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Enlargement of the scope of the carbon–carbon coupling reactions between Fischer-type metallaalkylidyne and organopalladium compounds

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Dedicated to Martin Bennett on the occasion of his retirement.

Abstract

The carbyne carbon atom of the 'Fischer-type' metallaalkylidyne complexes: $(\eta^5\text{-}C_5H_5)(CO)_2Mo{\equiv}C\text{-}pTol$ (**1**) is readily coupled with the palladated carbon atom of the organometallic compounds $[Me(PPh_3)Pd(\mu\text{-}X)]_2$, (X = Cl, I; **2**, **3**) affording novel stable μ-alkylidene complexes $[\{Cp(OC)(\mu\text{-}OC)Mo\}\{\mu\text{-}C(4\text{-}Tol)Me\}Pd(PPh_3)X]$ (X = Cl, I; **4**, **5**). Compound **4** has been fully characterised through a crystal structure analysis, which shows that a molybdaalkylidene unit is interacting with a palladium(triphenylphosphine)chloride unit via an alkylidene carbon, the molybdenum and the carbon atom of a carbonyl group. The phosphine and the halide ligands of these new dimetallic complexes can reversibly exchange their role in solution leading to a mixture of isomers in which the phosphine is either *cis* or *trans* to the alkylidene carbon atom bridging the two metals. $[Me(SEt_2)Pd(\mu\text{-}Cl)]_2$ (**6**) led to a chloride bridged dimer (**7**) through the C–C coupling reaction with **1**. Compound **7** allowed the entry into a larger class of μ-alkylidene species structurally related to **4** via bridge-splitting reactions by neutral ligands such as 4-methylpyridine for example to afford **8**. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Palladium; Molybdenum; Metallaalkylidyne; C–C coupling; Insertion

1. Introduction

We have recently shown that so-called 'Fischer-type' metallaalkylidyne complexes (also termed metallacarbyne compounds) may well lead to C–C coupling reactions when they are allowed to react with organopalladium compounds such as cyclopalladated derivatives, the reaction being analogous to the insertion of an alkyne into a Pd–C bond. The isolobal analogy between metallacarbynes and alkynes derivatives has mainly been successful for the development of the coordination chemistry of the former compounds. This has been amply demonstrated by Stone's group who has thus synthesised a wealth of polymetallic compounds [1]. Recent results from our group suggest that an organometallic chemistry of metallacarbynes akin to that of alkynes should also exist and the aim of the present paper is indeed to contribute to the definition of this new field of the chemistry of metallacarbynes [2]. Our previous studies [3–5], focusing on the reaction between metallacarbynes and organometallic compounds, dealt exclusively with Pd compounds derived from the well-known cyclopalladation reaction (i.e. obtained via an intramolecular C–H activation reaction of N-, S- or P-containing ligands) which were already known to exhibit a range of reactivity patterns towards alkynes [6]. We found that these compounds with a Pd–C σ-bond stabilised by intramolecular coordination of a Y atom to Pd, all led to the expected C–C bond formation through reaction with metallaalkylidynes. Moreover, it seemed that these reactions were even

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easier to perform with metallaalkylidynes than with alkynes [6]. We therefore decided to study the insertion of the M≡CR unit into the Pd–C bond of organopalladium compounds lacking an intramolecular coordination bond to the metal in order to check whether the existence of this Y to Pd bond is essential for the stability of the bridged-carbene heterodimetallic compounds. To this end we have chosen a series of halide-bridged compounds such as **2** and **3** as the starting organopalladium materials.

