189. Synthesis and Reactivity of Naphthalene Sandwich Complexes of Molybdenum. X-Ray Structure of [Mo(η^6-naphthalene){P(OMe)$_3$}$_3$] and [Mo(H)(η^6-naphthalene){P(OMe)$_3$}$_3$][BF$_4$]

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The sandwich complexes bis(η^6-naphthalene)molybdenum(0) (**1**), bis(η^6-1-methylnaphthalene)molybdenum(0) (**2**), and bis(η^6-1,4-dimethylnaphthalene)molybdenum(0) (**3**) are synthesized by cocondensation of Mo-atoms with the naphthalene ligands. Complexes **1**–**3** are also obtained by reduction of $MoCl_5$ or $MoCl_4 \cdot 2THF$ with highly activated Mg in the presence of the naphthalene ligands. Mg was activated by sublimation of the metal in a simple rotating solution reactor. Complex **2** exists as a mixture of regio- and stereoisomers. Three regioisomers, **3a**–**c**, are formed in reactions of Mo-atoms with 1,4-dimethylnaphthalene, whereas **3a**, the isomer with the Mo-atom coordinated to the unsubstituted rings, is formed selectively *via* the reductive method. The ligands in **1**–**3** are highly labile. CO displaces both naphthalene rings in **2** and **3** to give [Mo(CO)$_6$], while PF$_3$, P(OMe)$_3$, and PMe$_3$ displace only one coordinated naphthalene in **1** to yield the [Mo(η^6-naphthalene)L$_3$] complexes **4**–**6**. In toluene, arene exchange is a competitive process in reactions of **1** with PF$_3$. Complexes **5** (L = P(OMe)$_3$) and **6** (L = PMe$_3$) react with HBF$_4$ to give the cationic metal hydride complexes **8** and **9**. The X-ray crystal structures of [Mo(η^6-naphthalene){P(OMe)$_3$}$_3$] (**5**) and [Mo(H)(η^6-naphthalene){P(OMe)$_3$}$_3$][BF$_4$] (**8**) are reported.

1. Introduction. – The first comments on the lability of complexes of fused arenes can be found in *Fischer et al.*'s paper on the synthesis of [Cr(CO)$_3$(η^6-naphthalene)] in 1958 [1]. It is now well established that the arene–metal bond of condensed aromatics undergoes substitution reactions much more readily than that to benzene [2–9]. Theoretical [2] [9b], kinetic [3c] [6] [8b–11], and thermochemical studies [7b] [12] have shown that the enhanced reactivity of the naphthalene–metal bond over that of benzene (*'naphthalene effect'*) is due to kinetic as well as ground-state thermodynamic differences. The naphthalene–metal bond is more labile because the metal can undergo facile slippage, thereby freeing coordination sites at the metal center[1]) (*Fig. 1*). Ground-state thermodynamic differences contribute, because naphthalene binds less strongly to the metal. Determina-

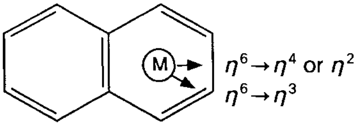

Fig. 1. *The* 'naphthalene effect'. Facile ring slippage in naphthalene transition-metal complexes generates coordination sites at the metal center.

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[1]) The 'ring slippage' mechanism in substitution reactions of η^6-arene complexes was first reported by *Basolo* and coworkers [13].

tion of bond-dissociation energies *via* calorimetric methods reveal the naphthalene–Cr bond in the $Cr(CO)_3$ complex to be 6 kcal/mol weaker than the benzene–Cr bond [12] [7b]. It is interesting to note that, while the benzene complexes of $Mo(CO)_3$, $W(CO)_3$, and $Mn(CO)_3^+$ have a well established and extensive chemistry, the naphthalene analogues are not known. Other benzo-fused π-ligands show a similar enhanced reactivity, with the indenyl ligand being the most thoroughly investigated [14].

The '*naphthalene effect*' is of practical use. The lability of η^6-naphthalene is a key-factor in the efficiency of [$Cr(CO)_3$(η^6-naphthalene)] and of [Ru(η^6-naphthalene)(η^4-cycloocta-1,5-diene)] in homogeneous catalysis under mild conditions [15–17] [8b]. In another application, [$Cr(CO)_3$(η^6-naphthalene)] gives access, *via* naphthalene exchange, to functionalized [Cr(arene)$(CO)_3$] complexes important in organic synthesis [3c] [18–21].

