



# Alkyne to carbyne coupling reactions of the unsaturated methoxycarbyne-bridged complex $[\text{Mo}_2(\eta^5\text{-C}_5\text{H}_5)_2(\mu\text{-COMe})(\mu\text{-PCy}_2)(\text{CO})_2]$

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## ABSTRACT

The 32-electron complex  $[\text{Mo}_2\text{Cp}_2(\mu\text{-COMe})(\mu\text{-PCy}_2)(\text{CO})_2]$  ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ ) reacts at 333 K with terminal alkynes  $\text{HC}\equiv\text{CR}$  to give the corresponding derivatives  $[\text{Mo}_2\text{Cp}_2\{\mu\text{-}\kappa^2\text{-}\eta^3\text{-CRCHC(OMe)}\}(\mu\text{-PCy}_2)(\text{CO})_2]$ , ( $\text{R} = p\text{-tol, CO}_2\text{Me}$ ), with good yields. These compounds are both obtained selectively as *trans*-dicarbonyl isomers and display a propenyl-ylidene type ligand bridging the dimetal centre, derived from the specific coupling of the alkyne to the carbyne ligand through the terminal carbon atom of the alkyne. The reaction with the internal alkyne  $(\text{MeO}_2\text{C})\text{C}\equiv\text{C}(\text{CO}_2\text{Me})$  gives the related derivative  $[\text{Mo}_2\text{Cp}_2\{\mu\text{-}\kappa^2\text{-}\eta^3\text{-C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\text{C(OMe)}\}(\mu\text{-PCy}_2)(\text{CO})_2]$ , but now this product is obtained as an equimolar mixture of the corresponding *trans*- and *cis*-dicarbonyl isomers. The structures of the new compounds are discussed on the basis of the available spectroscopic data in solution and an X-ray diffraction analysis of the product derived from *p*-tolylacetylene ( $\text{Mo}–\text{Mo} = 2.8646(8) \text{ \AA}$ ).

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## 1. Introduction

The chemistry of carbyne complexes is a well-developed field within the organometallic science. These complexes usually display a high reactivity derived from the multiple nature of their metal–carbon bonds in either the terminal or the edge-bridging coordination modes, which can be further increased in the latter case by the presence of multiple metal–metal bonds (Chart 1) [1], and they are also involved in several industrial processes of interest such as the Fisher–Tropsch (FT) synthesis of hydrocarbons from syngas ( $\text{CO} + \text{H}_2$ ) [2] and the alkyne metathesis [3]. In contrast, the chemistry of alkoxycarbyne compounds is considerably less developed, especially in the case of binuclear complexes having multiple metal–metal bonds. We thus initiated a systematic study of the reactivity of such unsaturated species, focused first on cationic binuclear complexes with 32- and 30-electron counts [4,5], and then on an electron-richer species, the neutral 30-electron complex  $[\text{Mo}_2\text{Cp}_2(\mu\text{-COMe})(\mu\text{-PCy}_2)(\mu\text{-CO})]$  (**1**) ( $\text{Cp} = \eta^5\text{-C}_5\text{H}_5$ , Chart 2) [6]. Although our experimental results indicate that compound **1** actually displays a remarkable multisite reactivity involving not only its multiple Mo–Mo and Mo–C bonds, but also the essentially single C–O and O–Me bonds of the methoxycarbyne ligand [7], it surprisingly failed to react with alkynes, even under forcing thermal or photochemical conditions. The addition of alkynes is a particularly interesting reaction of carbyne

complexes, it being a central step in the alkyne metathesis process, and it has been previously observed in a few electron-precise alkoxycarbyne-bridged complexes [8]. We thus suspected that the failure of **1** to react with alkynes might have a kinetic (rather than thermodynamic) origin, and therefore we turned our attention to the 32-electron complex  $[\text{Mo}_2\text{Cp}_2(\mu\text{-COMe})(\mu\text{-PCy}_2)(\text{CO})_2]$  (**2**), a derivative of **1** having a more open (and more accessible to external reagents), edge-bridging bioctahedral structure (Chart 2) [7a]. We have shown recently that compound **2** is electron-rich enough to add  $[\text{Au}(\text{PR}_3)]^+$  cations to give heterometallic  $\text{Mo}_2\text{Au}$  clusters [9]. In this paper we report that complex **2** indeed reacts with several alkynes under moderate thermal activation to give with good yields products resulting from the C–C coupling between the methoxycarbyne ligand and the incoming alkyne molecule.

## 2. Results and discussion

### 2.1. Reactions of the carbyne complex **2** with alkynes

The 32-electron complex **2** reacts at 333 K with terminal alkynes  $\text{HC}\equiv\text{CR}$  to give the corresponding derivatives  $[\text{Mo}_2\text{Cp}_2\{\mu\text{-}\kappa^2\text{-}\eta^3\text{-CRCHC(OMe)}\}(\mu\text{-PCy}_2)(\text{CO})_2]$ , [ $\text{R} = p\text{-tol}$  (**3a**),  $\text{CO}_2\text{Me}$  (**3b**)], with good yields (Chart 3). These compounds are both obtained selectively as *trans*-dicarbonyl isomers and display a propenyl-ylidene type ligand bridging the dimetal centre, derived from the specific coupling of the alkyne to the carbyne ligand through

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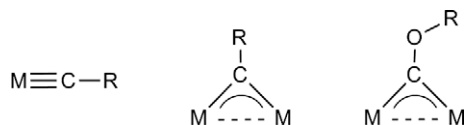


Chart 1.

