Synthesis, Structure and Reactivity of the Molybdenum Cycloheptatrienyl Tetrahydroborate Complex {(η^7-C$_7$H$_7$)Mo(η^2-BH$_4$)[P(*cyclo*-C$_6$H$_{11}$)$_3$]}

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Dedicated to Professor Wolfgang Jeitschko on the occasion of his 70th birthday

The reaction of the cycloheptatrienyl-toluene sandwich complex [(η^7-C$_7$H$_7$)Mo(η^6-C$_6$H$_5$Me)]BF$_4$ with tricyclohexylphosphine in acetonitrile furnishes the cationic half-sandwich cycloheptatrienyl complex {(η^7-C$_7$H$_7$)Mo[P(C$_6$H$_{11}$)$_3$](CH$_3$CN)$_2$}BF$_4$ (**1**). Treatment of **1** with NaBH$_4$ in ethanol results in the formation of the tetrahydroborate complex {(η^7-C$_7$H$_7$)Mo(η^2-BH$_4$)[P(*cyclo*-C$_6$H$_{11}$)$_3$]} (**2**), in which the borohydride ligand is coordinated to the molybdenum atom through two three-center, two-electron bonds. The complex is stable in ethanol and water. The expected formation of a metal trihydride of the type {(η^7-C$_7$H$_7$)MoH$_3$[P(*cyclo*-C$_6$H$_{11}$)$_3$]} as a hydrolysis product could not be observed. Since this behaviour differs from the reactivity reported for related cyclopentadienyl-ruthenium complexes, a comparative computational study on the model complexes [(η^5-C$_5$Me$_5$)RuH$_3$(PMe$_3$)] (**4**) and [(η^7-C$_7$H$_7$)MoH$_3$(PMe$_3$)] (**5**) was performed revealing that the classical trihydride form [MH$_3$] represents the global minimum for the ruthenium complex **4**, whereas the dihydrogen-hydride form [MH(η^2-H$_2$)] is more stable for the molybdenum counterpart.

Key words: Cycloheptatrienyl Ligands, Hydride Ligands, Dihydrogen Complexes, Density Functional Calculations

Introduction

Transition metal tetrahydroborate complexes have been studied extensively in the past [1, 2]. The interest in the monoanionic BH$_4$-ligand is primarily based on its rich and diverse coordination chemistry, which involves mono-, bi- or tridentate coordination through one, two or three bridging two-electron three-center B-H-M bonds, respectively [1 – 3]. Since BH$_4^-$ and CH$_4$ are isoelectronic, these different coordination modes might serve as prototype structures for the coordination and activation of saturated hydrocarbons such as methane [4, 5]. In addition, decomposition of tetrahydroborate complexes can be used as a convenient entry to transition metal hydride as well as dihydrogen complexes, and this reactivity is also of significance with regard to hydrogenation catalysis [6].

In the course of our studies on molybdenum complexes with linked cycloheptatrienyl-phosphine ligands [7], we have synthesized the tetrahydroborate complexes **III** as stable precursors for the generation of the cationic 14-electron complex fragment [(*o*-R$_2$PC$_6$H$_4$-η^7-C$_7$H$_6$)Mo(*P-Mo*)]$^+$ (R = *i*Pr, Ph), which can be used in catalytic carbon-carbon bond formation [7c]. The ease of isolation and stability of the tetrahydroborates **III** was somewhat surprising since the corresponding complexes [(η^5-C$_5$Me$_5$)Ru(η^2-BH$_4$)(PR$_3$)] (**I**, R = Me, Et, *i*Pr, *cyclo*-C$_6$H$_{11}$, Ph) containing the isolobal cyclopentadienyl-ruthenium moiety [7c, 7d, 8] are unstable in ethanol solution and undergo immediate protonolysis to form ruthenium trihydrides [(η^5-C$_5$Me$_5$)RuH$_3$(PR$_3$)] **II** [9]. In contrast, various attempts to convert **III** into the corresponding trihydride proved unsuccessful (Scheme 1). For complexes **II**, a pseudo-square-pyramidal arrange-

