

Molybdenum alkylidene complexes with linked cycloheptatrienyl–phosphane ligands for potential use in olefin metathesis

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Dedicated to Professor Ernst Otto Fischer on the occasion of his 85th birthday

Abstract

The synthesis of cycloheptatrienyl molybdenum complexes incorporating the linked cycloheptatrienyl–phosphane ligand [2-(diisopropylphosphanyl)phenyl]cycloheptatrienyl, *o*-*i*Pr₂P-C₆H₄-C₇H₆, is described. Reaction of the 17-electron dibromide [(*o*-*i*Pr₂PC₆H₄-η⁷-C₇H₆)MoBr₂(*P-Mo*)] (**1**) with NaBH₄ furnishes a tetrahydroborate complex, which can be directly converted into the acetate complex [(*o*-*i*Pr₂PC₆H₄-η⁷-C₇H₆)Mo(η²-O₂CCH₃)(*P-Mo*)] (**2**). The acetate ligand can be cleaved upon treatment with diazoalkanes, N₂CHR, in the presence of Me₃SiCl affording the molybdenum alkylidenes [(*o*-*i*Pr₂PC₆H₄-η⁷-C₇H₆)MoCl(=CHR)(*P-Mo*)] (**4a**, R = Ph; **4b**, R = SiMe₃). Complexes **4** might serve as a source for the preparation of potential olefin metathesis catalysts of the type [(*o*-*i*Pr₂PC₆H₄-η⁷-C₇H₆)Mo(=CHR)(*P-Mo*)]⁺ by halide abstraction. CH₂ insertion into the metal–carbon bond of the diphenylacetylene complex **5** resulted in the formation of the cationic η³-vinylcarbene complex **6**, which can be regarded as an alkene adduct of a 16-electron complex of just that kind. In addition, the X-ray crystal structures of **2** and **6** are reported. © 2003 Elsevier B.V. All rights reserved.

Keywords: Cycloheptatrienyl complexes; Molybdenum; Alkylidene complexes; Olefin metathesis; Diazoalkanes

1. Introduction

Since the first successful isolation and characterization of a stable transition metal carbene complex by Fischer and Maasböl in 1964 [1], numerous preparative routes for the synthesis of Fischer and Schrock type carbene complexes have been developed [2,3]. Among many other possible carbene sources, diazoalkanes are particularly useful for the preparation of non-heteroatom-stabilized carbene complexes due to their stability and ease of availability [4]. Established and extensively studied by Herrmann [5], diazoalkanes were frequently used in the synthesis of transition metal carbenes [6]. Recently, this method could be employed in the preparation of Grubbs-type ruthenium alkylidene com-

plexes [RuCl₂(=CHR)(PPh₃)₂] (R = alkyl, aryl) [7], which are among the most important (pre)catalysts for all types of olefin metathesis reactions [8]. The phenylcarbene complex **I** is even commercially available and constitutes a versatile starting material for further catalyst design by substitution of PPh₃ for other ligands among which stable *N*-heterocyclic carbenes [9,10] proved to be extremely useful for boosting the catalytic activity [11]. Although exceedingly sensitive towards dioxygen and moisture, Schrock's molybdenum-based alkylidene complexes of the general formula [Mo(=CHCMe₂Ph)(=NAr)(OR₂)] represent the second important class of potent molecular olefin metathesis catalysts, and the highly active compound **II** can also be obtained from commercial sources [12]. It is also noteworthy in this context that recent work by Hoffmann involves cationic ruthenium carbene complexes such as **III**, which exhibit much higher ring-opening metathesis polymerization (ROMP) activity in solution than any other Ru system [13] (Fig. 1).

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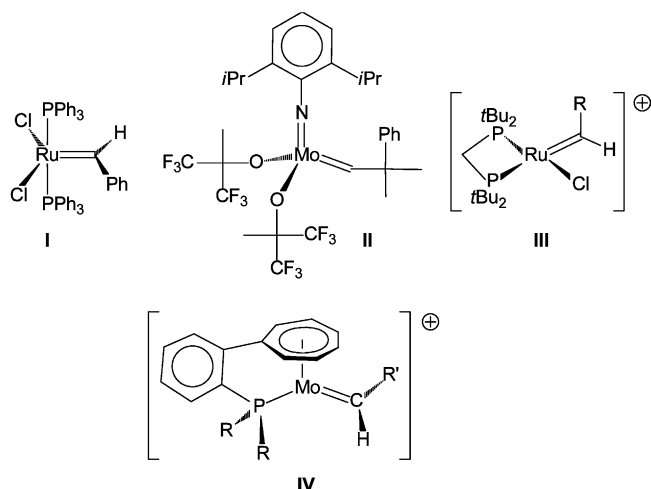


Fig. 1. Alkylidene transition metal complexes for use in olefin metathesis.