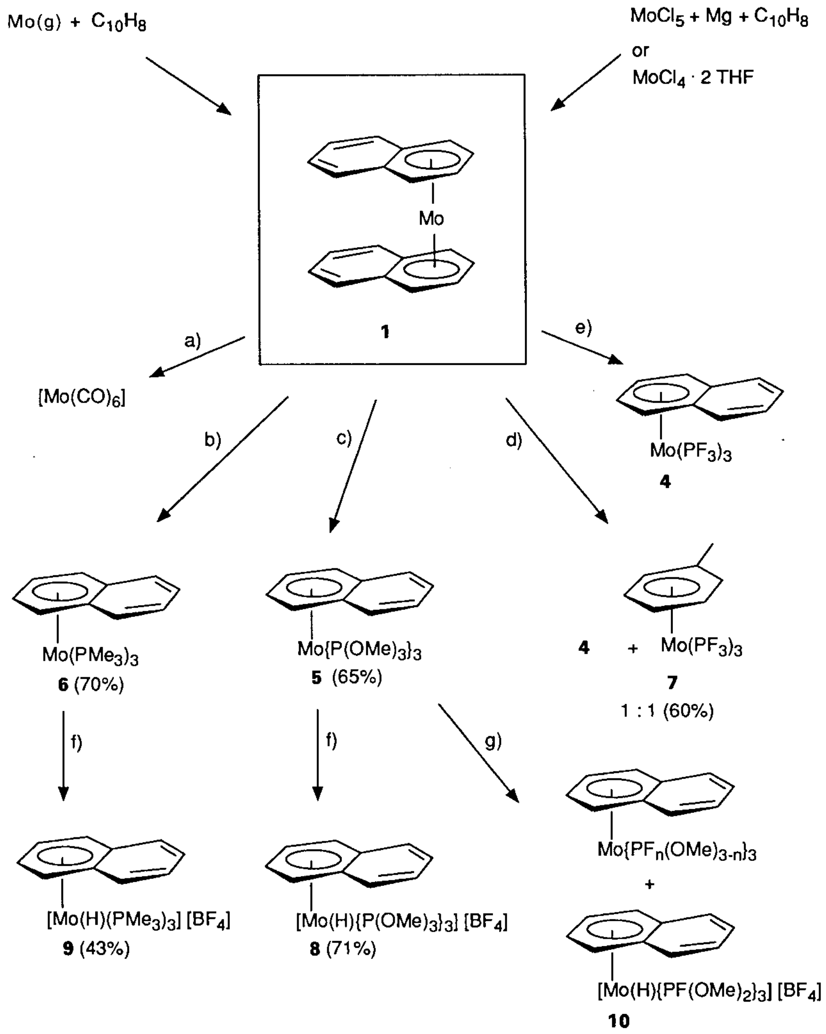
The sandwich complex [$Cr(naphthalene)_2$] provides an entry to half sandwich [CrL_3(naphthalene)] complexes [3b], to homoleptic [CrL_6] complexes [3b], and to mixed [Cr(arene)(naphthalene)] sandwich compounds [3c] [22]. When we consider the analogous Mo complex, the subject of this article, we have to keep in mind that although the metal–benzene bond in [Mo(η-benzene)$_2$] [23] is stronger (mean bond dissociation enthalpy $D = 50.4$ kcal/mol [24]) than that in [Cr(η-benzene)$_2$] ($D = 39.4$ kcal/mol [25]), the Mo complex is more labile and has a much richer substitution chemistry than the Cr analog [26–28]. The reactivity enhancement of naphthalene complexes, thus, makes [$Mo(naphthalene)_2$] a potentially very versatile precursor for a wide range of complexes.

General methods that give access to group-VI arene sandwich complexes are the classical *Fischer-Hafner* method and metal-vapor synthesis. The former fails when applied to the synthesis of naphthalene-chromium complexes as partial hydrogenation of the ligand is a competitive side reaction [29]. Metal-vapor synthesis [30] provides an efficient access to bis(naphthalene)chromium complexes [3] [4] [22a], and this route has also been used successfully in the preparation of monocyclic arene Mo sandwich complexes [31–34]. We here report details of the synthesis of homoleptic naphthalene-molybdenum complexes *via* this route. We also present an alternative, more convenient, reductive synthesis of these labile complexes and demonstrate their reactivity.