R = H, CH₃
R' = CH₃, *i*Pr, Ph

R = *i*Pr, Ph
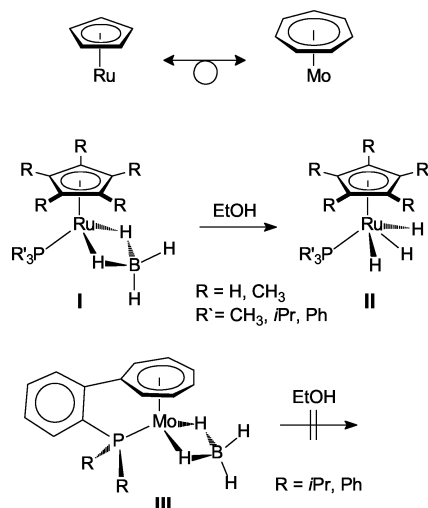
Scheme 1.

Scheme 2.

ment of the ligands was observed with the phosphine and the hydrides forming the basal plane. However, at temperatures above −80 ℃ only one ^{1}H NMR resonance was observed for the hydride atoms, and it could be assumed that their quick interconversion proceeds *via* a trigonal-bipyramidal arrangement, in which the hydrogen atoms are in equatorial and the Cp and phosphine ligands in axial positions. In complexes **III**, such interconversion is not possible due to the bridge between the cycloheptatrienyl and phosphanyl donor moiety. Accordingly, the absence of such linkage might enhance the reativity of cyclohepatrienyl tetrahydroborate complexes of the type [(η^7-C₇H₇)Mo(η^2-BH₄)(PR₃)] towards ethanol or other proton sources and, at the same time, the possibility to exchange the positions of the hydride ligands might lead to a stabilization of the corresponding trihydride derivatives [(η^7-C₇H₇)MoH₃(PR₃)]. Hence, we wish to report here on the synthesis and structural characterization of the tetrahydroborate complex [(η^7-C₇H₇)Mo(η^2-BH₄)(PCy₃)] (Cy = *cyclo*-C₆H₁₁, **2**) and on its reactivity towards potential proton sources such as ethanol or acetic acid. In addition, comparative theoretical calculations on trihydride complexes incorporating the isolobal complex fragments [(η^5-C₅Me₅)Ru(PR₃)] and [(η^7-C₇H₇)Mo(PR₃)] will be presented.

Results and Discussion

Complexes of type **III** have been prepared by the reduction of the molybdenum(I) dibromides [(*o*-R₂PC₆H₄-η^7-C₇H₆)MoBr₂(*P-Mo*)] with NaBH₄
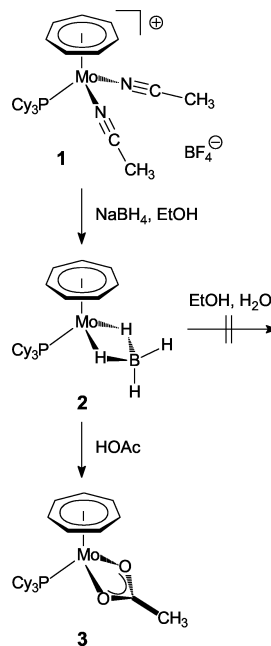
in ethanol solution. In contrast, the synthesis of **2** can be achieved from the readily available molybdenum(0) complex [(η^7-C₇H₇)Mo(CO)₃]BF₄ [10], which reacts in boiling toluene to afford the cationic sandwich complex [(η^7-C₇H₇)Mo(η^6-C₆H₅Me)]BF₄ [11]. Subsequent reaction in acetonitrile results in removal of the arene ligand and in the formation of [(η^7-C₇H₇)Mo(CH₃CN)₃]BF₄, in which the weakly coordinated acetonitrile ligands can easily be displaced by softer ligands such as mono- and diphosphines [12]. Accordingly, [(η^7-C₇H₇)Mo(PCy₃)(CH₃CN)₂]BF₄ (**1**) can be obtained from the reaction of the cycloheptatrienyl-toluene sandwich complex with acetonitrile in the presence of tricyclohexylphosphine, PCy₃ (Scheme 2). **1** is isolated as an air-sensitive brownish solid, which is stable only in acetonitrile solution and rapidly decomposes in other coordinating solvents such as THF, acetone or dichloromethane. The ^{1}H and ^{13}C NMR spectroscopic characterization of **1** reveals resonances at 5.13 and 88.2 ppm for the C₇H₇ hydrogen and carbon atoms, respectively. The ^{31}P NMR spectrum exhibits a single resonance at 28.7 ppm, which is about 18 ppm downfield from the resonance observed for the uncoordinated P(C₆H₁₁)₃ ligand.