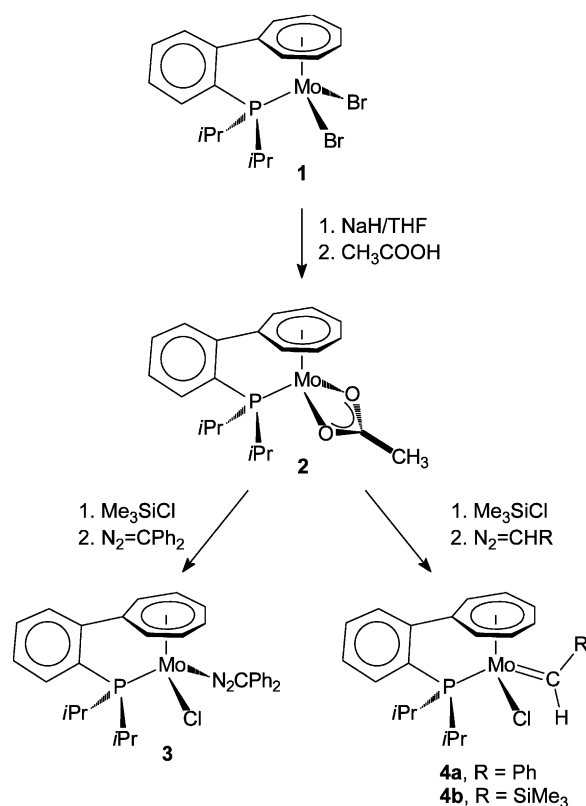
In continuation of our work on complexes containing linked cycloheptatrienyl–phosphane ligands [14], we became interested in cationic 16-electron molybdenum alkylidene complexes of type **IV** and their potential use in olefin metathesis. With Brunner, we have independently emphasized the similarity between the isoelectronic and isolobal fragments $[(\eta\text{-C}_5\text{R}_5)\text{Ru}]$ and $[(\eta\text{-C}_7\text{H}_7)\text{Mo}]$ [14–16], which has prompted us to pursue a general study on the possibility of replacing frequently used ruthenium catalysts by analogous but much cheaper molybdenum systems [14]. Consequently, we propose that alkylidene complexes such as **IV** can be regarded as a link between the two most popular catalyst systems **I** and **II** and might additionally exhibit a similar reactivity as observed for the cationic system **III**. In this contribution, we wish to present a preliminary report on the syntheses of molybdenum carbenes of type $[(o\text{-}i\text{Pr}_2\text{PC}_6\text{H}_4\text{-}\eta^7\text{-C}_7\text{H}_6)\text{MoCl}(=\text{CHR})(P\text{-}Mo)]$ ($R = \text{Ph}, \text{SiMe}_3$), which could provide the 16-electron complex fragments **IV** upon chloride abstraction.

2. Results and discussion

We had previously reported on the use of paramagnetic dialkyl complexes of the type $[(o\text{-}R_2\text{PC}_6\text{H}_4\text{-}\eta^7\text{-C}_7\text{H}_6)\text{Mo}(\text{CH}_2\text{SiMe}_3)_2(P\text{-}Mo)]$ ($R = \text{Ph}, i\text{Pr}$) in the ROMP of norbornene [14a]. We proposed that 17-electron alkylidene complexes $[(o\text{-}R_2\text{PC}_6\text{H}_4\text{-}\eta^7\text{-C}_7\text{H}_6)\text{Mo}(=\text{CHSiMe}_3)(P\text{-}Mo)]$ could have formed as the active species by intramolecular α -deprotonation and elimination of Me_4Si . However, we have not yet been able to prove the formation of such complexes. From our present point of view, cationic 16-electron metal carbenes such as **IV** are more likely to be catalytically active as they would allow to coordinate an additional alkene ligand and to further describe the

course of the metathesis polymerization by the Chauvin mechanism [17].