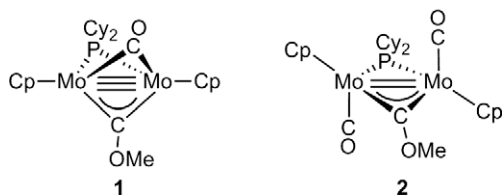


Chart 2.

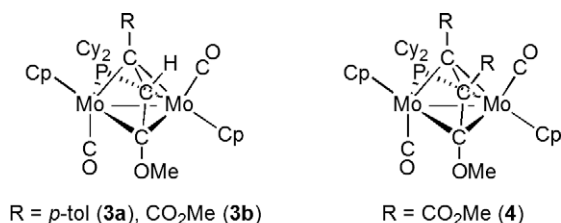


Chart 3.

the terminal carbon atom of the alkyne, possibly more favoured on steric grounds.

A similar reaction takes place between **2** and the internal alkyne  $(\text{MeO}_2\text{C})\text{C}\equiv\text{C}(\text{CO}_2\text{Me})$  to give the related derivative  $[\text{Mo}_2\text{Cp}_2\{\mu-\kappa^2:\eta^3-\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\text{C}(\text{OMe})\}(\mu-\text{PCy}_2)(\text{CO})_2]$ , but now this product is obtained as a roughly equimolar mixture of the corresponding *trans*- (**4**) and *cis*-dicarbonyl (**5**) isomers (Chart 3), that could be conveniently separated using conventional chromatographic techniques. In contrast, no reaction takes place between **2** and diphenylacetylene under the same experimental conditions (toluene solution, 333 K). We should note here that no more forcing conditions can be used when examining the reactivity of compound **2**, because extensive decomposition of this molecule takes place above 333 K whereas, on the other hand, decarbonylation to give complex **1** occurs rapidly under photochemical activation.

## 2.2. Crystal structure of compound **3a**

The structure of this complex in the crystal is depicted in Fig. 1 and the most relevant bond distances and angles are collected in Table 1. The molybdenum atoms are bridged by a rather symmetrical dicyclohexylphosphine ligand ( $\text{Mo}-\text{P}$  ca. 2.46 Å) and by a 5-electron donor  $\text{C}(p\text{-tol})-\text{CH}-\text{C}(\text{OMe})$  fragment, with the C(3) and C(5) atoms bonded to Mo(2) [ $\text{Mo}(2)-\text{C}(3) = 2.151(4)$  Å,  $\text{Mo}(2)-\text{C}(5) = 2.220(4)$  Å], and all three carbon atoms of the chain bonded to the other metal atom [ $\text{Mo}(1)-\text{C}(3) = 2.445(4)$  Å,

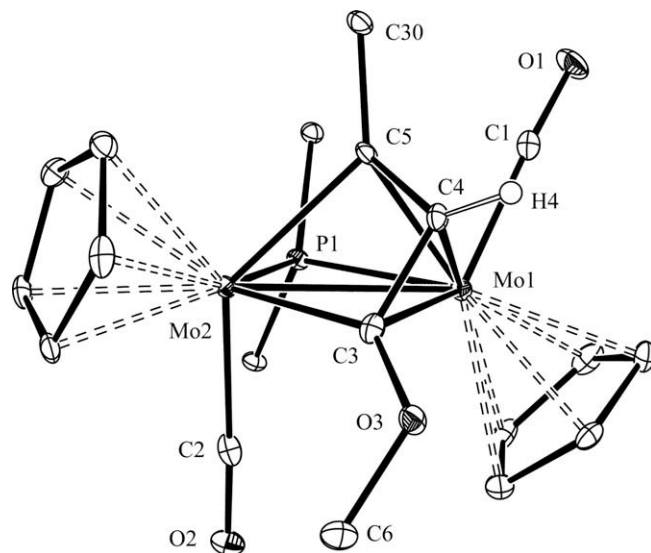


Fig. 1. ORTEP diagram (30% probability) of compound **3a**, with H atoms (except H4), Cy and *p*-tol rings (except C<sup>1</sup> atoms) omitted for clarity.

Table 1

Selected bond lengths (Å) and angles (°) for compound **3a**.