The two acetonitrile ligands in **1** can also be easily displaced by other ligands, and the reaction of **1** with sodium tetrahydroborate, NaBH₄, in ethanol so-

lution affords the tetrahydroborate complex **2** as a pale green crystalline solid after extraction with diethyl ether and evaporation of the solvent (Scheme 2). The broad high-field ^{1}H NMR resonance at −5.76 ppm reveals the presence of metal-coordinated hydride functions. Single crystals of **2** obtained from a diethyl ether/hexane solution at −30 °C have been subjected to an X-ray crystal structure determination, and the molecular structure of **2** is shown in Fig. 1. The cycloheptatrienyl ring is coordinated in a symmetric η^7-fashion with Mo-C distances in the range from 2.240(2) to 2.294(3) Å. The geometry around the metal atom can be interpreted as a two-legged piano stool with the centroid of the seven-membered ring and the Mo, P and B atoms in the same plane. In addition, the positions of all hydrogen atoms were refinable, indicating that the BH$_4$ anion is coordinated to the molybdenum atom through two three-center, two-electron bonds, thereby simultaneously blocking two coordination sites. This bidentate M(η^2-H$_2$BH$_2$) ligation represents the most common mode of bonding in transition metal tetrahydroborate complexes [1 – 3, 13]. It should be noted, however, that only a small number of mononuclear molybdenum-borohydride complexes have previously been structurally characterized [14], including one representative of complexes **III** (R = *i*Pr, Scheme 1) [7c], [MoH(η^2-BH$_4$)(PMe$_3$)$_4$] [14c] and [Mo(η^2-BH$_4$)(CO)$_4$]$^-$ [14d], in which the BH$_4$-ligand is also coordinated in a dihapto fashion. In addition, since most metal borohydrides contain metals in positive formal oxidation states [1, 2], **2** together with the linked cycloheptatrienyl-phosphine complexes **III** represents one of the few well-defined examples of zerovalent metal borohydrides, a class, which was previously limited to the monoanionic complexes [M(η^2-BH$_4$)(CO)$_4$]$^-$ (M = Cr, Mo) [14d] and [Ti(η^3-BH$_4$)(CO)$_4$]$^-$ [15].

In contrast to our supposition, the tetrahydroborate complex **2** behaves similarly to its linked cycloheptatrienyl-phosphine counterparts **III** (Scheme 1) with respect to its stability in ethanol solution and lack of reactivity towards the formation of a trihydride complex [(η^7-C$_7$H$_7$)MoH$_3$(PCy$_3$)]. **2** remains stable in ethanol solution for prolonged time even after the addition of water and/or catalytic amounts of alumina, whereas the addition of acetic acid results in the immediate cleavage of the Mo-H-B bonds and formation of the acetate complex **3**, which could be fully characterized by means of NMR spectroscopy and mass spectrometry (Scheme 2). The resonances observed for the
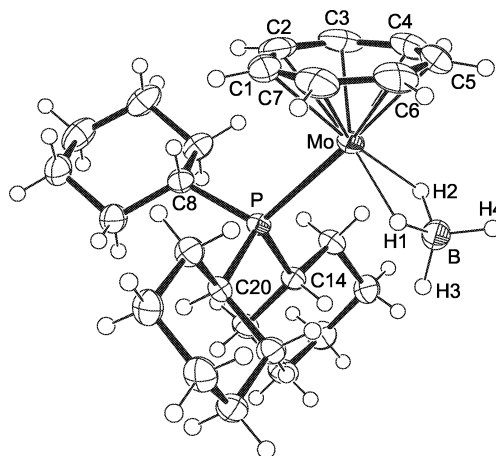