Our preparative route for making these alkylidene complexes available is outlined in Scheme 1. The 17-electron dibromide **1** is easily accessible [14d], and it can be reduced employing hydride sources such as NaBH_4 or NaH . Thus, treatment with sodium borohydride results in the formation of the tetrahydroborate complex $[(o\text{-}i\text{Pr}_2\text{PC}_6\text{H}_4\text{-}\eta^7\text{-C}_7\text{H}_6)\text{Mo}(\eta^2\text{-BH}_4)(P\text{-}Mo)]$ exhibiting a bidentate $M(\mu^2\text{-H}_2\text{BH}_2)$ ligation [14b], whereas chiral-at-metal monohydride complexes of the type $[(o\text{-}i\text{Pr}_2\text{PC}_6\text{H}_4\text{-}\eta^7\text{-C}_7\text{H}_6)\text{MoHL}(P\text{-}Mo)]$ ($L =$ phosphines, imidazol-2-ylidenes) are formed on reaction with sodium hydride in the presence of suitable Lewis bases L [14c]. In a similar fashion, the acetate complex **2** can be prepared in high yield by addition of a large excess of NaBH_4 to an ethanolic solution of **1**, followed by quenching this reaction mixture with acetic acid. In its $^1\text{H-NMR}$ spectrum **2** exhibits three cycloheptatrienyl resonances at 5.61, 4.55 and 4.50 ppm in a 2:2:2 ratio indicating that its structure is essentially C_s symmetric. Accordingly, the $^{13}\text{C-NMR}$ spectrum displays four resonances for the C_7H_6 carbon atoms. The resonances observed for the acetate ligand at 1.60 ppm (CH_3) and at 180.3 ppm ($^3J_{\text{C,P}} = 1.3$ Hz, COO) and 22.8 ppm (CH_3), respectively, are in good agreement with the values found for related carboxylate transition metal complexes [18].



Scheme 1.

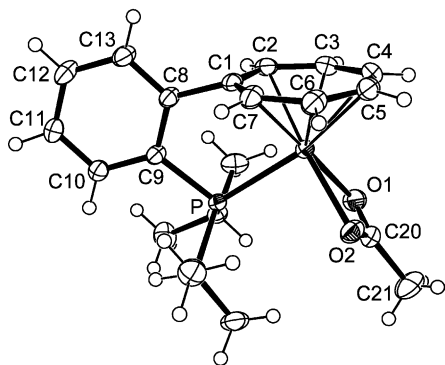


Fig. 2. ORTEP drawing of **2** with thermal ellipsoids drawn at 50% probability. Selected bond lengths [Å] and angles [°]: C1–C2 1.414(2), C1–C7 1.419(2), C2–C3 1.413(2), C3–C4 1.420(3), C4–C5 1.392(3), C5–C6 1.413(3), C6–C7 1.418(2), C20–O1 1.265(2), C20–O2 1.265(2), Mo–C1 2.2495(14), Mo–C2 2.2760(15), Mo–C3 2.2463(17), Mo–C4 2.3014(17), Mo–C5 2.3068(17), Mo–C6 2.2371(17), Mo–C7 2.2599(17), Mo–O1 2.2174(12), Mo–O2 2.2189(11), Mo–P 2.4710(4); O1–C20–O2 118.52(15).

To confirm the spectroscopic results, a single crystal of **2** was subjected to X-ray diffraction analysis. The molecular structure is depicted in Fig. 2, and it reveals that the cycloheptatrienyl–phosphane ligand does indeed coordinate in chelating $\eta^7:\eta^1$ -fashion with an almost perfectly perpendicular orientation of the six- and seven-membered rings. The molybdenum atom is symmetrically bound to the seven ring-carbon atoms with the shortest bond to C6 [2.2371(17) Å] and the longest bond to C5 [2.3068(17) Å]. The two Mo–O bonds are almost identical [Mo–O1 2.2174(12) Å, Mo–O2 2.2189(11) Å] confirming the η^2 -coordination mode for the acetate group. It should be noted that the positions of all hydrogen atoms could be refined for **2**. Therefore, it is possible to establish the angles between the centroid of the cycloheptatrienyl ring, the C₇ carbon atoms and the adjacent hydrogen atoms revealing a significant out-of-plane displacement for the C₇ hydrogen atoms. The average bending is about 9° toward the molybdenum center, and such a deviation has been attributed to a reorientation of the large seven-membered ring for a better metal overlap [19,20].