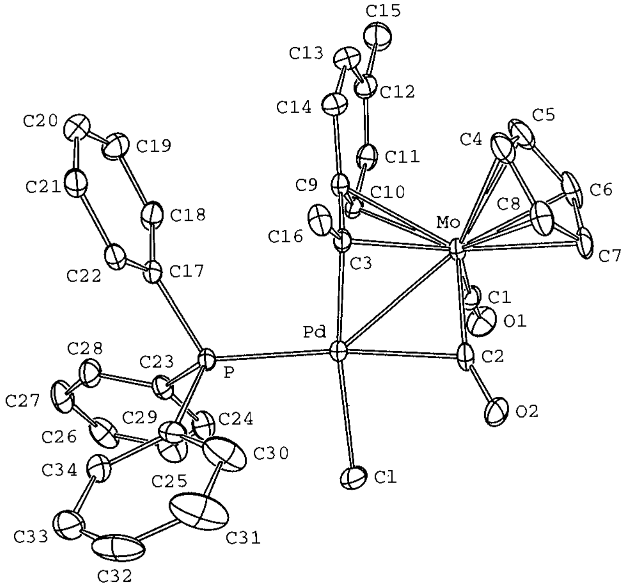


Fig. 1.

Table 1
Selected bond distances (Å) for **4a**

Mo–Pd	2.7763(4)	Pd–Cl	2.403(1)
Mo–C1	1.993(4)	Pd–P	2.321(1)
Mo–C2	1.995(4)	C1–O1	1.146(5)
Mo–C3	2.193(4)	C2–O2	1.167(5)
Mo–C9	2.382(4)	C3–C9	1.433(6)
Mo–C10	2.544(4)	C3–C16	1.511(6)
Mo···C14	3.362(4)	C9–C10	1.424(6)
Mo–Cp′ [a]	1.984(4)	C9–C14	1.444(5)
Pd···C1	3.302(4)	C10–C11	1.420(6)
Pd–C2	2.258(4)	C11–C12	1.357(5)
Pd–C3	2.007(3)	C12–C13	1.420(7)
Pd···C10	3.181(4)	C13–C14	1.364(7)

[a] Cp′, centroid of C_5H_5.

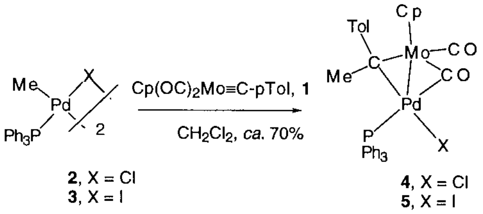
Table 2
Selected bond angles (°) for **4a**

Pd–Mo–C1	86.0(1)	Cl–Pd–P	93.39(4)
Pd–Mo–C2	53.5(1)	P–Pd–C2	164.1(1)
Pd–Mo–C3	45.80(8)	P–Pd–C3	94.9(1)
Pd–Mo–Cp′ [a]	150.9(1)	Mo–C1–O1	175.8(4)
C1–Mo–C2	83.8(2)	Mo–C2–O2	156.2(3)
C1–Mo–C3	121.0(2)	Mo–C3–Pd	82.6(1)
C2–Mo–C3	88.6(2)	Mo–C3–C9	79.1(2)
C3–Mo–Cp′ [a]	119.8(2)	Mo–C3–C16	125.7(3)
Mo–Pd–C3	51.6(1)	Pd–C3–C9	118.8(2)
C2–Pd–C3	86.1(1)	Pd–C3–C16	117.0(3)
C2–Pd–Cl	84.7(1)	C9–C3–C16	121.2(3)
Cl–Pd–C3	171.2(1)		

[a] Cp′, centroid of C_5H_5.

2. Results and discussion

Treating **2** or **3** with two equivalents of (η^5-C_5H_5)$(OC)_2$Mo≡C-pTol (**1**) in CH_2Cl_2 at room temperature (r.t.) led to a good yield (up to 70%) of compounds **4** and **5** which were isolated as brown–orange and yellow–orange solids, respectively. The course of the reaction could be followed by infrared spectroscopy, and thus revealed that the reaction was indeed complete after ca. 0.5 h as the CO stretching frequencies of **1** have disappeared and have been substituted by those of **4** or **5**. The new compounds were less stable in solution than the previous related bimetallic complexes of the series as they led to decomposition products after 2–3 h at r.t. However, they were stable as solids in the absence of air (Eq. (1)).