Fig. 1. ORTEP drawing of **2** with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å] and angles [°]: Mo–C1 2.280(3), Mo–C2 2.294(3), Mo–C3 2.268(3), Mo–C4 2.240(2), Mo–C5 2.289(2), Mo–C6 2.263(2), Mo–C7 2.254(2), Mo–P 2.5468(5), Mo–B 2.380(3), Mo–H1 1.88(3), Mo–H2 1.90(2), C1–C2 1.408(4), C1–C7 1.395(4), C2–C3 1.399(4), C3–C4 1.403(4), C4–C5 1.389(4), C5–C6 1.387(4), C6–C7 1.395(4); Mo–P–C8 114.17(7), Mo–P–C14 114.10(6), Mo–P–C20 112.70(7), C8–P–C14 109.18(9), C8–P–C20 102.59(9), C14–P–C20 102.94(9), H1–B–H2 103(2).

acetate ligand at 1.74 ppm (C*H$_3$*) and at 177.7 ppm (*C*OO) and 22.8 ppm (*C*H$_3$), respectively, are in good agreement with the values found for related transition metal carboxylate complexes [7a, 16], indicating an η^2-coordination mode for the acetate moiety.

From the results described above, it is obvious that there is a distinct difference in reactivity between cycloheptatrienyl-molybdenum and cyclopentadienyl-ruthenium tetrahydroborate complexes and that the corresponding molybdenum trihydrides can not be isolated under the same conditions as described for the ruthenium analogues [9]. Further experiments towards finding the right conditions and the appropriate acid for the generation of trihydride complexes of the type [(η^7-C$_7$H$_7$)MoH$_3$(PR$_3$)] from borohydrides such as **2** are in progress. In order to investigate the expected structure of such a molybdenum trihydride and in order to elucidate differences between hydride complexes containing the isolobal cyclopentadienyl-ruthenium and cycloheptatrienyl-molybdenum moieties, we have performed a comparative quantum chemical study on the model complexes [(η^5-C$_5$Me$_5$)RuH$_3$(PMe$_3$)] (**4**) and [(η^7-C$_7$H$_7$)MoH$_3$(PMe$_3$)] (**5**). The calculations were performed using the Gaussian03 package [17]. Both structures have been fully optimized
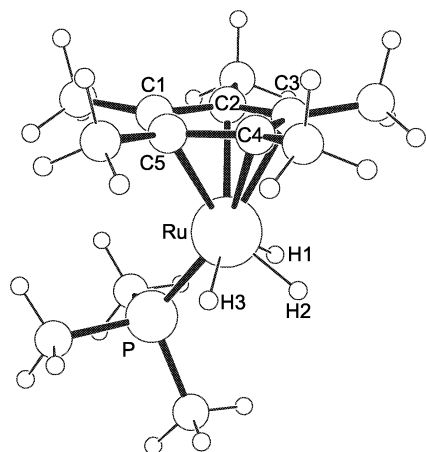
Fig. 2. Presentation of the calculated structure of **4**. Selected bond lengths [Å] and angles [°]: H1–H2 1.713, H2–H3 1.713, Ru–H1 1.599, Ru–H2 1.586, Ru–H3 1.599, Ru–P 2.279, Ru–C1 2.360, Ru–C2 2.307, Ru–C3 2.243, Ru–C4 2.243, Ru–C5 2.307, C1–C2 1.428, C1–C5 1.428, C2–C3 1.438, C3–C4 1.432, C4–C5 1.438, H1–Ru–H2 65.1, H1–Ru–H3 118.2, H2–Ru–H3 65.1, H1–Ru–P 76.1, H2–Ru–P 97.0, H3–Ru–P 76.1.
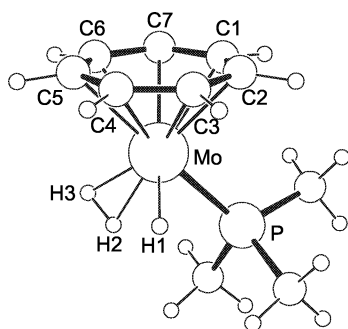