2. Preparation of Molybdenum Sandwich Complexes. – a) Via *Metal-Vapor Synthesis.* When Mo-atoms were cocondensed with an excess of naphthalene onto a liquid-N_2-cooled surface, a brown matrix was formed from which the sandwich complex bis(η^6-naphthalene)molybdenum(0) (**1**) was isolated as black, very oxygen-sensitive crystals (*Scheme 1*). The yield of **1** was poor, because its separation from elemental molybdenum and excess naphthalene involved extraction with hot toluene, sublimation of the free ligand, and crystallization. The 1-methyl- and 1,4-dimethylnaphthalene analogues, **2** and **3**, respectively, were readily prepared by the same route. The higher solubility of the complexes in apolar solvents and the fact that both ligands are liquids at room temperature facilitated isolation and improved yields.

Metal-vapor synthesis is a powerful and clean method for the synthesis of bis(η-arene)metal complexes. Most first row transition elements can be readily evaporated by resistance heating in simple apparatus. Metals of the second and third rows generally require much higher temperatures for evaporation (*e.g.* 2600° for molybdenum), and a focussed electron beam is usually employed to generate metal vapor for preparative work [30] [35] [36]. Considerable skill is required to construct the necessary apparatus, and even

Scheme 1



a) CO, THF, r.t. b) PMe_3, hexane, 35°. c) $P(OMe_3)$, toluene, 4°. d) PF_3, toluene, 4°. e) PF_3, hexane, 35°. f) HBF_4 1 equiv., CH_2Cl_2, −78–0°. g) HBF_4 excess, CH_2Cl_2, −78–0°.

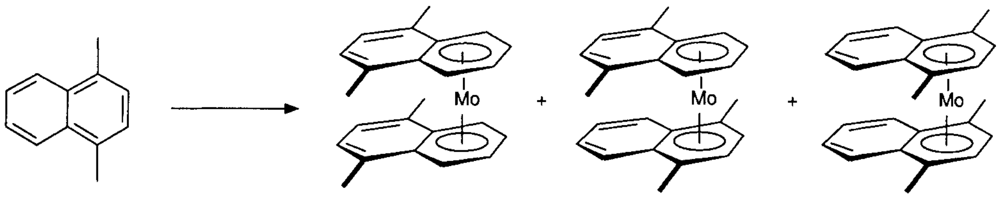
though it is commercially available, it is expensive. These are the key factors that have prevented metal-vapor synthesis of organometallics from becoming a routine method.

b) Via *Reductive Methods.* The reaction of transition-metal salts with reducing agents in the presence of suitable ligands has proved most useful for the synthesis of organo-transition-metal compounds. Shortly after the first synthesis of naphthalene sandwich complexes by the direct method [3a], we explored a reductive synthesis. A new method was developed which combined the simplicity of evaporation of main-group metals with the reductive synthesis. K-Atoms were generated (at 250°) and condensed into cold solutions of metal chlorides and arenes. Bis(arene)metal complexes of Ti, V, Cr, and Mo could be synthesized this way [37]. The drawbacks of this method are the hazards inherent in work with finely divided potassium, and the fact that bis(arene) complexes are further reduced by excess potassium which often results in product decomposition. For these reasons, we turned to Mg as reducing agent. This looked particularly promising, as the reduction of molybdenum halides by Mg suspensions has been widely used in the synthesis of low valent organo-molybdenum complexes [38–41].

Attempts to obtain complexes **1**–**3** by reaction of an anthracene-activated Mg slurry [42] with $MoCl_4 \cdot 2THF$ at −40° were not successful. We, therefore, turned to Mg slurries made by evaporation of the metal into THF. These are easily prepared in a modified rotavapor apparatus and have proven very useful in the formation of difficultly accessible *Grignard* reagents [43]. Addition of $MoCl_4 \cdot 2THF$ and naphthalene to a Mg suspension thus prepared yielded **1** in low yields (< 10%). A simpler and more efficient synthesis was devised by condensing Mg-atoms in the same apparatus directly into a −110° solution of naphthalene and $MoCl_5$ in THF. This gave, after workup, complex **1** in 19% yield. Compounds **2** and **3** were obtained likewise in 26% and 25% yield, respectively. To allow for complete reaction, a minimum two-fold excess of Mg was evaporated in all cases, and at the end of the Mg evaporation, the reaction mixture was brought to −40° and stirred overnight under Ar. Reduction of the halide occurred stepwise (at −110°) as indicated by color changes. The initially red-brown solution of $MoCl_5$ in THF turned green with the onset of condensation of Mg, then changed progressively to grayish brown, dark brown, and finally black. Similar yields were obtained when $MoCl_4 \cdot 2THF$ was used instead of $MoCl_5$.

