, the residue extracted with dichloromethane/petroleum ether (1/10) and the extracts chromatographed through an alumina column (activity IV). Elution with dichloromethane/petroleum ether (1/9) gave an orange fraction yielding, after removal of solvents under vacuum, compound

***trans*-3** as an orange microcrystalline solid (0.049 g, 93%). The crystals used in the X-ray study were grown by the slow diffusion of a layer of petroleum ether into a dichloromethane solution of the complex at 253 K. Anal. Calc. for $C_{31}H_{37}Mo_2O_2PS$: C, 53.45; H, 5.35; S, 4.60. Found: C, 53.58; H, 4.73; S, 4.47. ^{1}H NMR (400.13 MHz, 233 K): δ 7.16 [false t, J_{HH} = 7, 2H, H^3(Ph)], 7.05 [s, br, 2H, H^2(Ph)], 6.99 [t, J_{HH} = 7, 1H, H^4(Ph)], 5.23, 5.10 (2s, 2 × 5H, Cp), 2.20-0.80 (m, 22 H, Cy). ^{1}H NMR (400.13 MHz, 298 K): δ 7.12 [false t, J_{HH} = 7, 2H, H^3(Ph)], 7.04 [false d, J_{HH} = 7, 2H, H^2(Ph)], 6.96 [t, J_{HH} = 7, 1H, H^4(Ph)], 5.23, 5.07 (2s, 2 × 5H, Cp), 2.20-0.90 (m, 22 H, Cy). ^{13}C{^{1}H} NMR (100 MHz, 233 K): δ 242.8 (d, J_{CP} = 10, MoCO), 237.1 (d, J_{CP} = 10, MoCO), 151.1 [s, C^1(Ph)], 129.4 [s, br, C^2(Ph)], 127.4 [s, C^4(Ph)], 124.5 [s, C^3(Ph)], 99.9 (d, J_{CP} = 26, CS), 90.8, 89.9 (2s, Cp), 51.1 [s, C^1(Cy)], 51.0 [d, J_{CP} = 7, C^1(Cy)], 36.4 [s, C^2(Cy)], 36.2, 34.3, 33.4 [3d, J_{CP} = 4, C^2(Cy)], 28.7, 28.5, 28.4, 28.1 [4d, J_{CP} = 10, C^3(Cy)], 26.3, 26.2 [2s, C^4(Cy)].

*4.2. Preparation of cis-[$Mo_2Cp_2\{\mu$-η^2:η^2-C(Ph)S$\}(\mu$-$PCy_2)(CO)_2$] (**cis-3**).*

A tetrahydrofuran solution (5 mL) containing compound ***trans*-3** (0.050 g, 0.072 mmol) was irradiated with visible-UV light for 25 min with a gentle N_2 purge to give a brown solution. The solvent was then removed under vacuum, the residue extracted with dichloromethane/petroleum ether (1/10) and the extracts chromatographed through an alumina column (activity IV). Elution with dichloromethane/petroleum ether (1/1) gave a brown fraction yielding, after removal of solvents under vacuum, compound ***cis*-3** as an orange microcrystalline solid (0.047 g, 94%). The crystals used in the X-ray study were grown by the slow diffusion of a layer of petroleum ether into a concentrated diethyl ether solution of the complex at 253 K. Anal. Calc. for $C_{31}H_{37}Mo_2O_2PS$: C, 53.45; H, 5.35; S, 4.60. Found: C, 53.26; H, 4.97; S, 4.40. ^{1}H NMR: δ 7.09 [false t, J_{HH} = 7, 2H, H^3(Ph)], 6.93 [false d, J_{HH} = 7, 2H, H^2(Ph)], 6.86 [t, J_{HH} = 7, 1H, H^4(Ph)], 4.91 (s, 10H, Cp), 1.90-1.20 (m, 22 H, Cy). ^{13}C{^{1}H} NMR (233 K): δ 243.0 (d, J_{CP} = 10, MoCO), 155.5 [s, C^1(Ph)], 128.3 [s, C^{2,3}(Ph)], 123.3 [s, C^4(Ph)], 89.5 (s, Cp), 87.0 [d, br, J_{CP} = 22, CS), 51.8 [d, J_{CP} = 11, C^1(Cy)], 51.7 [d, br, J_{CP} = 19, C^1(Cy)], 35.0 [s, C^2(Cy)], 34.4 [d, J_{CP} = 4, C^2(Cy)], 28.6 [d, J_{CP} = 10, 2C^3(Cy)], 26.6, 26.5 [2s, C^4(Cy)].