Fig. 3. Presentation of the calculated structure of **5**. Selected bond lengths [Å] and angles [°]: H1–H2 1.941, H2–H3 0.850, Mo–H1 1.743, Mo–H2 1.806, Mo–H3 1.871, Mo–P 2.494, Mo–C1 2.321, Mo–C2 2.327, Mo–C3 2.285, Mo–C4 2.309, Mo–C5 2.353, Mo–C6 2.344, Mo–C7 2.392, C1–C2 1.421, C1–C7 1.414, C2–C3 1.409, C3–C4 1.422, C4–C5 1.405, C5–C6 1.417, C6–C7 1.410, H1–Mo–H2 66.3, H1–Mo–H3 88.2, H2–Mo–H3 26.7, H1–Mo–P 78.7, H2–Mo–P 73.0, H3–Mo–P 91.5.

with DFT methods employing the B3LYP hybrid functional (Figs 2 and 3). For all main-group elements (C, H and P) the all-electron triple-ζ basis set (6-311G**) was used, whereas for the group 6 and group 8 transition metals Ru and Mo a small-core relativistic ECP together with the corresponding triple-ζ valence basis set was employed (Stuttgart RSC 1997 ECP) [18, 19].

The calculated gas phase geometry of the ruthenium trihydride complex **4** is in good agreement with

the solid state structure of the corresponding triphenylphosphine complex [(η^5-C$_5$Me$_5$)RuH$_3$(PPh$_3$)], which has been determined by X-ray diffraction analysis [9]. To our surprise, the optimized structure of the analogous molybdenum complex **5** reveals a slightly different geometry with respect to the arrangement of the three hydrogen atoms around the molybdenum center. Whereas the equilibrium Ru-H distances in **4** point to three regular ruthenium-hydride single bonds, the molybdenum-bonded hydrogen atoms in complex **5** exhibit one very short H-H distance of 0.850 Å suggesting a dihydrogen ligand, H$_2$, in addition to a single hydride, H$^-$, coordinated to the molybdenum center. Since atom-atom distances are not always valid bond strength descriptors [20], we further investigated the intramolecular forces in **4** and **5** by means of the generalized compliance constants [21] in order to unambiguously differentiate between hydridic and dihydrogen bonding. Compliance constants, whether recorded experimentally [22] or computed theoretically, measure the displacement of a single internal coordinate due to an external force. While all Ru-H bond strengths in **4** are approximately the same, namely 0.41 Å/mdyne for the Ru-H1 and Ru-H3 bonds and 0.39 Å/mdyne for the Ru-H2 bond, respectively, all H···H contacts between the metal-bonded hydrogen atoms are weaker by one order of magnitude (4.03 Å/mdyne). This is in line with the absence of any covalent dihydrogen bonding in **4**. Turning to complex **5**, the two-electron bond of the dihydrogen ligand H2-H3 is weakened but still intact (H2-H3 compliance constant: 0.61 Å/mdyne). Furthermore, the Mo-H2 and Mo-H3 interactions are weak bonds (1.10 Å/mdyne and 1.06 Å/mdyne, respectively) while the Mo-H1 bond is twice as strong and hydridic in nature (compliance constant: 0.58 Å/mdyne). Finally, the interaction between the dihydrogen ligand H2-H3 and the single hydride shows a compliance constant of 5.87 Å/mdyne, substantiating the claim for a mixed dihydrogen-hydride ligand pattern in **5**, which should thus be formulated as [(η^7-C$_7$H$_7$)MoH(η^2-H$_2$)(PMe$_3$)].