Mo(1)–Mo(2)	2.8646(8)	Mo(2)–C(3)	2.151(4)
Mo(1)–P(1)	2.455(1)	Mo(2)–C(5)	2.220(4)
Mo(2)–P(1)	2.466(1)	C(30)–C(5)	1.478(5)
Mo(1)–C(1)	1.951(4)	C(5)–C(4)	1.444(5)
Mo(2)–C(2)	1.986(4)	C(4)–C(3)	1.405(6)
Mo(1)–C(3)	2.445(4)	C(3)–O(3)	1.356(5)
Mo(1)–C(4)	2.267(4)	O(3)–C(6)	1.440(5)
Mo(1)–C(5)	2.213(4)		
Mo(1)–C(1)–O(1)	176.8(4)	C(4)–C(5)–Mo(2)	96.3(2)
Mo(2)–C(2)–O(2)	176.3(3)	C(5)–Mo(2)–C(3)	60.9(2)
Mo(2)–Mo(1)–C(1)	117.2(1)	P(1)–Mo(1)–C(3)	101.5(1)
Mo(1)–Mo(2)–C(2)	83.8(1)	P(1)–Mo(1)–C(4)	111.6(1)
Mo(1)–P(1)–Mo(2)	71.19(4)	P(1)–Mo(1)–C(5)	78.1(1)
Mo(1)–C(3)–Mo(2)	76.8(1)	P(1)–Mo(1)–C(1)	94.2(1)
Mo(1)–C(5)–Mo(2)	80.5(1)	P(1)–Mo(2)–C(2)	81.6(1)
Mo(2)–C(3)–C(4)	100.6(3)	P(1)–Mo(2)–C(3)	110.3(1)
C(3)–C(4)–C(5)	102.1(3)	P(1)–Mo(2)–C(5)	77.7(1)

$\text{Mo}(1)-\text{C}(4) = 2.267(4)$  Å,  $\text{Mo}(1)-\text{C}(5) = 2.213(4)$  Å]. The intermetallic distance in **3a** [2.8646(8) Å] is some ca. 0.1 Å shorter than that found in the related and isoelectronic cation  $[\text{Mo}_2\text{Cp}_2\{\mu-\kappa^2:\eta^3-\text{CHC}^t\text{BuC}(\text{OH})\}(\mu-\text{Me}_2\text{PCH}_2\text{PMe}_2)(\text{CO})_2]^+$  (2.963(1) Å) [10], a shortening effect expected from the replacement of a diphosphine by a phosphide ligand, and it is nearly identical to that measured in the also isoelectronic formimidoyl complex  $[\text{Mo}_2\text{Cp}_2(\mu-\eta,\kappa:\eta,\kappa-\text{HCN}^t\text{Bu})(\mu-\text{PCy}_2)(\text{CO})_2]$  (2.883(2) Å) [11]. In any case all these values are in agreement with the single Mo–Mo bond that should be proposed for these 34-electron complexes on the basis of the EAN rule. In compound **3a** the hydrocarbon chain and the Mo(2) atom can be alternatively regarded as a metallacyclobutadiene fragment coordinated to the Mo(1) atom. Actually these four atoms lie roughly in the same plane, with the sum of chain angles within the  $\text{MoC}_3$  cycle adding up 359.9°, as graphically illustrated on the left of Fig. 2. This coordination environment is similar to those determined crystallographically for the  $\text{Mo}_2$  cation mentioned above and for the heterodinuclear complexes  $[\text{MoFeCp}\{\mu-\text{C}(p\text{-tol})\text{C}(\text{Me})\text{C}(\text{O})\text{Me}\}(\text{CO})_5]$  and  $[\text{MoFeCp}\{\mu-\text{C}(p\text{-tol})\text{C}(\text{OMe})\text{C}(\text{H})\}(\text{CO})_5]$  [12a,b]. A feature to be noted in the structure of **3a** is the strong asymmetry in the coordination of the hydrocarbon bridge. Since the distances from C(5) to both metal atoms are quite similar (ca. 2.22 Å), the electron density at the dimetal centre would be

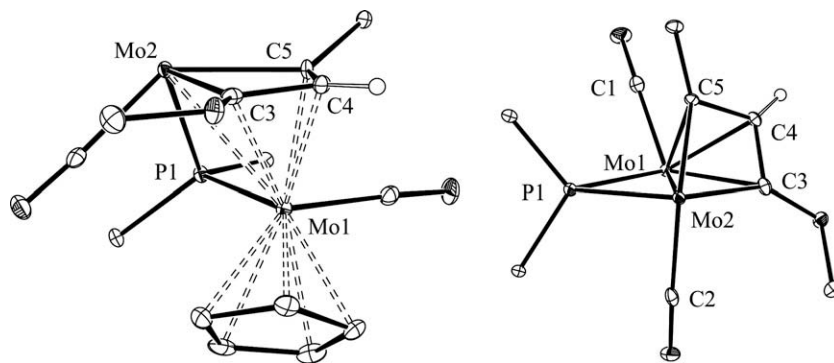


Fig. 2. Simplified ORTEP diagrams (30% probability) of compound **3a**, viewed along the MoC<sub>3</sub> plane (left), or the intermetallic bond (right), with H atoms (except H4), and most of the rings omitted for clarity.

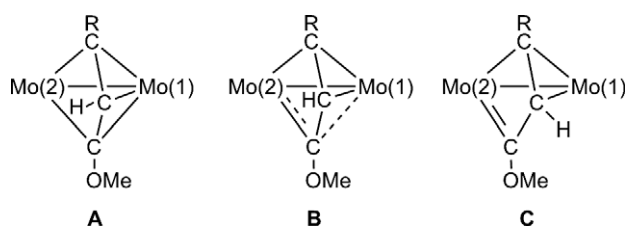


Fig. 3. Coordination modes for bridging CRHC(OMe) ligands at binuclear centres (see text).

unevenly distributed because of the binding of the central C(4) atom to only one of the metal centres (**A** in Fig. 3). This effect seems to be counterbalanced in compound **3a** by the asymmetric coordination of C(3), much closer (by ca. 0.3 Å) to Mo(2) (**B** in Fig. 3). Taken to its final point, this distortion would transform the bridging ligand into an alkenyl-carbene group, and this also would imply an asymmetric distribution of the electron density (**C** in Fig. 3), but now just opposite to the initial situation.