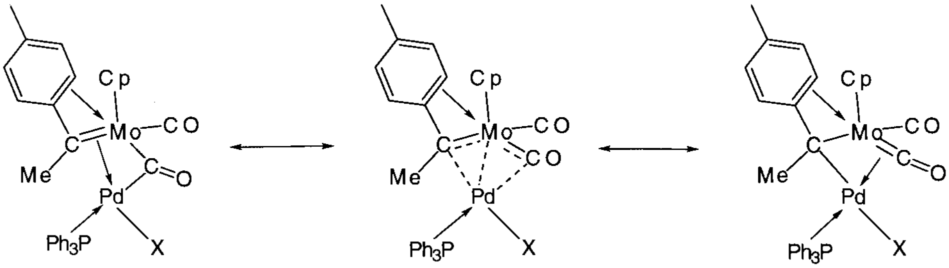


(1)

In order to fully ascertain the geometry of this novel class of compounds the crystal structure of **4** has been determined. The ORTEP of **4** is shown in Fig. 1 and selected bond lengths and angles are given in Tables 1 and 2.

It is clear that the reaction between **2** and **1** has led to a C–C formation between the carbyne carbon atom of **1** and the methyl σ-bonded to Pd in **2** affording a bimetallic complex bridged with a μ-alkylidene ligand. The palladium atom is within bonding distances of P, Mo [7], C2, C3 and I. The phosphorus, C3, C2 and iodine atoms are arranged in a normal square plane arrangement around Pd. The C3 atom strongly interacts with both the Pd and the Mo atoms, the Pd–C3 distance (2.007(3) Å) being close to a normal Pd–C covalent bond whereas the Mo–C3 distance (2.193(4) Å) is significantly shorter than usual Mo–C single bonds [8]. The Mo–C3–Pd (82.6(1)°) angle is as expected for μ-alkylidene complexes [9].

Other noticeable features of the structure are similar to those observed previously for related molecules, such as the semi-bridging property of the CO ligand between the palladium and the molybdenum atoms (C2O2) and



Scheme 1.

the strong interaction of the C9–C10 vector to molybdenum which was identified recently [10]. This interaction is evidenced by unusually high chemical shifts of C9 and C10 (107.3 and 82.4 ppm for C9 and C10, respectively) and by short contacts of these carbons with the molybdenum atom (2.382(4) and 2.544(4) Å for Mo–C9 and Mo–C10, respectively).

Among the various limit formulae that can be drawn for the complex **4** we are inclined to think that those presented in Scheme 1 should be the most likely as they are in accord with most of the crystallographic data provided above.

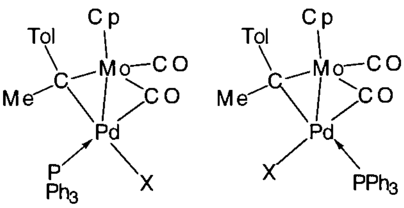
A careful examination of the ^{1}H-NMR spectrum of **4** showed it to be a 14:1 mixture of the two isomers **4a** and **4b**, respectively. A similar observation was made in the ^{31}P-NMR spectrum of **4** which displays two signals at $\delta = 27.0$ and 20.3 with an intensity ratio identical to that observed in ^{1}H-NMR. Unfortunately, in the ^{13}C-NMR spectrum the minor isomer was not detected probably because of its extremely low concentration. In this spectrum the doublet at $\delta = 232.2$ with a $^{2}J_{P-C} = 21.5$ Hz can be assigned to the semi-bridging CO group, i.e. the CO *trans* to the PPh_3 ligand. This result is in line with previous observations for a related compound having a PPh_2CH_2Ar unit *trans* to the semi-bridging CO (Ar = orthopalladated phenyl ring) [5]. We could thus unambigously assign to the major isomer **4a** the structure that was determined by the crystal structure analysis depicted above. The structure of the second isomer **4b** should be related to that of **4a** by exchanging the roles of the PPh_3 and the chloride ligands on the palladium atom (Scheme 2).

The ^{1}H-NMR spectrum of **5** also shows the presence of two isomeric forms: a minor isomer **5a** which has chemical shifts analogous to those of **4a**, and a major isomer **5b** whose chemical shifts and coupling constants are close to those of **4b** (**5a**:**5b** = 1:2). The ^{13}C-NMR spectrum of **5** at 232 K showed this time that two isomers are present and it provided further evidence for their structures.