In order to measure the energy difference between the dihydrogen-hydride and the corresponding trihydride structure of complex **5**, we have tried to locate a stationary point on the potential energy surface associated with the latter structure. The calculation revealed that the C_s symmetric trihydride with Mo-H compliance constants of about 0.5 Å/mdyne represents a transition state ($\Delta H^{\#} = 4.66$ kcal/mol; imaginary frequency $= -208$ cm^{-1}) connecting the two degenerate
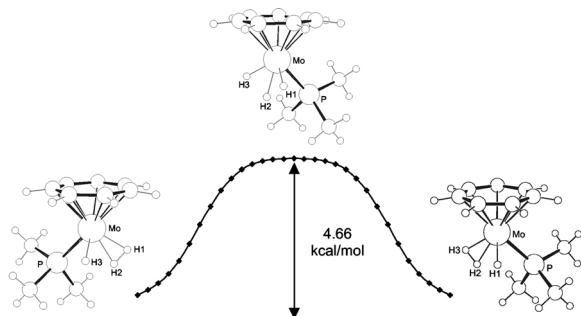
Fig. 4. The reaction path for the interconversion of the dihydrogen-hydride enantiomers of **5** followed by an IRC (intrinsic reaction coordinates) calculation.

dihydrogen-hydride enantiomers. Following this reaction path by an IRC (intrinsic reaction coordinates) calculation reveals that this interconversion proceeds *via* an extremely flat, plateau-like transition region [23], and no intermediate minimum could be localized (Fig. 4). These findings differ from the experimental and theoretical results reported for other trihydride systems. In cationic molybdenocene complexes for instance, both the trihydride $[MH_3]$ and the dihydrogen-hydride species $[MH(\eta^2\text{-}H_2)]$ represent either global or local minima on the respective potential energy surface [24].

Conclusion

With this contribution, we have reported a convenient access to cycloheptatrienyl-molybdenum tetrahydroborate complexes such as $[(\eta^7\text{-}C_7H_7)Mo(\eta^2\text{-}BH_4)(PCy_3)]$ (**2**). The reaction of the latter with potential proton sources such as ethanol or acetic acid did not result in the formation of the expected trihydride complex. Our theoretical calculations suggest, however, that, in contrast to the classical trihydride $[MH_3]$ arrangement observed for $[(\eta^5\text{-}C_5Me_5)RuH_3(PR_3)]$ complexes, the formation of non-classical hydride-dihydrogen $[MH(\eta^2\text{-}H_2)]$ complexes should be expected upon substitution of the cyclopentadienyl-ruthenium for the isolobal cycloheptatrienyl-molybdenum moiety. Further studies are in progress to synthesize and fully characterize such species.

Experimental Section

All operations were performed in an atmosphere of dry argon by using Schlenk and vacuum techniques. All solvents were purified by standard methods and distilled prior to use. The complexes $[(\eta^7\text{-}C_7H_7)Mo(CO)_3]BF_4$

[10, 25], $[(\eta^7\text{-}C_7H_7)Mo(\eta^6\text{-}C_6H_5Me)]BF_4$ [11], and $[(\eta^7\text{-}C_7H_7)Mo(CH_3CN)_3]BF_4$ [12] were prepared according to published procedures.

*Preparation of $\{(\eta^7\text{-}C_7H_7)Mo[P(cyclo\text{-}C_6H_{11})_3]\text{-}(CH_3CN)_2\}BF_4$ (**1**)*