The coordination spheres around the Mo atoms in **3a** are completed by terminal cyclopentadienyl and carbonyl ligands, the latter groups arranged *trans* to each other and placed in very different environments. Thus, the carbonyl group on Mo(1) points away from the dimetal centre [C(1)–Mo(1)–Mo(2) = 117.2(1)°], while the one bound to Mo(2) points towards the intermetallic region [C(2)–Mo(2)–Mo(1) = 83.8(1)°]. This structural effect is also present in the above mentioned Mo<sub>2</sub> complexes and seems to have a steric origin. Thus, in the case of **3a**, the carbonyl ligand bound to the Mo(1) atom would be pointing away from the dimetal centre to avoid unfavourable repulsions with the C(*p*-tol) group, the latter being placed almost in the same plane than the average Mo<sub>2</sub>C plane defined by the carbonyl ligands (Fig. 2, right).

### 2.3. Solution structure of the *trans*-dicarbonyl complexes **3a,b** and **4**

The spectroscopic data in solution for compound **3a** (Table 2) are fully consistent with the structure found in the crystal. Moreover, these data are similar to those for the complexes **3b** and **4**, and therefore it is assumed that all these three complexes have the same structure. The *trans*oid arrangement of the carbonyl ligands in solution is evidenced by the presence in each case of two C–O stretching bands in the corresponding IR spectrum, with medium and strong relative intensities (in order of decreasing frequency), as expected from dicarbonyl oscillators with angles ( $\alpha$ ) between the CO ligands in the range 90° <  $\alpha$  < 180° [13]. The distinct environments of the two CO ligands in each case is reflected in the appearance of quite separated <sup>13</sup>C resonances (ca. 250 and

Table 2  
Selected IR<sup>a</sup> and <sup>31</sup>P{<sup>1</sup>H} NMR<sup>b</sup> data for new compounds.

Compound	$\nu(\text{CO})$	$\delta_{\text{P}}$
[Mo <sub>2</sub> Cp <sub>2</sub> { $\mu$ - $\kappa^2$ : $\eta^3$ -C( <i>p</i> -tol)CHC(OMe)}]( $\mu$ -PCy <sub>2</sub> )-(CO) <sub>2</sub> ] ( <b>3a</b> )	1887 (m, sh), 1869 (vs)	134.7
[Mo <sub>2</sub> Cp <sub>2</sub> { $\mu$ - $\kappa^2$ : $\eta^3$ -C(CO <sub>2</sub> Me)CHC(OMe)}]( $\mu$ -PCy <sub>2</sub> )-(CO) <sub>2</sub> ] ( <b>3b</b> )	1903 (m, sh), 1883 (vs) <sup>c</sup>	142.2 <sup>d</sup>
<i>trans</i> -[Mo <sub>2</sub> Cp <sub>2</sub> { $\mu$ - $\kappa^2$ : $\eta^3$ -C(CO <sub>2</sub> Me)C(CO <sub>2</sub> Me)C(OMe)}]( $\mu$ -PCy <sub>2</sub> )(CO) <sub>2</sub> ] ( <b>4</b> )	1922 (s), 1892 (vs) <sup>e</sup>	144.3
<i>cis</i> -[Mo <sub>2</sub> Cp <sub>2</sub> { $\mu$ - $\kappa^2$ : $\eta^3$ -C(CO <sub>2</sub> Me)C(CO <sub>2</sub> Me)C(OMe)}]( $\mu$ -PCy <sub>2</sub> )(CO) <sub>2</sub> ] ( <b>5</b> )	1936 (vs), 1887 (w) <sup>f</sup>	152.1

<sup>a</sup> Recorded in dichloromethane solution, unless otherwise stated,  $\nu$  in cm<sup>-1</sup>.

<sup>b</sup> Recorded in CD<sub>2</sub>Cl<sub>2</sub> solutions at 290 K and 121.50 MHz, unless otherwise stated,  $\delta$  in ppm relative to external 85% aqueous H<sub>3</sub>PO<sub>4</sub>.

<sup>c</sup>  $\nu(\text{C}=\text{O})$ : 1673 (w), 1658 (w).

<sup>d</sup> In C<sub>6</sub>D<sub>6</sub>.

<sup>e</sup>  $\nu(\text{C}=\text{O})$ : 1682 (m).

<sup>f</sup>  $\nu(\text{C}=\text{O})$ : 1691 (w), 1666 (w).