The notable features of the ^{1}H-NMR spectrum of **1** are the two sets of symmetrical *multiplets* corresponding to the two *AA'BB'* systems for the H-atoms on the coordinated and the uncoordinated ring. They are assigned in analogy to the Cr complex [3b]. In substituted naphthalenes, the metal can coordinate to either the substituted or the unsubstituted ring. With 1-methylnaphthalene, both direct and reductive methods give rise to a mixture of complexes with the expected eight signals of magnetically distinct Me groups. The signals associated with ring H-atoms of the coordinated and uncoordinated rings integrate in a 5:4 ratio. Metal incorporation into the unsubstituted ring is, thus, slightly favored. This bias is more pronounced in 1,4-dimethylnaphthalene. Molybdenum evaporation resulted in a mixture of the three isomers **3a**–**c** in a ratio of 1.6:2.4:1, whereas the reductive method gave **3a** exclusively (*Scheme 2*). While we cannot exclude that this

Scheme 2



	3a		**3b**		**3c**
Mo(g):	1.6	:	2.4	:	1
$MoCl_5$ / Mg :	1		-		-

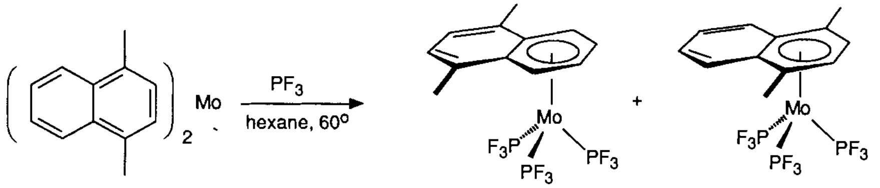
selection occurred during workup which included crystallization, it is unlikely as no enrichment of one of the three isomers was found when the mixture of **3a–c** was recrystallized. Preferred or exclusive coordination to the unsubstituted ring of 1-alkyl-, 1,4-dialkyl-, and 1,4-dialkoxynaphthalene has precedent in the synthesis of $[Cr(CO)_3(naphthalene)]$ complexes [44] [45] and in metal-vapor synthesis of Cr [3b] and Fe [46] naphthalene sandwich complexes.

3. Arene Displacement Reactions (*Scheme 1*). – Treatment of a solution of **3** in THF with CO gave $[Mo(CO)_6]$ as only product. When a reaction of **2** with CO in hexane was monitored by IR, no evidence for a $[Mo(CO)_3(naphthalene)]$ intermediate was found. Provided that, as in the Cr analogue, the reaction involves a stepwise replacement of the naphthalene rings, the result shows that the second naphthalene is displaced faster than the first. In $[Cr(naphthalene)_2]$, the situation is reversed although the rates of displacement of the two naphthalenes are similar. In the course of the reaction, bands due to both $[Cr(CO)_3(naphthalene)]$ and $[Cr(CO)_6]$ appear in the $\nu(CO)$ region of the IR spectra [3b].

As in the Cr complex, treatment of **1** with PF_3, $P(OMe)_3$, or PMe_3 gave the half sandwich complexes $[MoL_3(naphthalene)]$ ($L=PF_3$ (**4**)[2]), $P(OMe)_3$ (**5**), PMe_3 (**6**)). The ^{31}P-NMR spectra of **4–6** show the three phosphorous ligands to be equivalent due to rapid rotation around the metal–arene bond. The ^{31}P-NMR spectrum of **5** recorded at −73° remained a *singlet* attesting to the low activation barrier between conformers having different orientations of the phosphites with respect to the condensed aromatic ligand.

Reactions of the Me-substituted derivatives **2** and **3** were slower and, in alkane solvents, required heating. The reaction of PF_3 with the isomer mixture of **3a–c** gave a 3:1 mixture of **4a** and **4b** (*Scheme 3*). The bias for coordination to the unsubstituted ring is higher than that of the mixture of **3a–c** where only 56% of the metal is bound to the unsubstituted ring. This demonstrates that the naphthalene bound to Mo *via* its substituted ring is more labile. The other possibility, that the product undergoes haptotropic rearrangement [48] to give a 3:1 equilibrium mixture, is unlikely as the same reaction with **3a** gave **4a** as single compound.