For **5a** the signal of the COs and the bridging alkylidene carbon were found at $\delta = 232.2$ with $^{2}J_{P-C} = 21.5$ Hz for C2, a singlet at $\delta = 230.5$ and a singlet at $\delta = 158.9$ for C1 and C3, respectively.

For **5b**, C1 and C2 were at $\delta = 238.8$ and 231.5 without a $^{2}J_{P-C}$ coupling and C3 was at $\delta = 171.5$ with $^{2}J_{P-C} = 81.2$ Hz. This latter coupling constant is related to that found earlier for a cationic derivative of a compound closely related to **5b** having a phosphine ligand *trans* to the bridging alkylidene carbon atom [10]. The ^{13}C-NMR signal for the corresponding bridging alkylidene carbon atom of this latter was seen at $\delta = 155.1$ with a $^{2}J_{P-C}$ coupling constant of 56.4 Hz. Thus, it is clear that in **5b** the PPh_3 ligand is *trans* to the bridging alkylidene carbon whereas in **5a** it is *cis* to this carbon.

A magnetisation transfer (or spin saturation) experiment on **4** proved that **4a** and **4b** are in equilibrium with one another in $CDCl_3$ solution. Indeed irradiating the signal at $\delta = 2.12$, for the methyl group on the alkylidene bridge in **4a**, led to the disappearance of the corresponding signal at $\delta = 3.09$ in **4b**. Further evidence for this dynamic process was brought about by a ROESY experience on **5** which showed unambiguously that the methyl groups at the bridging carbons (at $\delta = 2.13$ and 3.30, respectively) and the *ortho* protons (H10 and H14) of the tolyl group of **5a** and **5b** are indeed correlated. Moreover, we found that the equilibrium between **5a** and **5b** is temperature dependent as the ratio **5b**:**5a** decreased with decreasing the temperature. The ROESY experiment also confirmed another interesting aspect pertaining to the structure of **5** as it showed an intense nOe effect between the methyl groups and the H14 *ortho* proton of the tolyl unit only (both on the bridging carbon atom). This result points to a lack of free rotation of the tolyl group around the C3–C9 bond thereby emphasising the importance of



4a, X = Cl
5a, X = I

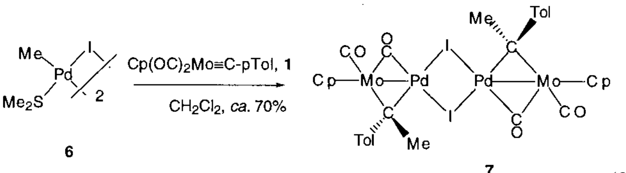
4b, X = Cl
5b, X = I

Scheme 2.

the interaction between C9–C10 and the molybdenum atom in both **5a** and **5b**.

The results described above may be rationalised by considering that in compounds **4** and **5** the triphenylphosphine ligand is more or less destabilised when coordinated *trans* to the bridging alkylidene unit. This effect was first described by Pearson who established that a ligand with a large *trans* influence bound to a soft metal is destabilised when coordinated *trans* to another soft ligand [11]. The reluctance of a phosphine ligand to bind *trans* to a σ-bound carbyl unit that was encountered later [12] is in line with observations made recently by Vicente et al. who showed that such 'transphobia' occurred quite systematically [13]. The difference between **4** and **5** is essentially due to the nature of the halide, i.e. a chloride versus an iodide, respectively. In **4** the most abundant isomer has the chloride anion *trans* to the alkylidene unit whereas in **5** the reverse situation occurs with the iodide preferentially *cis* to this latter carbon atom. This result is easily rationalised using the antisymbiotic (or transphobia) effect as the iodide ligand is known to have a larger *trans* influence compared to chloride. Thus, in **5** the iodide and the phosphine ligand are almost equally destabilised *trans* to the alkylidene carbon atom, whereas in **4** this conflicting situation is not occurring as **4a** is by far the most abundant isomer. This behaviour is also reflected by the lower stability in the solution of **5** versus **4**.