*4.3. Preparation of trans-[$Mo_2Cp_2\{\mu$-η^2:η^2-C(Ph)Se$\}(\mu$-$PCy_2)(CO)_2$] (**trans-4**).*

The procedure is identical to that described for ***trans*-3**, but using grey Se (0.010 g, 0.0125 mequiv) instead of S_8. After similar workup, compound ***trans*-4** was isolated as an orange microcrystalline solid (0.053 g, 92%). Anal. Calc. for $C_{31}H_{37}Mo_2O_2PSe$: C, 50.08; H, 5.02. Found: C, 49.68; H, 5.20. ^{1}H NMR: δ 7.07 [m, 4H, H^{2,3}(Ph)], 6.95 [m, 1H, H^4(Ph)], 5.22, 5.12 (2d, J_{HH} = 1, 2 × 5H, Cp), 2.10-1.00 (m, 22 H, Cy). ^{13}C{^{1}H} NMR (75.46 MHz): δ 242.8 (d, J_{CP} = 11, MoCO), 238.5 (d, J_{CP} = 7, MoCO), 155.2 [s,

C^1(Ph)], 130.7 [s, C^3(Ph)], 127.5 [s, C^2(Ph)], 124.8 [s, C^4(Ph)], 91.0, 90.4 (2s, Cp), 89.6 (s, CSe), 51.7 [d, J_{CP} = 22, C^1(Cy)], 51.6 [s, C^1(Cy)], 36.8, 36.5 [2d, J_{CP} = 4, C^2(Cy)], 34.8, 33.9 [2d, J_{CP} = 5, C^2(Cy)], 29.3, 29.1, 28.8 [3d, J_{CP} = 11, C^3(Cy)], 28.6 [d, J_{CP} = 10, C^3(Cy)], 26.9, 26.8 [2s, C^4(Cy)].

*4.4. Preparation of cis-[$Mo_2Cp_2\{\mu$-η^2:η^2-C(Ph)Se$\}(\mu$-$PCy_2)(CO)_2$] (**cis-4**).*

The procedure is identical to that described for ***cis*-3**, but using ***trans*-4** (0.050 g, 0.067 mmol) instead of ***trans*-3**. After similar workup, compound ***cis*-4** was isolated as an orange microcrystalline solid (0.046 g, 92%). Anal. Calc. for $C_{31}H_{37}Mo_2O_2PSe$: C, 50.08; H, 5.01. Found: C, 49.80; H, 4.82. ^{1}H NMR: δ 7.06 [false t, J_{HH} = 7, 2H, H^3(Ph)], 6.96 [false d, J_{HH} = 7, 2H, H^2(Ph)], 6.85 [t, J_{HH} = 7, 1H, H^4(Ph)], 4.91 (s, 10H, Cp), 1.90-1.20 (m, 22 H, Cy).

*4.5. X-ray data collection, structure determination and refinements for compounds **trans-3** and **cis-3**.*

The X-ray intensity data for both compounds were collected on a Kappa-Appex-II Bruker diffractometer using graphite-monochromated Mo K_α radiation at 100 K. The software APEX was used for collecting frames with the ω/ϕ scans measurement method [21]. The Bruker SAINT software was used for data reduction [22], and a multi-scan absorption correction was applied with SADABS [23]. Using the program suite WinGX [24], the structures were solved by Patterson interpretation and phase expansion using SHELXL2014 [25], and refined with full-matrix least squares on F^2 using SHELXL2014. All hydrogen atoms were geometrically placed and refined using a riding model, and all positional parameters and anisotropic temperature factors for all non-H atoms were anisotropically refined in general. In complex ***trans*-3**, one cyclopentadienyl ligand was disordered over two positions, satisfactorily refined with 0.7/0.3 occupancies. For compound ***cis*-3**, two independent but otherwise similar molecules were present in the asymmetric unit and one of the cyclohexyl groups was disordered over two positions, satisfactorily refined with 0.8/0.2 occupancies. In both compounds the carbon atoms involved in disorder were refined isotropically to prevent their temperature factors from becoming non-positive definite.

Table 4. Crystal data for compounds **3**.