Scheme 3



3 **4a** **4b**

	4a		**4b**
3a	1		-
3a/b/c	3	:	1

In toluene, arene exchange is a competitive process in reactions with PF_3. Thus, treatment of **1** with PF_3 in toluene at 0° gave $[Mo(PF_3)_3(toluene)]$ (**7**) in equal amount

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[2] For a review of PF_3 complexes of transition metals, see [47].

together with the expected complex **4** (*Scheme 1*). In contrast, no arene exchange is observed in analogous reactions with $P(OMe)_3$ or PMe_3. It is reasonable to ascribe this to the stronger metal–arene bond in complexes containing the more electron-rich phosphorous ligands, as these ligands facilitate π-backbonding to the arene. Also, the metal center is less susceptible to *Lewis*-base assistance of arene displacement. In support of this, we note that in $[Cr(CO)_2(naphthalene)\{PR(OR')_2\}]$ complexes arene exchange reactions occur much less readily than the $Cr(CO)_3$ complex [49]. PF_3 and CO have very similar ligand characteristics, both being strong π acids. The finding that arene exchange in **4** takes place under very mild conditions was expected on the grounds of earlier observations. The temperatures at which $[M(\eta\text{-arene})(CO)_3]$ complexes undergo uncatalyzed arene-exchange reactions is 140–160° for M=Cr [50] [26] and 60–80° for M=Mo [50]. Exchange between $[Cr(CO)_3(\eta^6\text{-naphthalene})]$ and free arene is much more facile [3c] [9b] than in $[Cr(benzene)(CO)_3]$, and, by extrapolation, must be rapid at ambient temperature in $[Mo(CO)_3(\eta^6\text{-naphthalene})]$. The parent complex has not yet been isolated, its only known characterized derivative is the octamethyl complex $[Mo(CO)_3(\eta^6\text{-}C_{10}Me_8)]$ [51].

Bis(naphthalene)molybdenum (**1**) undergoes cleavage of the metal–arene bond somewhat more readily than the analogous Cr complex. In reactions of the latter, THF is often the solvent of choice. The high affinity of Mo for oxygen ligands, while resulting in rapid naphthalene displacement, leads to low product yields in this solvent. Alkane solvents are better but at the price of longer reaction times and higher temperatures.

The higher reactivity of **1** compared to $[Mo(\eta\text{-benzene})_2]$ is very evident: substitution of both benzene rings by PF_3 to give $[Mo(PF_3)_6]$ takes place at 100° under high PF_3 pressure (600 bar) [52]. Displacement of one arene in the benzene complex by phosphine and phosphite ligands requires temperatures in the range 90–120° [53a]. The highly basic alkyl phosphines have been reported not to react with the benzene complex [53a] and $[Mo(\eta\text{-benzene})(PMe_3)_3]$ was made *via* an indirect route [53e].

4. Reaction of 5 and 6 with HBF_4 (*Scheme 1*). – Complexes $[Mo(\eta^6\text{-}C_{10}H_8)\{P(OMe)_3\}_3]$ (**5**) and $[Mo(\eta^6\text{-}C_{10}H_8)(PMe_3)_3]$ (**6**), when treated with 1 equiv. of $HBF_4 \cdot Et_2O$ in CH_2Cl_2 at −78° gave the stable hydrides **8** and **9** which were isolated as red-orange crystalline compounds. Protonation of electron rich $[M(\eta^6\text{-arene})(PR_3)_n]$ complexes is well documented (n=2, M=Ru, Os [54]; n=3, M=Mo,W [27] [53]). The ^1H-NMR spectra of **8** and **9** show the characteristic MoH signals which appear as *quartets*, centered at −8.5 ppm for **8** and −7.8 ppm for **9**, with the large P,H coupling (48 and 53 Hz, respectively) expected from the proximity of the H and PR_3 ligands. The ^{31}P-NMR spectrum of **8** showed a *doublet* (J(PH) = 48 Hz) at ambient temperature which broadened on cooling to −90° to a broad *singlet* ($w_{1/2}$ = 300 Hz). The coupling pattern of these formally seven-coordinate complexes is consistent with either a pseudo-trigonal-bypyramidal ground state (local C_{3v} symmetry) or a highly fluxional pseudo-square based pyramidal structure. As in other $[Mo(arene)L_4]$ complexes, the square based pyramidal structure is found in the X-ray structure of **8** (*vide infra*). Reaction of **5** with an excess of $HBF_4 \cdot Et_2O$ gave an orange oil. The ^1H-NMR spectra of the crude product indicated a complex mixture of naphthalenemolybdenum compounds. Addition of Et_2O to a CH_2Cl_2 solution of the products precipitated a solid which ^1H-, ^{31}P-, and ^{19}F-NMR spectroscopy showed to be $[Mo(H)(\eta^6\text{-naphthalene})\{PF(OMe)_2\}_3][BF_4]$ (**10**). P–F Bond formation was indicated by the 1160 Hz ^1J(P,F) coupling of the ^{31}P-NMR signal at 133.6 ppm. In the ^1H-NMR, the assignment is supported by the integral of the $P(OMe)_3$ resonance and by the observation of the metal-hydride signal as a *quartet* of *quartets* with $^2J(H,P) = 48$ and $^3J(H,F) = 6$ Hz. It is interesting to note that in the Cr analog, no metal-hydride species were observed under these conditions. Instead, the reaction yielded a single product $[Cr(PF_2OMe)_3(naphthalene)]$ [55]. With **5**, the P–O bond cleavage and P–F bond-forming reaction is more sluggish. Presumably, this can be ascribed to the higher stability of the metal–H bond in the Mo system. Mono OR/F exchange at phosphorous was recently reported for $[Mo(bpy)(CO)_2P(OR)_3]$ on treatment with $BF_3 \cdot OEt_2$ [56] and fluorination by HBF_4 *via* a P–C cleavage reaction has been found in a benzene-molybdenum-phosphine complex [57].