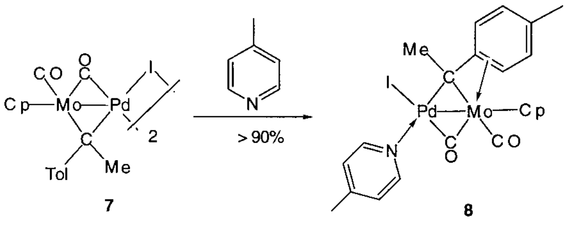
Another starting material, **6**, in which the phosphine ligand has been substituted by a dimethylsulfide group, could be used to synthesise polymetallic compounds related to the one described above. However, reaction of **1** with **6** led to a product **7** with a different geometry to that of **4** or **5**.



(2)

Compound **7** was much less soluble in common organic solvents than **4** or **5**. Moreover its combustion analysis and ^{1}H-NMR spectrum indicated that it no longer contained the dimethylsulfide ligand. We thus assigned for this new compound **7** the iodide-bridged dimeric structure. Due to the presence of the iodide bridges and the chiral carbon alkylidene centre, eight different isomers could be encountered. However, the spectroscopic data indicated the presence of only one isomeric form, thus the reaction between **1** and **6** must occur with a high degree of stereoselectivity. It is reasonable to assume that the most likely structure for **6** might be that in which the steric effects between the substituents of the bridging alkylidene units are minimised and thus the *trans anti* structure depicted in Eq. (2) is the most likely.

Further evidence for the dimeric nature of **7** was provided by the iodide bridge-splitting reaction with neutral nucleophiles. Indeed with two equivalents of PPh_3, **7** afforded good yields of **5**. With 4-methylpyridine a new compound **8** could be obtained as shown in Eq. (3). The structure of **8** is readily assigned through its ^{1}H-NMR spectrum, because the chemical shift of the methyl group of the alkylidene bridge is at $\delta = 3.16$, which is close to that of the corresponding methyl in **5b**.



(3)

This latter result is noteworthy because we attempted the direct synthesis of **8**, via reaction of **1** with *bis*(*p*-methylpyridine)dimethyldi(μ-iodo)dipalladium. This reaction was unsuccessful as we only obtained decomposition products. Thus, **7** might allow an interesting entry into a much larger class of bimetallic compounds by varying the nature of the ligand to cleave the iodide bridges.

3. Conclusion

This study is a further illustration that metallacarbyne units can indeed formally insert into Pd–C bonds via C–C bond formation leading to novel bimetallic compounds bridged by an alkylidene moiety. Although the thermal stability of the new series of compounds is somewhat lower than that of the previous series, it is clear now that an intramolecular interaction is not necessary for the inserted compounds to be isolated. This opens new perspectives for either the synthesis of novel polymetallic species or towards new ways of functionalising metallaalkylidyne units.

4. Experimental

4.1. General

All reactions were performed in Schlenck-type flasks under oxygen and water free nitrogen. Solvents were dried and distilled under nitrogen prior to use: diethyl ether and tetrahydrofuran over sodiumbenzophenone ketyl, *n*-hexane over sodium and dichloromethane over P_2O_5. The starting materials $(\eta^5\text{-}C_5H_5)(OC)_2Mo{\equiv}Cp$-tolyl (**1**) [14], $[(CH_3)LPd(\mu\text{-}X)]_2$ ($L = PPh_3$, $X = Cl$, **2**; $L = PPh_3$, $X = I$, **3**; $L = 4\text{-}MePy$, $X = I$ [15], and $L =$

SMe_2, X = I, **6** [16]) were obtained using published procedures. The ^{1}H-NMR spectra were recorded at r.t. unless otherwise stated, at 300 and 400 MHz, $^{13}C\{^1H\}$-NMR spectra at 75 and 100 MHz on FT-Bruker instruments (AC-300 and AM 400) and $^{31}P\{^1H\}$-NMR at 121.5 MHz on a FT-Bruker (AC 300) using deuterated solvents dried on molecular sieves (4 Å) prior to use. All ^{13}C-NMR spectra were run after ^{13}CO was bubbled through the solutions for ca. 10 s, this leading to enrichment of the CO groups in ^{13}C of up to 5–10% (no $^3J_{C-C}$ could be seen). δ are given in ppm referring to external $SiMe_4$ (^{1}H and ^{13}C), or H_3PO_4 (^{31}P). Infrared spectra were measured on a Brucker IFS 66 spectrometer. Elemental analyses were performed by the Service Central d'Analyse du CNRS (Lyon).