	***trans*-3**	***cis*-3**
Mol formula	$C_{31}H_{37}Mo_2O_5PS$	$C_{31}H_{37}Mo_2O_5PS$
Mol weight	696.52	696.52
Cryst syst	Monoclinic	Monoclinic
Space group	*P* 2_1/n	*P* 2_1/c
Radiation (λ, Å)	0.71073	0.71073
a (Å)	11.6663(6)	24.2091(8)
b (Å)	18.8450(9)	10.6337(4)
c (Å)	13.1517(6)	22.3230(10)
α (°)	90	90
β (°)	93.777(2)	97.2100(10)
γ (°)	90	90
V (Å^3)	2885.1(2)	5701.2(4)
Z	4	8
Calcd density (g cm^{-3})	1.604	1.623
Absorp coeff. (mm^{-1})	1.024	1.036
Temperature (K)	100.0(1)	100.0(1)
θ range (°)	1.89 to 28.45	1.70 to 26.02
index ranges (*h*, *k*, *l*)	–15, 15; 0, 25 0, 17	–29, 29; 0, 13 0, 27
No. of reflns collected	32588	46123
No. of indep reflns (R_{int})	7223 (0.1226)	11225 (0.0899)
Reflns with [$I > 2\sigma(I)$]	4058	7804
R indexes [data with I > 2σ(I)][a]	R_1 = 0.0522, wR_2 = 0.1217 [b]	R_1 = 0.0516, wR_2 = 0.0882[c]
R indexes (all data)[b]	R_1 = 0.0883, wR_2 = 0.1104[b]	R_1 = 0.0837 wR_2 = 0.097[c]
GOF	0.994	1.018
No. of restraints/params	0/329	0/657
$\Delta\rho$(max., min.), eÅ^{-3}	0.753 / –0.702	0.897 / –0.712

[a] $R_1 = \Sigma\|Fo| - |Fc\|/\Sigma|Fo|$. $wR_2 = [\Sigma w(|Fo|^2 - |Fc|^2)^2/\Sigma w|Fo|^2]^{1/2}$. $w = 1/[\sigma^2(Fo^2) + (aP)^2 + bP]$ where $P = (Fo^2 + 2Fc^2)/3$.
[b] a = 0.0315, b = 0.0000.
[c] a = 0.0296, b = 0.0000.

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Appendix A. Supplementary Data

CCDC 1507413-1507414 contain the supplementary crystallographic data for compounds ***trans*-3** and ***cis*-3**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] M.A. Alvarez, M.E. García, S. Menéndez, M.A. Ruiz, Organometallics 30 (2011) 3694.

[2] M.A. Alvarez, M.E. García, D. García-Vivó, S. Menéndez, M.A. Ruiz, Organometallics 32 (2013) 218.

[3] Thioacyl-bridged complexes having Mo atoms: (a) H. Alper, F.W.B. Einstein, F.W. Hartstock, A.C Willis, J. Am. Chem. Soc. 107 (1985) 173. (b) H. Alper, F.W.B. Einstein, F.W. Hartstock, A.C. Willis, Organometallics 5 (1986) 9. (c) M.E. García, J.C. Jeffery, P. Sherwood, F.G.A. Stone, J. Chem. Soc., Chem. Commun. (1986) 802. (d) P.G. Byrne, M.E. García, J.C. Jeffery, P. Sherwood, F.G.A. Stone, J. Chem. Soc., Dalton Trans. (1987) 1215. (e) P. Mathur, C. Srinivasu, S.M. Mobin, J. Organomet. Chem. 665 (2003) 226.

[4] For thioacyl-bridged complexes having other metal atoms see, for instance: (a) H. Umland, F. Edelmann, D. Wormsbacher, U. Behrens, Angew. Chem., Int. Ed. Engl. 22 (1983) 153. (b) W. Ziegler, H. Umland, U. Behrens, J. Organomet. Chem. 344 (1988) 235. (c) A. Martin, M.J. Mays, P.R. Raithby, G.A. Solan, J. Chem. Soc., Dalton Trans. (1993) 1789. (d) Y.-C. Shi, Y. Shi, Inorg. Chim. Acta 434 (2015) 92.

[5] R. Aumann, H. Heinen, G. Henkel, M. Dartmann, B. Krebs. Z. Naturforsch., B. 38 (1983) 1325.