Werner and coworkers have shown that reaction of the ruthenium methallyl complex [(η -C₅H₅)Ru(PPh₃)(η^3 -2-MeC₃H₄)] with acetic acid leads to the formation of the closely related acetate complex [(η -C₅H₅)Ru(PPh₃)(η^2 -O₂CCH₃)] [18]. Cleavage of the carboxylate ligand is observed on treatment with diaryl diazoalkanes in the presence of halide sources such as [Et₃NH]Cl or Me₃SiCl, and ruthenium alkylidene complexes of type [(η -C₅H₅)RuCl(PPh₃)(=CRR')] are formed [18b,21]. We anticipated that **2** should react in a similar manner to produce alkylidene complexes [(*o*-iPr₂PC₆H₄- η^7 -C₇H₆)MoCl(=CRR')(P-Mo)]. The reaction of **2** with diphenyl diazoalkane in the presence of Me₃SiCl, however, did not give the desired product.

Instead, characterization of the reddish-brown compound isolated from the reaction mixture indicates the formation of the diazoalkane complex **3** [22]. This assumption could be supported by X-ray diffraction analysis revealing that the N₂CPh₂ ligand is coordinated through the terminal nitrogen atom [23].

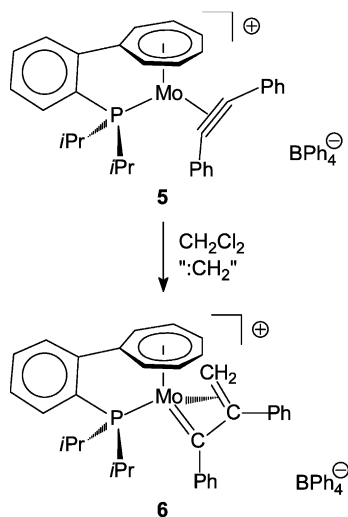
Due to our failure to convert **3** into a diphenylalkylidene complex, the monosubstituted N₂CHPh was used instead leading to an instantaneous evolution of dinitrogen and the formation of the phenylcarbene complex **4a** in good yield. Similarly, the trimethylsilylcarbene derivative **4b** was quantitatively isolated employing N₂CHSiMe₃. Indicative of metal alkylidene formation are the low-field ¹³C NMR resonances of **4a** and **4b** [24], which are observed at 318 (²J_{C,P} = 23 Hz) and 354 ppm (²J_{C,P} = 23 Hz), respectively. In their ¹H-NMR spectra, both complexes exhibit characteristic doublets for the Mo=CHR protons at 13.61 (**4a**, ³J_{H,P} = 26 Hz) and 15.35 ppm (**4b**, ³J_{H,P} = 32 Hz). In **4a** and **4b**, the pseudotetrahedrally coordinated molybdenum center has four different ligands, and so the complexes are obtained as racemic mixtures of two enantiomers. As these representatives of so-called “chiral-at-metal” half-sandwich compounds [15,25] are configurationally stable, the diastereotopic cycloheptatrienyl hydrogen atoms of each complex give rise to six different ¹H-NMR resonances. Accordingly, seven ¹³C-NMR resonances are observed for the C₇H₆ carbon atoms together with six resonances each for the phenylene-bridge as well as for the isopropyl groups. Finally, one single ³¹P-NMR resonance is found for each complex at 50.3 (**4a**) and 51.7 ppm (**4b**).

Complexes **4** are ideal precursors for the generation of 16-electron alkylidene complexes of type **IV** (vide supra), and treatment of **4a** or **4b** with halide abstracting agents such as trimethylsilyl triflate or complex silver(I) and thallium(I) salts should result in the formation of the cations [(*o*-iPr₂PC₆H₄- η^7 -C₇H₆)Mo(=CHR)(P-Mo)]⁺ (R = Ph, SiMe₃). In fact, preliminary studies indicate that a highly active ROMP catalyst can be generated upon addition of TlPF₆ to a solution of **4b** in dichloromethane. An initial experiment has been carried out in the following manner: A solution of **4b** (3 mg, 6 μmol) in CH₂Cl₂ (0.5 ml) was treated with an excess of TlPF₆ (10 mg, 29 μmol). The resulting mixture was filtered to remove thallium(I) chloride and added to a solution of norbornene (300 mg, 3.18 mmol). Rapid formation and precipitation of poly(norbornene) could be observed, and the reaction seemed to be over within 90 s. These reactions are currently under further investigation, and we hope to present novel homogeneous cycloheptatrienyl transition metal catalysts in the near future.

By chance, we have been able to isolate and crystallographically characterize a complex, which can be regarded as an olefin adduct of a type **IV** complex.