4.2. *[(η^5-C_5H_5)(OC)Mo]{μ-CO}{μ-C(p-tolyl)(CH$_3$)}-[(PPh$_3$)PdCl]* (**4**)

[(CH_3)(PPh_3)Pd(μ-Cl)]$_2$ (**2**) (0.346 g, 0.410 mmol) was added to a solution of (η^5-C_5H_5)(OC)$_2$Mo≡C-(*p*-tolyl) (**1**) (0.259 g, 0.81 mmol) in CH_2Cl_2 (25 ml) at r.t. The reaction was complete within 0.5 h as checked by IR (disappearence of the CO stretching frequencies of **1** at 1991 and 1917 cm^{-1}) leading to a deep red solution. The solvent was partially removed in vacuo and addition of *n*-hexane (35 ml) induced the precipitation of **4** as an orange–brown powder. It was washed with *n*-hexane (2 × 10 ml) and dried in vacuo. Yield 0.434 g, 72%. Orange–red crystals suitable for an X-ray diffraction analysis were obtained by slow diffusion of *n*-hexane into a saturated solution of **4** in CH_2Cl_2. IR (CH_2Cl_2): $\nu = 1964$ (vs), 1846 (s), 1814 (sh); (KBr pellet): $\nu = 1958$ (vs), 1947 (sh), 1865 (vs), 1841 (vs) (CO). Calc. for $C_{34}H_{30}ClMoO_2PPd$ (739.4): C, 55.23; H, 4.09. Found: C, 55.20; H, 4.38%. **4a**: ^{1}H-NMR ($CDCl_3$): $\delta = 7.7$–7.1 (m, 15H$_{arom}$, PPh_3), 7.08 (m, 2H, H11 and H13), 6.76 (d, $^3J = 8.2$ Hz, H14), 6.45 (d, $^3J = 5.8$ Hz, H10), 4.31 (s, 5H, C_5H_5), 2.26 (s, 3H, CH_3 (tolyl)), 2.12 (d, $^4J_{P-H} = 6.3$, 3H, μ-C–CH_3). ^{13}C-NMR ($CDCl_3$): $\delta = 232.2$ (d, $^2J_{P-C} = 21.5$, μ-CO)), 230.6 (CO), 156.1 (μ-C), 137.0–125.0 (19 C$_{arom}$), 107.3 (C9), 94.8 (C_5H_5), 82.4 (C10), 28.2 (d, $^3J_{P-C} = 4.4$, μ-C–*C*H_3), 21.4 (CH_3 (tolyl)). ^{31}P-NMR ($CDCl_3$): $\delta = 27.0$. **4b**: ^{1}H-NMR ($CDCl_3$): $\delta = 3.09$ (d, $^4J_{P-H} = 7.0$, 3H, μ-C–CH_3), 2.31 (s, 3H, CH_3 (tolyl)), the other signals were too weak to be observed. ^{31}P-NMR ($CDCl_3$): $\delta = 20.3$.

4.3. *[(η^5-C_5H_5)(OC)Mo]{μ-CO}{μ-C(p-tolyl)(CH$_3$)}-[(PPh$_3$)PdI]* (**5**)