235 ppm) in the corresponding NMR spectra, with the most deshielded resonance exhibiting a stronger coupling to the P nucleus (13 versus 7 Hz, see Section 3). The latter resonance is thus assigned to the (incipiently semibridging) carbonyl ligand pointing towards the intermetallic bond (C(2) in the structure of **3a**), in agreement with its position defining a more acute C–Mo–P angle (81.6(2)° versus 94.2(2)°). It should be recalled here that for complexes of type [MoCpXYL<sub>2</sub>] it is well established that <sup>2</sup>J<sub>PY</sub> coupling constants increase algebraically with the X–Mo–Y angle, they being usually negative at acute angles [14]. As for the hydrocarbon chain, the central CH carbon gives rise to a quite shielded resonance ( $\delta$  ca. 70 ppm) weakly coupled to the phosphorus nucleus, in agreement with its relatively large C–Mo–P angle (111.6(1)° for **3a**), whereas the former carbyne resonance is now identified as the singlet resonance appearing at ca. 200–225 ppm on the basis of its similarly low P–C coupling (C(3)–Mo–P angles ca. 105° for **3a**). Finally, the resonance for the internal carbon of the former alkyne molecule gives rise to a resonance at ca. 80 ppm, strongly coupled to the P nucleus (ca. 28 Hz) in agreement with its positioning closer to the dicyclohexylphosphide bridge, this implying a much more acute C–Mo–P angle (C(5)–Mo–P ca. 78° for **3a**).

### 2.4. Solution structure of the *cis*-dicarbonyl complex **5**

The main structural difference between compound **5** and its isomer **4** is derived from the distinct relative arrangement of the Cp and CO ligands in each case, this being of the *cis*oid type for **5**. Such a circumstance is readily apparent in the corresponding IR spectrum, now displaying two C–O stretching bands of strong and weak relative intensities (in order of decreasing frequency), as

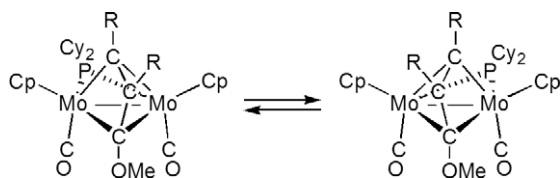


Fig. 4. Fluxional process proposed for compound **5** in solution ( $R = \text{CO}_2\text{Me}$ ).

expected for a  $\text{Mo}_2(\text{CO})_2$  oscillator with carbonyl ligands almost parallel to each other, and crystallographically verified for the related C,C,O-bonded alkenyl complex *cis*- $[\text{Mo}_2\text{Cp}_2\{\mu-\eta^1, \kappa:\eta^2-\text{C}(\text{CO}_2\text{Me})\text{CH}(\text{CO}_2\text{Me})\}(\mu\text{-PCy}_2)(\text{CO})_2]$  [15]. In this sort of structure, the Cp ligands are placed close to the intermetallic axis, and the carbonyl ligands are almost perpendicular to that axis. Therefore, out of the two possible arrangements of the terminal ligands relative to the hydrocarbyl bridging ligand, we propose for compound **5** the one having the CO ligands distal from that bridge, presumably more favoured on steric grounds (Chart 3), as found for the mentioned alkenyl complex. As for the hydrocarbon chain in **5**, the three metal-bound C atoms display shieldings and P–C couplings comparable to those observed for the *trans*-dicarbonyl complexes **3** and **4**, and thus deserve no further comments. However, the fact that both the pairs of carbonyl ( $\delta_{\text{C}} = 240.1$  ppm,  $J_{\text{PC}} = 8$  Hz) and the cyclopentadienyl ligands ( $\delta_{\text{C}} = 88.9$  ppm,  $\delta_{\text{H}} = 5.16$  ppm) give rise in each case to a single  $^{13}\text{C}$  (or  $^1\text{H}$ ) NMR resonance is inconsistent with the static structure proposed for this complex (Chart 3) and therefore suggests the operation of a fluxional process in solution for this molecule. Although we have not investigated the corresponding process in detail, it seems likely that such a process would just involve the alternate binding of the central atom of the hydrocarbon chain to each molybdenum atom thus yielding, on the fast exchange limit, equivalent carbonyl and cyclopentadienyl ligands (Fig. 4). Since such a process is an intramolecular, nondissociative rearrangement, the P–C couplings are preserved in the averaged spectrum, thus explaining the great similarity between the averaged data for **5** and the data for complexes **3** and **4**. We must note, however, that a similar rearrangement could not be completely excluded for the *trans*-dicarbonyl complexes **3** and **4** (this would be an isomerisation process here), although no spectroscopic evidence would follow from it, because in those cases the carbonyl and cyclopentadienyl ligands would remain inequivalent in the fast exchange limit.

### 3. Experimental

All manipulations and reactions were carried out under a nitrogen (99.995%) atmosphere using standard Schlenk techniques. Solvents were purified according to literature procedures, and distilled prior to use [16]. Compound **2** was prepared as described previously [7a], and all other reagents were obtained from the usual commercial suppliers and used as received, unless otherwise stated. Petroleum ether refers to that fraction distilling in the range 338–243 K. Chromatographic separations were carried out using jacketed columns cooled by tap water at ca. 288 K or by a closed 2-propanol circuit, kept at the desired temperature with a cryostat. Commercial aluminium oxide (activity I, 150 mesh) was degassed under vacuum prior to use. The latter 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  $\text{CaF}_2$  windows and are referred to as  $\nu(\text{CO})$ . Nuclear magnetic resonance (NMR) spectra were routinely recorded at 300.13 ( $^1\text{H}$ ), 121.50 ( $^{31}\text{P}\{^1\text{H}\}$ ) or 75.47 MHz ( $^{13}\text{C}\{^1\text{H}\}$ ), at 290 K in  $\text{CD}_2\text{Cl}_2$  solutions unless otherwise stated. Chemical shifts ( $\delta$ ) are given in ppm, relative to internal tetramethylsilane ( $^1\text{H}$ ,  $^{13}\text{C}$ ) or external

85% aqueous  $\text{H}_3\text{PO}_4$  solutions ( $^{31}\text{P}$ ). Coupling constants ( $J$ ) are given in Hertz.