Recrystallization of the diphenylacetylene complex **5** [26] from CH_2Cl_2 afforded single crystals of the alkylidene complex **6**, which must have formed by insertion of a methylene group, CH_2 , into one of the acetylenic molybdenum–carbon bonds (Scheme 2). It is a matter of fact that the CH_2 moiety must stem from the dichloromethane solvent, the mechanism of its insertion, however, cannot yet be fully explained. The spectroscopic characterization of **6** is still in progress, but the structural parameters give clear evidence for the formation of a η^3 -vinylcarbene complex (vide infra) [27,28]. Dinuclear complexes containing exactly the same alkylidene ligand, the 1,2-diphenylpropenyldiene, have been described previously. Interestingly, they have either formed by addition of CH_2 (from diazoalkane) to a dinuclear diphenylacetylene complex or by addition of just the same alkyne to a bridged methylene complex [29,30].

The molecular structure of the cation in **6** is shown in Fig. 3. The asymmetric unit contains two independent complexes **6**, and the two cations exhibit an identical molybdenum–alkylidene bond length of 1.969(6) Å, which is comparable to values for related cationic vinylidene complexes, such as $[(\eta^7\text{-C}_7\text{H}_7)\text{Mo}(=\text{CHR})(\text{dppe})]\text{PF}_6$ [$\text{R}=\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$, 1.91(1) Å; $\text{R}=\text{Ph}$, 1.93(1) Å] [24b,31]. The only other structurally characterized carbene derivative of any cycloheptatrienyl metal system, the cyclic oxacarbene complex $[(\eta^7\text{-C}_7\text{H}_7)\text{Mo}(=\text{CCH}_2\text{CH}_2\text{CH}_2\text{O})(\text{dppe})(\text{Mo}-\text{O})]\text{PF}_6$ displays a longer Mo–C bond length of 2.04(3) Å [24b]. Surprisingly, the carbon–carbon bond distances within the $\text{Mo}=\text{C}(\text{Ph})-\text{C}(\text{Ph})=\text{CH}_2$ moiety of the two independent cations differ quite significantly (Fig. 3), the formulation of **6** as a η^3 -vinylcarbene complex, however, is unequivocally justified.



Scheme 2.

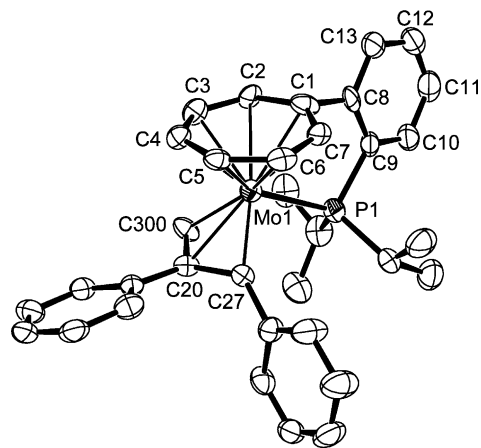


Fig. 3. ORTEP drawing of **6** with thermal ellipsoids drawn at 50% probability. The hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°] for molecule 1 [molecule 2]: Mo1–C300 2.368(6) [2.384(6)], Mo1–C20 2.336(6) [2.319(6)], Mo1–C27 1.969(6) [1.969(6)], Mo1–P1 2.5467(16) [2.5611(15)]; Mo1–C300–C20 71.3(3) [75.9(4)], C300–C20–C27 113.1(5) [114.5(5)], C20–C27–Mo1 85.8(4) [84.2(4)], C300–Mo1–C27 65.1(2) [64.6(2)].

3. Conclusion

With this contribution, we have presented a preliminary account of the preparation of cycloheptatrienyl molybdenum alkylidene complexes, which might allow the generation and isolation of cationic 16-electron complexes of the type $[(o\text{-}i\text{Pr}_2\text{PC}_6\text{H}_4\text{-}\eta^7\text{-C}_7\text{H}_6)\text{Mo}(=\text{CHR})(\text{P-Mo})]^+$ for applications in olefin metathesis in the near future. With these systems, we hope to show again that cycloheptatrienyl complexes can indeed be potentially useful for applications in homogeneous transition metal catalysis. This work is part of our general goal to extend the chemistry of cycloheptatrienyl complexes and to raise their level of significance in comparison with that of cyclopentadienyl and benzene complexes.