5. X-Ray Crystal Structures of 5 and 8. – To our knowledge, although many $[M(L)_3(\eta\text{-arene})]$ complexes have been well investigated [2] (arene = η^6-benzene or substituted benzene, M = Mo [57–60]; arene = η^4-naphthalene, M = Fe [46], Ru [61], Ta [62], Mn [63]; arene = η^6-naphthalene, M = Cr [2] [3c] [64] [65], Ru [66]), complexes **5** and **8**, reported here, are the first structurally characterized Mo(η^6-naphthalene) complexes.

$[Mo(H)(\eta^6\text{-naphthalene})\{P(OMe)_3\}_3][BF_4]$ (**8**) crystallizes with two independent molecules in the asymmetric unit which differ essentially by the orientation of the MeO groups.

Both $[Mo(\eta^6\text{-naphthalene})\{P(OMe)_3\}_3]$ (**5**) and its hydride **8** adopt a staggered conformation of the phosphite groups with respect to the ring C-atoms. The naphthalene ring shows a bending along C(15)–C(18). This deformation, with the second ring bent away from the metal atom, is weak for **5** (4.8(3)°) and more accentuated for the hydride complex **8** (11.3(6)° and 10.2(8)°; *Fig. 2*). A similar deformation of the naphthalene ring was observed in $[Ru(\eta^4\text{-1,5-cod})(\eta^6\text{-}C_{10}H_8)]$ [66]. Because of this deformation, the distance between Mo and the coordination plane of the naphthalene (1.823(3) and 1.829(7) Å for **5**

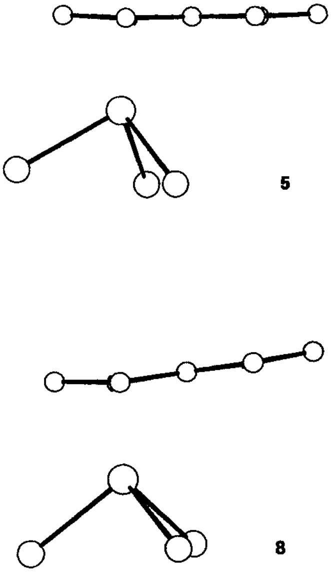


Fig. 2. *Projection of partial structures of* **5** *and* **8** *along the central C(14)–C(19) bond showing the bending deformation of the naphthalene ring*

and **8** respectively) is more accurately described with respect to the plane formed by C(15)–C(18) (*Table 1*).