[6] L.M. Caldwell, R.L. Cordiner, A.F. Hill, J. Wagler, Organometallics 29 (2010) 1526.

[7] (a) M.D. Bermudez, E. Delgado, G.P. Elliot. N.H. Tran-Huy, F. Mayor-Real, F.G.A. Stone, M.J. Winter, J. Chem. Soc., Dalton Trans. (1987) 1235. (b) E. Delgado, J. Hein, J.C. Jeffery, A.L. Rattermann, F.G.A. Stone, L.J. Farrugia, J. Chem. Soc., Dalton Trans. (1987) 1191. (c) A.F. Hill, B.A. Nasir, F.G.A. Stone, Polyhedron 8 (1989) 179. (d) S. Anderson, A.F. Hill, B.A. Nasir, Organometallics 14 (1995) 2987.

[8] (a) M.A. Alvarez, M.E. García, A. Ramos, M.A. Ruiz, Organometallics 26 (2007) 1461. (b) M.A. Alvarez, M.E. García, D. García-Vivó, M.A. Ruiz, M.F. Vega, Organometallics 32 (2013) 4543.

[9] M.A. Alvarez, M.E. García, D. García-Vivó, M.E. Martínez, A. Ramos, M.A. Ruiz, Dalton Trans. 43 (2014) 7780.

[10] (a) M.A. Alvarez, M.E. García, D. García-Vivó, A. Ramos, M.A. Ruiz, Inorg. Chem. 50 (2011) 2064. (b) M.A. Alvarez, M.E. García, D. García-Vivó, A. Ramos, M.A. Ruiz, Inorg. Chem. 51 (2012) 11061. (c) M.A. Alvarez, M.E. García, D. García-Vivó, R. Lozano, A. Ramos, M.A. Ruiz, Inorg. Chem. 52 (2013) 9005.

[11] M.A. Alvarez, M.E. García, D. García-Vivó, M.E. Martínez, M.A. Ruiz, Organometallics 30 (2011) 2189.
[12] B. Cordero, V. Gómez, A.E. Platero-Prats, M. Revés, J. Echeverría, E. Cremades, F. Barragán, S. Alvarez, Dalton Trans. (2008) 2832.
[13] P. Pyykkö, M. Atsumi, Chem. Eur. J. 15 (2009) 12770.
[14] M.A. Alvarez, M.E. García, M.E. Martínez, M.A. Ruiz, Organometallics 29 (2010) 904.
[15] P.S. Braterman, Metal Carbonyl Spectra, Academic Press, London, U.K., 1975.
[16] M.E. García, D. García-Vivó, M.A. Ruiz, S. Alvarez, G. Aullón, Organometallics 26 (2007) 5912.
[17] M.E. García, V. Riera, M.A. Ruiz, M.T. Rueda, D. Sáez, Organometallics 21 (2002) 5515.
[18] (a) C.J. Jameson, in Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis, J.G. Verkade, L.D. Quin, Eds., VCH, New York, 1987, Chapter 6. (b) B. Wrackmeyer, H.G. Alt, H.E. Maisel, J. Organomet. Chem. 399 (1990) 125.
[19] R.C.S. Wong, M. L. Ooi, S.W. Ng, private communication to the Cambridge Crystallographic Data Centre (2013, deposition No. CCDC 934025).
[20] W.L.F. Armarego, C.C.C. Chai, Purification of Laboratory Chemicals, 7th ed., Butterworth-Heinemann, Oxford, U. K., 2012.
[21] APEX 2, version 2.0-1, Bruker AXS Inc, Madison, WI, 2005.
[22] SMART & SAINT Software Reference Manuals, version 5.051, Bruker Analytical X-ray Instruments, Madison, WI, 1998.
[23] G.M. Sheldrick, SADABS, Program for Empirical Absorption Correction, University of Göttingen, Göttingen, Germany, 1996.
[24] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.
[25] G.M. Sheldrick, Acta Crystallogr., Sect. A, 64 (2008) 112.

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Synopsis

C–E coupling (E = S, Se) takes place in the reactions of the title benzylidyne-bridged complex with elemental chalcogens to give the corresponding chalcogenoacyl-bridged derivatives, which can be isomerized photochemically with little perturbation of the bridging ligand, specifically placed with the chalcogen atom *trans* to P.

Pictogram for Graphical Abstract