4. Experimental

All operations were performed in an atmosphere of dry Ar by using Schlenk and vacuum techniques. Solvents were dried by standard methods and distilled prior to use. The synthesis of **1** has been described previously [14d]. The diazoalkanes were prepared according to published procedures [4]. Elemental analyses (C, H, N) were performed on a Heraeus CHNO-Rapid elemental analyzer. EI and ESI mass spectra were recorded on a Varian MAT 212 or on a Micromass Quattro LCZ mass spectrometer, respectively. ^1H - and ^{13}C -NMR spectra were measured on Bruker AC 200, Bruker AMX 400 or Varian U 600 spectrometers using the solvent as internal standard, whereas ^{31}P -NMR measurements were run on a Bruker AC 200 spectro-

meter using aqueous H_3PO_4 (85%) as an external reference. IR spectra were recorded on a Bruker Vector 22 instrument. For the atomic numbering schemes used in Section 4, see Fig. 2.

4.1. $[(o\text{-}i\text{Pr}_2\text{P-C}_6\text{H}_4\text{-}\eta^7\text{-C}_7\text{H}_6)\text{Mo}(\text{O}_2\text{CCH}_3)(\text{P-Mo})]$ (**2**)

A solution of **1** (500 mg, 0.93 mmol) in EtOH was treated at 0°C with NaBH_4 (250 mg, 6.52 mmol) and stirred for 3 h at ambient temperature, followed by quenching the reaction mixture with acetic acid. The solvent was removed in vacuo, and the residue was extracted with Et_2O /hexane (1:1). After evaporation of the solvent, **2** could be isolated as a light green solid. Purification by recrystallization from Et_2O –hexane was possible, affording green crystals of **2**. Yield: 350 mg (86%). $^1\text{H-NMR}$ (benzene- d_6 , 600 MHz): δ 7.92 (t, 1H, C_6H_4), 7.29 (d, 1H, C_6H_4), 7.61 (m, 2H, C_6H_4), 5.61 (s, 2H, C_7H_6), 4.55 (m, 2H, C_7H_6), 4.50 (s, 2H, C_7H_6), 2.05 (sep., 2H, $i\text{Pr}$: CH), 1.60 (s, 3H, O_2CCH_3), 1.04 (dd, 6H, $i\text{Pr}$: CH_3), 0.66 (dd, 6H, $i\text{Pr}$: CH_3). $^{13}\text{C-NMR}$ (benzene- d_6 , 150.7 MHz): δ 180.3 (d, $^3J_{\text{C,P}} = 1.3$ Hz, O_2C), 158.0 (d, $^3J_{\text{C,P}} = 25.5$ Hz, C-8), 136.4 (d, $^2J_{\text{C,P}} = 36.0$ Hz, C-9), 131.6 (s, C-11), 130.3 (d, $^2J_{\text{C,P}} = 1.5$ Hz, C-10), 128.9 (s, C-13), 128.8 (s, C-12), 109.3 (d, $^3J_{\text{C,P}} = 2.6$ Hz, C-1), 93.5 (d, $^2J_{\text{C,P}} = 5.9$ Hz, C-4,5), 85.5 (d, $^3J_{\text{C,P}} = 1.8$ Hz, C-3,6), 79.9 (s, C-2,7), 23.7 (d, 2C, $^1J_{\text{C,P}} = 16.4$ Hz, $i\text{Pr}$: CH), 22.8 (s, O_2CCH_3), 18.7 (s, 2C, $i\text{Pr}$: CH_3), 18.6 (s, 2C, $i\text{Pr}$: CH_3). $^{31}\text{P-NMR}$ (benzene- d_6 , 81 MHz): δ 67.8. MS (EI): m/z (%) = 438 (78) [M^+]. IR (CH_2Cl_2): $\tilde{\nu}$ (OCO_{asym}) = 1532, $\tilde{\nu}$ (OCO_{sym}) = 1454 cm^{-1} . Anal. calc. for $\text{C}_{21}\text{H}_{27}\text{MoO}_2\text{P}$ (438.41): C, 57.53; H, 6.20. Found C, 57.30; H, 6.15%.