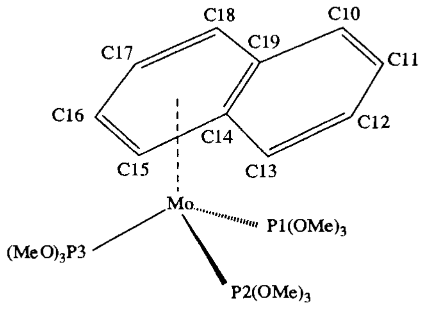
The slippage of the Mo-atom away from the central junction (C(14)–C(19)) of the naphthalene ring, leading to a slight deformation of the idealized η^6- towards a η^4-co-

Table 1. *Selected Geometrical Parameters* ([Å] and [°]) *for Compounds* **5** *and* **8**

		5	**8**	
			Molecule 1	Molecule 2
Metal-Arene Geometry	Mo–C(14)	2.417(6)	2.505(9)	2.46(1)
	Mo–C(15)	2.314(5)	2.32(1)	2.32(1)
	Mo–C(16)	2.297(6)	2.348(9)	2.36(1)
	Mo–C(17)	2.314(7)	2.346(9)	2.33(1)
	Mo–C(18)	2.291(8)	2.285(8)	2.28(1)
	Mo–C(19)	2.407(7)	2.446(8)	2.452(9)
	Dist. Mo···mean plane:			
	plane C(14)···C(19)	1.857(1)	1.907(2)	1.901(3)
	plane C(15)···C(18)	1.823(3)	1.829(6)	1.829(8)
	Eccentricity[a])	0.09	0.13	0.09
Naphthalene Ring Geometry	C(14)–C(15)	1.446(9)	1.42(1)	1.46(1)
	C(15)–C(16)	1.397(9)	1.38(2)	1.38(2)
	C(16)–C(17)	1.416(9)	1.43(2)	1.32(2)
	C(17)–C(18)	1.42(1)	1.41(1)	1.41(2)
	C(18)–C(19)	1.413(8)	1.44(1)	1.42(2)
	C(19)–C(14)	1.445(8)	1.42(1)	1.43(1)
	Average C–C	1.41(4)	1.41(3)	1.39(5)
	Bending angle[b])	+4.8(3)	+11.3(6)	+10.2(8)
Metal-Phosphite Geometry	Mo–P(1)	2.350(1)	2.420(3)	2.422(3)
	Mo–P(2)	2.362(2)	2.365(3)	2.375(3)
	Mo–P(3)	2.325(2)	2.354(3)	2.345(3)
	P(1)–Mo–P(2)	92.72(5)	85.29(9)	88.3(1)
	P(1)–Mo–P(3)	87.77(6)	82.92(9)	83.2(1)
	P(2)–Mo–P(3)	90.69(6)	104.8(1)	102.0(1)
	Average P–O	1.62(1)	1.59(2)	1.60(3)
	Average O–P–O	99(3)	101(3)	101(4)

[a]) Distance [Å] between the projection of the Mo-atom on the mean plane C(14)···C(19) to the centre of gravity of C(14)···C(19).

[b]) Dihedral angle [°] between the mean plane passing through C(15)···C(18) and the mean plane C(10)···C(15), C(18), C(19); + indicates bending away from Mo-atom.



ordination, has been found to be a common feature in complexes of condensed arene ligands with group-VI metals [2]. This eccentricity is very evident in both **5** (0.09 Å) and **8** (0.09 and 0.13 Å).

The coordination sphere of the Mo-atom can be described as distorted octahedral with the η^6-naphthalene moiety occupying one face. The MoP_3 tripod of **5** can be considered as regular (2.33 Å ≤ Mo–P ≤ 2.36 Å; 87.8° ≤ P–Mo–P ≤ 92.7°), whereas it is distorted in **8** (*Figs. 3* and *4*). Although the H-atom of the hydride complex **8** was not observed, it can be inferred that it is located between the two P-atoms for which the P–Mo–P angle is the more open. For both molecules of the asymmetric unit, this is clearly between P(2) and P(3): (P(2)–Mo–P(3) = 104.8(1); 102.0(1)°). These angles are very similar to that found in $[Mo(\eta^6\text{-}C_6H_6)(H)(PPh_2CH_2PPh_2)(PPh_2F)][BF_4]$ (P–Mo–P = 104.1(2)°) for which the position of the H-atom was observed [57]. Moreover, the *trans*-influence of the hydride ligand [57] [67] leads to a lengthening of the