#### 3.1. Preparation of $[\text{Mo}_2\text{Cp}_2\{\mu-\kappa^2:\eta^3-\text{C}(p\text{-tol})\text{CHC}(\text{OMe})\}(\mu\text{-PCy}_2)(\text{CO})_2]$ (**3a**)

Neat  $\text{HC}\equiv\text{C}(p\text{-tol})$  (50  $\mu\text{L}$ , 0.394 mmol;  $p\text{-tol} = 4\text{-C}_6\text{H}_4\text{Me}$ ) was added to a solution of compound **2** (0.050 g, 0.081 mmol) in toluene (15 mL), and the mixture was stirred for 2.5 h at 333 K to yield an orange solution. After removal of the solvent under vacuum, the residue was extracted with dichloromethane–petroleum ether (1:5) and the extracts were chromatographed through alumina (activity IV) at 263 K. An orange fraction was eluted with the same solvent mixture which gave, after removal of solvents under vacuum, compound **3a** as an orange microcrystalline solid (0.038 g, 64%). Crystals suitable for X-ray diffraction analysis were obtained by the slow diffusion of a layer of petroleum ether into a concentrated solution of the compound in dichloromethane at 253 K. Anal. Calc. for  $\text{C}_{35}\text{H}_{43}\text{Mo}_2\text{O}_3\text{P}$ : C, 57.23; H, 5.90. Found: C, 57.12; H, 5.71%.  $^1\text{H}$  NMR (400.13 MHz)  $\delta$  6.88 (d,  $J_{\text{HH}} = 7.5$ ,  $\text{C}_6\text{H}_4$ , 2H), 6.57 (d,  $J_{\text{HH}} = 7.5$ ,  $\text{C}_6\text{H}_4$ , 2H), 5.64 (d,  $J_{\text{HP}} = 2$ , CH, 1H), 5.08, 4.97 (2s, Cp,  $2 \times 5\text{H}$ ), 3.66 (s, OMe, 3H), 2.24 (s, Me, 3H), 2.20–0.70 (m, Cy, 22H).  $^{13}\text{C}\{^1\text{H}\}$  NMR  $\delta$  248.4 (d,  $J_{\text{CP}} = 13$ , MoCO), 240.1 (d,  $J_{\text{CP}} = 7$ , MoCO), 201.3 (s,  $\mu\text{-COMe}$ ), 147.3 [s,  $\text{C}^1(\text{C}_6\text{H}_4)$ ], 133.3 [s,  $\text{C}^4(\text{C}_6\text{H}_4)$ ], 127.4 [s,  $\text{C}^2$  and  $\text{C}^3(\text{C}_6\text{H}_4)$ ], 90.3, 88.6 (2s, Cp), 89.9 [d,  $J_{\text{CP}} = 28$ ,  $\mu\text{-C}(\text{C}_6\text{H}_4)$ ], 72.6 (d,  $J_{\text{CP}} = 5$ , CH), 59.8 (s, OMe), 51.8 [d,  $J_{\text{CP}} = 14$ ,  $\text{C}^1(\text{Cy})$ ], 48.1 [d,  $J_{\text{CP}} = 3$ ,  $\text{C}^1(\text{Cy})$ ], 38.2 [s,  $\text{C}^2(\text{Cy})$ ], 36.2 [d,  $J_{\text{CP}} = 6$ ,  $\text{C}^2(\text{Cy})$ ], 36.0 [d,  $J_{\text{CP}} = 4$ ,  $\text{C}^2(\text{Cy})$ ], 35.6 [d,  $J_{\text{CP}} = 2$ ,  $\text{C}^2(\text{Cy})$ ], 29.9 [d,  $J_{\text{CP}} = 7$ ,  $\text{C}^3(\text{Cy})$ ], 29.5, 28.9, 28.1 [3d,  $J_{\text{CP}} = 10$ ,  $\text{C}^3(\text{Cy})$ ], 27.0, 26.9 [2s,  $\text{C}^4(\text{Cy})$ ], 21.0 (s, Me).

#### 3.2. Preparation of $[\text{Mo}_2\text{Cp}_2\{\mu-\kappa^2:\eta^3-\text{C}(\text{CO}_2\text{Me})\text{CHC}(\text{OMe})\}(\mu\text{-PCy}_2)(\text{CO})_2]$ (**3b**)