4.2. $[(o\text{-}i\text{Pr}_2\text{PC}_6\text{H}_4\text{-}\eta^7\text{-C}_7\text{H}_6)\text{MoCl}(=\text{CHC}_6\text{H}_5)(\text{P-Mo})]$ (**4a**)

A solution of **2** (200 mg, 0.45 mmol) in 20 ml of toluene was treated with 0.1 ml Me_3SiCl and stirred for 30 min at room temperature (r.t.). The reaction mixture was cooled to 0°C , and a freshly prepared solution of PhHCN_2 in hexane (6.4 ml of a 0.1 M solution, 0.64 mmol) was added. After stirring for 3 h at ambient temperature, the solvent was removed in vacuo and the residue extracted with hexane. Purification by recrystallization from hexane afforded dark green crystals of **4a**. Yield 80% (184 mg). $^1\text{H-NMR}$ (THF- d_8 , 600 MHz): δ 13.61 (d, 1H, $^3J_{\text{H,P}} = 26$ Hz, CHPh), 7.68 (m, 2H, C_6H_4), 7.62 (d, 2H, $o\text{-C}_6\text{H}_5$), 7.53 (m, 2H, C_6H_4), 7.31 (t, 2H, $m\text{-C}_6\text{H}_5$), 7.04 (t, 2H, $p\text{-C}_6\text{H}_5$), 5.55 (t, 1H, C_7H_6), 5.40 (d, 1H, C_7H_6), 5.15 (t, 1H, C_7H_6), 4.94 (t, 1H, C_7H_6), 4.43 (t, 1H, C_7H_6), 4.24 (t, 1H, C_7H_6), 2.79 (sep., 1H, $i\text{Pr}$: CH), 2.52 (sep., 1H, $i\text{Pr}$: CH), 1.41 (dd, 6H, $i\text{Pr}$: CH_3), 0.95 (dd, 6H, $i\text{Pr}$: CH_3). $^{13}\text{C-NMR}$ (THF- d_8 , 150.7 MHz): δ 317.5 (d, $^2J_{\text{C,P}} = 23.1$ Hz,

CHPh), 152.8 (d, $^2J_{\text{C,P}} = 29.0$ Hz, C-8), 149.6 (d, $^3J_{\text{C,P}} = 7.0$ Hz, $ipso\text{-C}_6\text{H}_5$), 138.3 (d, $^2J_{\text{C,P}} = 33.9$ Hz, C-9), 131.9 (s, $o\text{-C}_6\text{H}_5$), 131.3 (s, C-13), 131.1 (s, C-12), 129.2 (s, $p\text{-C}_6\text{H}_5$), 128.8 (d, $^2J_{\text{C,P}} = 6.7$ Hz, C-10), 128.7 (d, $^3J_{\text{C,P}} = 3.8$ Hz, C-11), 127.9 (s, $m\text{-C}_6\text{H}_5$), 107.9 (d, $^2J_{\text{C,P}} = 2.0$ Hz, C-1), 102.3 (s, C_7H_6), 97.0 (t, 2 C, C_7H_6), 93.7 (d, C_7H_6), 84.7 (s, C_7H_6), 81.6 (s, C_7H_6), 25.1 (d, $^1J_{\text{C,P}} = 15.6$ Hz, $i\text{Pr}$: CH), 24.6 (d, $^1J_{\text{C,P}} = 15.6$ Hz, $i\text{Pr}$: CH), 18.6 (s, $i\text{Pr}$: CH_3), 18.3 (m, 2C, $i\text{Pr}$: CH_3), 17.3 (s, 2C, $i\text{Pr}$: CH_3). $^{31}\text{P-NMR}$ (THF- d_8 , 81 MHz): δ 50.3. MS (EI): m/z (%) = 505(28) [M^+].

4.3. $[(o\text{-}i\text{Pr}_2\text{PC}_6\text{H}_4\text{-}\eta^7\text{-C}_7\text{H}_6)\text{MoCl}(=\text{CHSiMe}_3)(\text{P-Mo})]$ (**4b**)