[(CH_3)(PPh_3)Pd(μ-I)]$_2$ (**2**) (0.100 g, 0.10 mmol) was added to a solution of (η^5-C_5H_5)(OC)$_2$Mo≡C-(*p*-tolyl) (**1**) (0.67g g, 0.21 mmol) in CH_2Cl_2 (10 ml) at r.t. IR spectra of the solution showed that the reaction was complete after 45 min leading to a deep orange–red solution. The volume of the solvent was reduced to 2 ml in vacuo. Addition of *n*-hexane at −80°C and removal of the solvents in vacuo allowed the isolation of **5** as a yellow–orange powder which was washed with *n*-hexane (2 × 10 ml) and dried in vacuo. Yield: 0.124 g, 71%. IR (CH_2Cl_2): $\nu = 1958$ (vs), 1854 (m), 1808 (s); (KBr pellet): $\nu = 1964$ (vs), 1826 (vs) (CO). Calc. for $C_{34}H_{30}IMoO_2PPd$ (830.8): C, 49.15; H, 3.64. Found: C, 48.88; H, 3.57%. **5a**: ^{1}H-NMR ($CDCl_3$): $\delta = 7.7$–7.2 (m, 15H$_{arom}$, PPh_3), 7.12 (m, 2H, H11 and H13), 6.79 (d, $^3J = 8.8$ Hz, H14), 6.46 (d, $^3J = 5.8$ Hz, H10), 4.32 (s, 5H, C_5H_5), 2.28 (s, 3H, CH_3 (tolyl)), 2.13 (d, $^4J_{P-H} = 6.5$, 3H, μ-C–CH_3). ^{13}C-NMR ($CDCl_3$, 232 K): $\delta = 232.2$ (d, $^2J_{P-C} = 21.2$, μ-CO)), 231.5 (CO), 158.9 (μ-C), 138.0–125.0 (C$_{arom}$), 107.5 (C9), 95.0 (C_5H_5), 80.8 (C10), 27.9 (μ-C–*C*H_3), 21.4 (CH_3 (tolyl)). ^{31}P-NMR ($CDCl_3$): $\delta = 28.2$. **5b**: ^{1}H-NMR ($CDCl_3$): $\delta = 7.7$–7.2 (m, 15H$_{arom}$, PPh_3), 6.22 (d, $^3J = 5.2$ Hz, H10), 4.30 (s, 5H, C_5H_5), 3.30 (d, $^4J_{P-H} = 6.9$, 3H, μ-C–CH_3), 2.32 (s, 3H, CH_3 (tolyl)). ^{13}C-NMR ($CDCl_3$, 232 K): $\delta = 238.8$ (CO), 230.5 (CO), 171.8 (d, $^2J_{P-C} = 81.2$, μ-C), 138.0–125.0 (C$_{arom}$), 106.6 (C9), 94.5 (C_5H_5), 87.7 (C10), 32.7 (μ-C–*C*H_3), 21.6 (CH_3 (tolyl)). ^{31}P-NMR ($CDCl_3$): $\delta = 19.2$.

4.4. *{[(η^5-C_5H_5)(OC)Mo]{μ-CO}{μ-C(p-tolyl)(CH$_3$)}-[(PPh$_3$)Pd(μ-I)]}$_2$* (**7**)

[(CH_3)(Me_2S)Pd(μ-I)]$_2$ (**6**) (0.162 g, 0.26 mmol) was added to a suspension of (η^5-C_5H_5)(OC)$_2$Mo≡C-(*p*-tolyl) (**1**) (0.168 g, 0.52 mmol) in Et_2O (20 ml). After 2 h stirring at r.t., the deep-red precipitate thus obtained was filtered, washed with Et_2O (4 ml) and *n*-hexane (4 ml) and dried in vacuo. Yield: 0.243 g, 74%. IR (CH_2Cl_2): $\nu = 1969$ (vs), 1819 (vs); (KBr pellet): $\nu =$ 1974 (s), 1949 (s), 1819 (sh), 1812 (s) (CO). Calc. for $C_{32}H_{30}I_2Mo_2O_4Pd_2$ (1137.1): C, 33.80; H, 2.66. Found: C, 33.96; H, 2.75%. ^{1}H-NMR ($CDCl_3$): $\delta = 7.3$–7.1 (m, 3H, H11, H13 and H14) 6.77 (br. s, 1H, H10), 4.36 (s, 5H, C_5H_5), 3.08 (s, 3H, μ-C–CH_3), 2.33 (s, 3H, CH_3 (tolyl)). ^{13}C-NMR (CD_2Cl_2): $\delta = 237.7$ (br, μ-CO)), 230.9 (CO), 139.1, 133.3, 131.8, 126.9 (C (tolyl)), 105.6 (C9), 94.9 (C_5H_5), 90.0 (C10), 32.1 (μ-C–*C*H_3), 21.6 (CH_3 (tolyl)) (the signal of μ-C was not observed).