Neat  $\text{HC}\equiv\text{C}(\text{CO}_2\text{Me})$  (40  $\mu\text{L}$ , 0.450 mmol) was added to a solution of compound **2** (0.050 g, 0.081 mmol) in toluene (15 mL), and the mixture was stirred for 2 h at 333 K to yield an orange solution. After removal of the solvent under vacuum, the residue was extracted with dichloromethane–petroleum ether (1:5) and the extracts were chromatographed through alumina (activity IV) at 273 K. An orange fraction was eluted with dichloromethane–petroleum ether (2:1) which gave, after removal of solvents under vacuum, compound **3b** as an orange microcrystalline solid (0.039 g, 68%). Anal. Calc. for  $\text{C}_{30}\text{H}_{39}\text{Mo}_2\text{O}_5\text{P}$ : C, 51.29; H, 5.59. Found: C, 51.37; H, 5.76%.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  5.75 (d,  $J_{\text{HP}} = 3$ , CH, 1H), 4.96, 4.74 (2s, Cp,  $2 \times 5\text{H}$ ), 3.52, 3.27 (2s, OMe,  $2 \times 3\text{H}$ ), 2.60–0.70 (m, Cy, 22H).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ )  $\delta$  250.2 (d,  $J_{\text{CP}} = 13$ , MoCO), 236.8 (d,  $J_{\text{CP}} = 7$ , MoCO), 203.9 (s,  $\mu\text{-COMe}$ ), 177.5 (s,  $\text{CO}_2\text{Me}$ ), 89.9, 88.0 (2s, Cp), 76.9 [d,  $J_{\text{CP}} = 27$ ,  $\mu\text{-C}(\text{CO}_2\text{Me})$ ], 73.1 (d,  $J_{\text{CP}} = 5$ , CH), 59.7, 50.9 (2s, OMe), 51.7 [d,  $J_{\text{CP}} = 13$ ,  $\text{C}^1(\text{Cy})$ ], 47.0 [d,  $J_{\text{CP}} = 5$ ,  $\text{C}^1(\text{Cy})$ ], 37.7 [d,  $J_{\text{CP}} = 2$ ,  $\text{C}^2(\text{Cy})$ ], 37.2 [d,  $J_{\text{CP}} = 6$ ,  $\text{C}^2(\text{Cy})$ ], 35.5 [m,  $2\text{C}^2(\text{Cy})$ ], 29.3 [d,  $J_{\text{CP}} = 10$ ,  $\text{C}^3(\text{Cy})$ ], 29.2, 28.6 [2d,  $J_{\text{CP}} = 11$ ,  $\text{C}^3(\text{Cy})$ ], 28.7 [d,  $J_{\text{CP}} = 9$ ,  $\text{C}^3(\text{Cy})$ ], 27.4, 26.8 [2s,  $\text{C}^4(\text{Cy})$ ].

#### 3.3. Reaction of compound **2** with $\text{C}_2(\text{CO}_2\text{Me})_2$

Neat  $(\text{MeO}_2\text{C})\text{C}\equiv\text{C}(\text{CO}_2\text{Me})$  (50  $\mu\text{L}$ , 0.407 mmol) was added to a solution of compound **2** (0.050 g, 0.081 mmol) in toluene (15 mL), and the mixture was stirred for 2.5 h at 333 K to yield an orange solution containing a roughly equimolar mixture of the isomers *trans*- and *cis*- $[\text{Mo}_2\text{Cp}_2\{\mu-\kappa^2:\eta^3-\text{C}(\text{CO}_2\text{Me})\text{C}(\text{CO}_2\text{Me})\text{C}(\text{OMe})\}(\mu\text{-PCy}_2)(\text{CO})_2]$  (**4** and **5**, respectively). After removal of the solvent under vacuum, the residue was extracted with tetrahydrofuran–petroleum ether (1:4) and the extracts were chromatographed through alumina (activity IV) at 253 K. An orange fraction was eluted with the same solvent mixture which gave, after removal

**Table 3**  
Crystal data for compound **3a**.

Molecular formula	C <sub>35</sub> H <sub>43</sub> Mo <sub>2</sub> O <sub>3</sub> P
Molecular weight	734.54
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
Radiation ( $\lambda$ , Å)	0.71073
<i>a</i> (Å)	9.513(2)
<i>b</i> (Å)	10.040(3)
<i>c</i> (Å)	16.723(5)
$\alpha$ (°)	95.616(14)
$\beta$ (°)	103.66(3)
$\gamma$ (°)	92.203(18)
<i>V</i> (Å <sup>3</sup> )	1541.5(8)
<i>Z</i>	2
Calculated density (g cm <sup>-3</sup> )	1.583
Absorption coefficient (mm <sup>-1</sup> )	0.9
Temperature (K)	120
$\theta$ Range (°)	1.26–26.41
Index ranges ( <i>h</i> , <i>k</i> , <i>l</i> )	–11, 11; –12, 12; 0, 20
Reflections collected	16 720
Independent reflections [ <i>R</i> <sub>int</sub> ]	6288 [0.0484]
Reflections with $I > 2\sigma(I)$	4559
<i>R</i> indexes [ $I > 2\sigma(I)$ ] <sup>a</sup>	<i>R</i> <sub>1</sub> = 0.0369, <i>wR</i> <sub>2</sub> = 0.0906 <sup>b</sup>
<i>R</i> indexes (all data) <sup>a</sup>	<i>R</i> <sub>1</sub> = 0.0617, <i>wR</i> <sub>2</sub> = 0.0985 <sup>b</sup>
Goodness-of-fit (GOF)	1.005
Restraints/parameters	0/370
$\Delta\rho$ (max, min) (e Å <sup>-3</sup> )	0.819, –0.709

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ,  $wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum w|F_o|^2]^{1/2}$ ;  $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ , where  $P = (F_o^2 + 2F_c^2)/3$ .