A solution of **2** (150 mg, 0.34 mmol) in 20 ml of toluene was treated with 0.1 ml Me_3SiCl and stirred for 30 min at r.t. The reaction mixture was cooled to 0°C , and a solution of $\text{N}_2\text{CHSiMe}_3$ in hexane (0.23 ml of a 2 M solution, 0.46 mmol) was added. After stirring for 3 h at ambient temperature, the solvent was removed in vacuo, and the residue was extracted with hexane. Purification by recrystallization from hexane afforded brown crystals of **4b**. Yield: 99% (170 mg). $^1\text{H-NMR}$ (THF- d_8 , 400 MHz): δ 15.35 (d, 1H, $^3J_{\text{H,P}} = 32$ Hz, CHSiMe_3), 7.43 (m, 1H, C_6H_4), 7.35 (m, 1H, C_6H_4), 7.30 (m, 2H, C_6H_4), 5.40 (t, 1H, C_7H_6), 5.19 (dd, 2H, C_7H_6), 4.74 (t, 1H, C_7H_6), 4.38 (t, 1H, C_7H_6), 4.27 (t, 1H, C_7H_6), 2.47 (sep., 1H, $i\text{Pr}$: CH), 2.30 (sep., 1H, $i\text{Pr}$: CH), 1.23 (dd, 3H, $i\text{Pr}$: CH_3), 1.06 (dd, 3H, $i\text{Pr}$: CH_3), 0.80 (m, 6H, $i\text{Pr}$: CH_3), 0.00 (s, 9H, SiMe_3). $^{13}\text{C-NMR}$ (THF- d_8 , 100.6 MHz): δ 352.1 (d, $^2J_{\text{C,P}} = 23.3$ Hz, CHSiMe_3), 152.6 (d, $^2J_{\text{C,P}} = 28.1$ Hz, C-8), 135.8 (d, $^2J_{\text{C,P}} = 35.0$ Hz, C-9), 130.0 (s, 2C, C_6H_4), 127.4 (dd, 2C, C_6H_4), 103.3 (d, $^2J_{\text{C,P}} = 2.1$ Hz, C-1), 99.7 (s, C_7H_6), 97.7 (s, C_7H_6), 95.9 (d, C_7H_6), 91.6 (d, C_7H_6), 82.5 (s, C_7H_6), 81.0 (s, C_7H_6), 29.4 (s, 2 C, $i\text{Pr}$: CH), 18.0 (d, $^2J_{\text{C,P}} = 2.8$ Hz, $i\text{Pr}$: CH_3), 16.9 (d, $^2J_{\text{C,P}} = 3.4$ Hz, $i\text{Pr}$: CH_3), 16.5 (d, $^2J_{\text{C,P}} = 5.4$ Hz, $i\text{Pr}$: CH_3), 16.0 (s, $i\text{Pr}$: CH_3), 0.1 (s, 3C, SiMe_3). $^{31}\text{P-NMR}$ (benzene- d_6 , 81 MHz): δ 51.6.

4.4. X-ray crystallography

All data sets were collected at -120°C with a Bruker AXS APEX diffractometer equipped with a rotating anode using Mo- K_α radiation ($\lambda = 0.71073 \text{ \AA}$). Empirical absorption correction with SADABS [32] was applied to the raw data. Structure solution in all cases with SHELXS [33] and refinement with SHELXL [34] with anisotropic thermal parameters for all atoms. Hydrogen atoms for **2** and for the cation in **6** were located by difference Fourier techniques and were refined with isotropic thermal parameters, the hydrogen atoms for the BPh_4 counterions in **6** were added to the structure model on calculated positions and are unrefined. ORTEP

Table 1
Crystallographic data for **2** and **6**

	2	6
Formula	C ₂₁ H ₂₇ MoO ₂ P	C ₅₈ H ₅₆ BMoP
Formula weight (amu)	438.34	890.75
<i>a</i> (Å)	15.0825(15)	9.8870(18)
<i>b</i> (Å)	14.373(2)	17.054(3)
<i>c</i> (Å)	18.223(3)	27.011(5)
α (°)	90	90
β (°)	90	93.349(3)
γ (°)	90	90
<i>V</i> (Å ³)	3950.6(10)	4546.6(14)
<i>D</i> _{calc} (g cm ⁻³)	1.474	1.301
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Pbca</i>	<i>P2</i> ₁
<i>Z</i>	8	4
μ (mm ⁻¹)	0.756	0.362
Unique data	5758	11 846
Observed data $\{I > 2\sigma(I)\}$	4901	10 204
<i>R</i> ₁ (obs. data) (%)	2.57, <i>wR</i> ₁ = 6.36	4.26, <i>wR</i> ₁ = 9.16
<i>R</i> ₂ (all data) (%)	3.27, <i>wR</i> ₂ = 6.65	5.52, <i>wR</i> ₂ = 9.76
Goodness-of-fit	1.050	0.998
Number of variables	334	1387
Res. electr. dens. (e Å ⁻³)	0.596/−0.223	0.411/−0.607

[35] was used for all drawings. Additional crystallographic data are listed in Table 1.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 205582 (**2**) and 205583 (**6**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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