A solution of the toluene complex $[(\eta^7\text{-}C_7H_7)Mo(\eta^6\text{-}C_6H_5Me)]BF_4$ (1.0 g, 2.73 mmol) in acetonitrile (50 ml) is stirred at 80 °C for one hour. After the addition of tricyclohexylphosphine (1.53 g, 5.46 mmol), the brownish reaction mixture is stirred at 110 °C for additional 12 h. The resulting solution is filtered hot and concentrated *in vacuo*. Addition of the remaining solution to rapidly stirred diethyl ether precipitates the product as a brown solid, which is isolated by filtration. Yield: 84% (1.46 g, 2.29 mmol). ^{1}H NMR (400 MHz, CD$_3$CN): $\delta = 5.13$ (s, 7 H, C$_7$H$_7$), 2.18 (s br, 6 H, C$_6$H$_{11}$), 1.79 (s br, 12 H, C$_6$H$_{11}$), 1.71 (s br, 3 H, C$_6$H$_{11}$), 1.38 – 1.25 (m br, 12 H, C$_6$H$_{11}$); the resonances for the CH_3 hydrogen atoms of the acetonitrile ligands could not be detected due to fast solvent exchange. – ^{13}C $\{^1$H$\}$ NMR (100.6 MHz, CD$_3$CN): $\delta = 88.2$ (s, C$_7$H$_7$), 36.4 (d, $J_{CP} = 13.3$ Hz, PC$_6$H$_{11}$), 30.9 (s, PC$_6$H$_{11}$), 28.5 (d, $J_{CP} = 10.0$ Hz, PC$_6$H$_{11}$), 27.2 (s, PC$_6$H$_{11}$); the resonances for the acetonitrile ligands could not be detected due to fast solvent exchange. – ^{31}P NMR (162 MHz, CD$_3$CN): $\delta = 28.7$.

*Preparation of $\{(\eta^7\text{-}C_7H_7)Mo(\eta^2\text{-}BH_4)\text{-}[P(cyclo\text{-}C_6H_{11})_3]\}$ (**2**)*

A suspension of NaBH$_4$ (104 mg, 2.75 mmol) in ethanol (25 ml) is treated with **1** (250 mg, 0.39 mmol) at 0 °C, resulting in instantaneous gas evolution. The reaction mixture is allowed to warm up to r.t., and stirring is continued for 20 min. The solvent is evaporated and the residue extracted with diethyl ether/hexane (1:1). Cooling of this solution to −30 °C gives pale green crystals. Yield: 75% (141 mg, mmol). ^{1}H NMR (400 MHz, C$_6$D$_6$): $\delta = 5.19$ (s, 7 H, C$_7$H$_7$), 1.66 – 1.11 (m br, 33 H, C$_6$H$_{11}$), −5.76 (s br, 2 H, MoH_2BH_2); the resonances for two of the BH$_4$ protons could not be detected at ambient temperature – they are expected to appear as very broad resonances $\delta > 0$ ppm [7c, 9]. – ^{13}C $\{^1$H$\}$ NMR (100.6 MHz, C$_6$D$_6$): $\delta = 84.4$ (s, C$_7$H$_7$), 34.3 (d, $J_{CP} = 14.5$ Hz, PC$_6$H$_{11}$), 30.7 (s, PC$_6$H$_{11}$), 28.0 (d, $J_{CP} = 9.7$ Hz, PC$_6$H$_{11}$), 27.0 (s, PC$_6$H$_{11}$). – ^{31}P NMR (162 MHz, CD$_3$CN): $\delta = 28.7$. – C$_{25}$H$_{44}$BMoP (482.32): calcd. C 62.25, H 9.19; found C 62.10, H 9.26.

*Preparation of $\{(\eta^7\text{-}C_7H_7)Mo(\eta^2\text{-}O_2CCH_3)\text{-}[P(cyclo\text{-}C_6H_{11})_3]\}$ (**3**)*

A solution of **2** (100 mg, 0.21 mmol) in ethanol (20 ml) is treated with an excess of acetic acid at 0 °C. The reaction mixture is allowed to warm up to r.t., and stirring is continued until the gas evolution has ceased. The solvent is evap-

Table 1. Summary of the crystal data and details of data collection and refinement for compound **2**.