<sup>b</sup>  $a = 0.0532$ ,  $b = 0.0000$ .

of solvents under vacuum, compound **5** as an orange solid (0.027 g, 44%). Elution with tetrahydrofuran–petroleum ether (1:1) gave a second orange fraction yielding, after similar workup, compound **4** as an orange solid (0.024 g, 39%). *Data for compound 4*: Anal. Calc. for C<sub>32</sub>H<sub>41</sub>Mo<sub>2</sub>O<sub>7</sub>P: C, 50.54; H, 5.43. Found: C, 50.72; H, 5.75%. <sup>1</sup>H NMR  $\delta$  5.13 (s, Cp, 5H), 4.87 (d, *J*<sub>HP</sub> = 1, Cp, 5H), 3.83, 3.52, 2.36 (3s, OMe, 3  $\times$  3H), 2.20–1.00 (m, Cy, 22H). <sup>13</sup>C{<sup>1</sup>H} NMR  $\delta$  249.2 (d, *J*<sub>CP</sub> = 13, MoCO), 232.6 (d, *J*<sub>CP</sub> = 7, MoCO), 225.6 (s,  $\mu$ -COMe), 176.6, 166.4 (2s, CO<sub>2</sub>Me), 91.3, 89.2 (2s, Cp), 80.4 [d, *J*<sub>CP</sub> = 28,  $\mu$ -C(CO<sub>2</sub>Me)], 66.3 [d, *J*<sub>CP</sub> = 6, C(CO<sub>2</sub>Me)], 62.4, 51.1, 50.4 (3s, OMe), 52.2 [d, *J*<sub>CP</sub> = 14, C<sup>1</sup>(Cy)], 47.2 [d, *J*<sub>CP</sub> = 5, C<sup>1</sup>(Cy)], 37.2, 35.2, 34.7 [3d, *J*<sub>CP</sub> = 4, C<sup>2</sup>(Cy)], 36.8 [d, *J*<sub>CP</sub> = 5, C<sup>2</sup>(Cy)], 29.3, 28.9, 28.7 [3d, *J*<sub>CP</sub> = 10, C<sup>3</sup>(Cy)], 28.6 [d, *J*<sub>CP</sub> = 13, C<sup>3</sup>(Cy)], 27.0, 26.7 [2s, C<sup>4</sup>(Cy)]. *Data for compound 5*: Anal. Calc. for C<sub>32</sub>H<sub>41</sub>Mo<sub>2</sub>O<sub>7</sub>P: C, 50.54; H, 5.43. Found: C, 50.67; H, 5.64%. <sup>1</sup>H NMR  $\delta$  5.16 (s, Cp, 10H), 3.88, 3.59, 3.45 (3s, OMe, 3  $\times$  3H), 2.10–1.10 (m, Cy, 22H). <sup>13</sup>C{<sup>1</sup>H} NMR  $\delta$  240.1 (d, *J*<sub>CP</sub> = 8, 2  $\times$  MoCO), 205.0 (s,  $\mu$ -COMe), 178.6, 166.1 (2s, CO<sub>2</sub>Me), 88.9 (s, Cp), 75.6 [d, *J*<sub>CP</sub> = 6, C(CO<sub>2</sub>Me)], 65.9 [d, *J*<sub>CP</sub> = 29,  $\mu$ -C(CO<sub>2</sub>Me)], 61.4, 51.2, 51.1 (3s, OMe), 50.9 [d, *J*<sub>CP</sub> = 16, C<sup>1</sup>(Cy)], 48.4 [d, *J*<sub>CP</sub> = 8, C<sup>1</sup>(Cy)], 35.5 [d, *J*<sub>CP</sub> = 3, C<sup>2</sup>(Cy)], 34.8 [d, *J*<sub>CP</sub> = 4, C<sup>2</sup>(Cy)], 28.8, 28.5 [2d, *J*<sub>CP</sub> = 11, C<sup>3</sup>(Cy)], 27.7 [s, C<sup>4</sup>(Cy)].

### 3.4. X-ray structure determination of compound **3a**

The X-ray intensity data were collected on a Smart-CCD-1000 BRUKER diffractometer using graphite-monochromated Mo  $K\alpha$  radiation at 120 K. Cell dimensions and orientation matrixes were initially determined from least-squares refinements on reflections measured in 3 sets of 30 exposures collected in 3 different  $\omega$  regions and eventually refined against all reflections. The software SMART [17] was used for collecting frames of data, indexing reflections, and determining lattice parameters. The collected frames were then processed for integration by the software SAINT [17], and a multi-scan absorption correction was applied with SADABS [18]. Using the program suite WINGX [19] the structure was solved by Patterson interpretation and phase expansion, and refined with full-matrix least-squares on  $F^2$  with SHELXL97 [20]. All non-hydrogen

atoms were refined anisotropically. All the hydrogen atoms were fixed at ideal geometries and were given an overall isotropic thermal parameter. During the final stages of the refinement, all the positional parameters and the anisotropic temperature factors of all the non-H atoms were refined. After convergence, the strongest residual peaks (0.819, –0.709 e Å<sup>-3</sup>) were located around the metal centres. Crystallographic data and structure refinement details for **3a** are collected in Table 3.

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### Appendix A. Supplementary material

CCDC 763494 contains the supplementary crystallographic data for **3a**. 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). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2010.03.020.

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