4.5. *[(η^5-C_5H_5)(OC)Mo]{μ-CO}{μ-C(p-tolyl)(CH$_3$)}-[(4-MePy)PdI]* (**8**)

A solution of 4-methylpyridine (4-MePy) (0.70 ml of a 0.515 M solution in CH_2Cl_2, 0.36 mmol) was added to a solution of **7** (0.224 g, 0.36 mmol) in CH_2Cl_2. The solution became instantaneously darker and it was stirred for 0.5 h. The solution was then concentrated in vacuo (to ca. 2 ml) and the precipitation of **8** was induced by the addition of *n*-hexane (10 ml). The thus obtained yellow–brown precipitate was washed with *n*-hexane and dried in vacuo. Yield: 0.236 g, 91%. IR (CH_2Cl_2): $\nu = 1951$ (vs), 1802 (vs); (KBr pellet): $\nu = 1950$ (s), 1795 (vs) (CO). Calc. for $C_{45}H_{46}Cl_2I_2Mo_2$-$N2O_4Pd_2$ (**8** × 2 + CH_2Cl_2: 1408.3): C, 38.38; H, 3.29; N, 1.99. Found: C, 38.76; H, 3.29; N, 2.09% (the amount of CH_2Cl_2 was determined by ^{1}H-NMR). ^{1}H-NMR ($CDCl_3$): $\delta = 8.60$ (d, $^3J = 5.5$, 2H, 2,2′-H of 4-MePy), 7.36 (d, 1H, H13), 7.27 (d, $^3J = 6.0$, 1H, H11), 7.18 (d, $^3J = 8.6$, 1H, H14), 7.13 (d, 2H, 3,3′-H of 4-MePy), 6.50 (d, 1H, H10), 4.39 (s, 5H, C_5H_5), 3.16 (s, 3H, μ-C–CH_3), 2.34 and 2.33 (2s, 6H, CH_3 (tolyl and 4-MePy)). ^{13}C-NMR (CD_2Cl_2): $\delta = 241.0$ (μ-CO)), 232.9 (CO), 165.3 (μ-C), 154.6, 150.8, 148.7, 138.2, 132.1, 131.5, 126.7, 125.4 (*p*-tolyl and 4-MePy), 106.1 (C9), 94.3 (C_5H_5), 90.7 (C10), 32.7 (μ-C–CH_3), 21.5 and 21.2 (CH_3 of tolyl and 4-MePy).

*4.6. X-ray crystal structure determination of **4***

The X-ray data were collected on an Enraf-Nonius CAD4-F diffractometer using Mo–K_α graphite monochromated radiation ($\lambda = 0.7107$ Å, −100°C, $\theta/2\theta$ scans). Absorption corrections derived from the ψ-scans of four reflections were applied. The structures were solved using direct methods and refined against $|F|$. Hydrogen atoms were introduced as fixed contributors ($d_{C-H} = 0.95$ Å, $B_H = 1.3\ B_{equiv}$ for the atom to which it was attached). Non-hydrogen atoms were refined anisotropically. For all computations the Enraf-Nonius MOLEN package was used [17].

Crystal data for **4**: red crystals, crystal dimensions $0.40 \times 0.26 \times 0.22$ mm^3: $C_{34}H_{30}ClIMoO_2PPd$, $M = 739.4$, monoclinic, space group $P2_1/n$, $a = 10.989(3)$, $b = 20.137(6)$, $c = 13.954(4)$ Å, $\beta = 105.38(2)°$, $\gamma = 90.03(2)°$, $V = 2977.2$ Å^3, $Z = 4$, $D_{calc} = 1.649$ g cm^{-3}, $\mu = 11.801$ cm^{-1}. A total of 6919 reflections was collected, $2° < \theta < 26°$. 4853 reflections having $I > 3\sigma(I)$. Transmission factors: 0.93/1.00. Final results: $R(F) = 0.033$, $Rw(F) = 0.047$, GoF = 0.984.

5. Supplementary material

Crystallographic data for the structural analysis (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 104049. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Rd., Cambridge CB2 1EX, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.com.ac.uk or www: http://www.ccdc.cam.ac.uk).

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