Empirical formula	$C_{25}H_{44}BMoP$
Formula mass	482.32
Crystal system	monoclinic
Space group	$P2_1/n$ (no. 14)
A [Å]	14.4453(1)
B [Å]	11.9472(1)
C [Å]	15.1406(1)
β [°]	110.6221(4)
V [Å^3]	2445.55(3)
Z	4
ρ_{calcd} [g cm^{-3}]	1.31
μ [mm^{-1}]	0.6
T [K]	143
$F(000)$	1024
Crystal size [mm]	$0.46 \times 0.30 \times 0.08$
θ-Range [°]	1.68/25.37
Index ranges	h: ±17 / k: ±14 / l: ±18
Reflections collected	48102
Independent reflections	3994/4496/0.043
$[I_o > 2\sigma(I_o)$/all data/$R_{int}]$	
Data / parameters	4496/429
$R1$ $[I_o > 2\sigma(I_o)$/all data]	0.0233/0.0296
$wR2$ $[I_o > 2\sigma(I_o)$/all data]	0.0513/0.0537
GOF	1.039
Weights a/b	0.0176/2.0625
$\Delta\rho_{max/min}$ [e·Å^{-3}]	0.47/−0.32

orated and the residue extracted with diethyl ether/hexane (1 : 1). Recrystallization from a diethyl ether/hexane solution affords **3** as a green crystalline solid. Yield: 68% (74 mg, 0.14 mmol). ^{1}H NMR (400 MHz, C$_6$D$_6$): $\delta = 5.37$ (s, 7 H, C$_7H_7$), 1.84 – 1.14 (m br, 33 H, C$_6H_{11}$), 1.74 (s, 3 H, CHH$_3$). – ^{13}C $\{^1$H$\}$ NMR (100.6 MHz, C$_6$D$_6$): $\delta = 177.7$ (s, O$_2C$), 85.2 (s, C_7H$_7$), 33.9 (d, $J_{CP} = 11.1$ Hz, PC_6H$_{11}$), 30.0 (s, PC_6H$_{11}$), 28.2 (d, $J_{CP} = 9.4$ Hz, PC_6H$_{11}$), 26.7 (s, PC_6H$_{11}$), 22.8 (s, CH$_3$). – ^{31}P NMR (162 MHz, CD$_3$CN): $\delta = 38.6$. – MS (CI): m/z (%) = 511 (25) [M$^+$-CH$_3$].

Single crystal X-ray structure determination of compound **2**

Crystal data and details of the structure determination are presented in Table 1. Suitable single crystals for the X-ray diffraction study were grown from a diethyl ether/hexane (1 : 1) solution at −30 °C. A clear pale green plate was stored under perfluorinated ether, transferred in a Lindemann capillary, fixed, and sealed. Preliminary examination and data collection were carried out on an area detecting system (NONIUS, MACH3, κ–CCD) at the window of a rotating anode (NONIUS, FR591) and graphite monochromated Mo-K$_\alpha$ radiation ($\lambda = 0.71073$ Å). The unit cell parameters were obtained by full-matrix least-squares refinement of 4732 reflections. Data collection were performed at 143 K (OXFORD CRYOSYSTEMS) within a θ-range of $1.68° < \theta < 25.37°$. Nine data sets were measured in rotation scan modus with $\Delta\varphi/\delta\Omega = 1.0°$. A total number of 48102 intensities were integrated. Raw data were corrected for Lorentz polarization, and, arising from the scaling procedure, for latent decay and absorption effects. After merging ($R_{int} = 0.043$) a sum of 4496 (all data) and 3994 $[I > 2\sigma(I)]$, respectively, remained and all data were used. The structure was solved by a combination of direct methods and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atom positions were found in the difference map calculated from the model containing all non-hydrogen atoms. The hydrogen positions were refined with individual isotropic displacement parameters. Full-matrix least-squares refinements with 429 parameters were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with SHELXL-97 weighting scheme and stopped at shift/err < 0.001. The final residual electron density maps showed no remarkable features. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*. All calculations were performed on an Intel Pentium II PC, with the STRUX-V system, including the programs PLATON, SIR92, and SHELXL-97 [26].

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