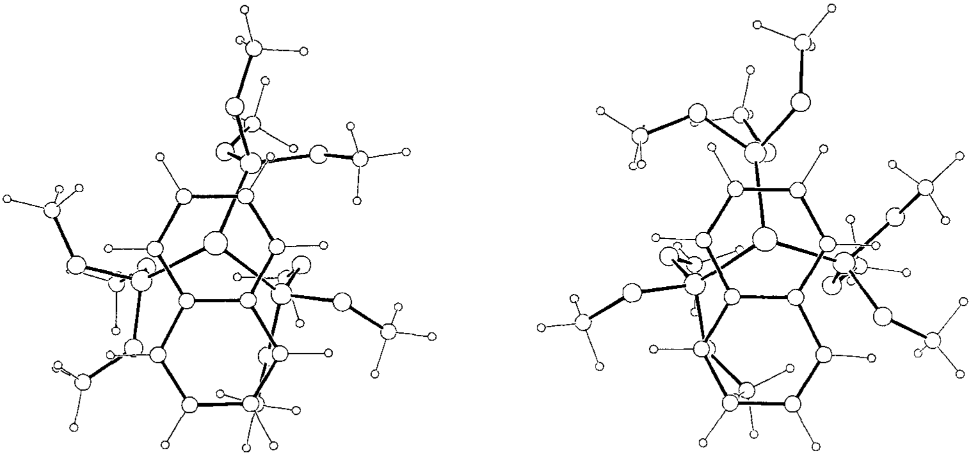


Fig. 3. *Projection of molecular structures of* **5** (right) *and* **8** (left) *perpendicularly to the* η^6 *mean plane.* Atoms are represented with arbitrarily-fixed atomic radii for clarity.

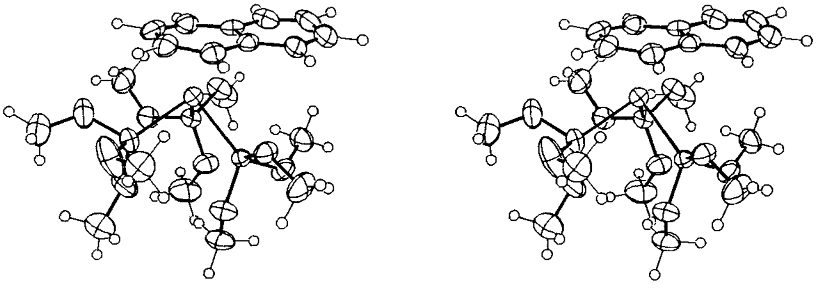


Fig. 4. *Stereoscopic drawing of complex* **5**. Ellipsoids are represented with 50% probability.

Mo–P(1) bond (2.420(3); 2.422(3) Å) relatively to the two others (average Mo–P 2.36(1) Å) and confirms the location of the H-atom between P(2) and P(3).

Within the η^6-ring ligand, the C–C bond distances vary in a nonalternant fashion between 1.32(2) and 1.46(1) Å; the shorter observed distances are of the C(15)–C(16) and C(16)–C(17) bonds whereas the longer are the C(14)–C(15) and C(18)–C(19) bonds. This is consistent with the slight deformation of the naphthalene ring toward the η^4-coordination.

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Experimental Part

1. *General.* All manipulations involving organometallics were carried out under an atmosphere of purified N_2 or Ar with use of standard *Schlenk* techniques or in a glovebox (*GB80, Mecaplex*). Mg (99.95%, bloc) and Mo (99.9%, rod) and $MoCl_5$ were obtained from *Alfa-Ventron*. $MoCl_4 \cdot 2THF$ [68] and PF_3 [69] were prepared by literature methods. Metal-vapor synthesis with Mo was carried out on a *G. V. Planar* apparatus model *VSP 500* equipped with a positive hearth 3.5-kW electron beam furnace. The design is similar to that described by *Cloke* and *Green* [36]. Syntheses *via* Mg evaporation were carried out in a rotating soln. reactor described in [43b]. Yields in metal-vapor synthesis are based on evaporated metal, they are not corrected for the 30–50% of metal which does not reach the reaction zone and is deposited on furnace parts or at the top of the bell shaped reactor. Et_2O solvents were distilled from 'sodium-benzophenone ketyl' immediately prior to use. Toluene was refluxed for 4 h over Na before distillation. Alkanes were distilled from CaH_2. NMR Spectra were recorded on a *Bruker-VM-360* spectrometer (^1H at 360 MHz, ^{13}C at 90.6 MHz, ^{31}P at 146 MHz) and a *Varian-XL-200* spectrometer (^1H at 200 MHz, ^{13}C at 50.3 MHz, ^{31}P at 81 MHz, ^{19}F at 188 MHz). Chemical shifts (δ) are given in ppm relative to TMS, HPO_4, or $CFCl_3$. Elemental analyses were performed by *H. Eder*, Service de Microchimie, Institut de Chimie Pharmaceutique, Université de Genève.

2. *Synthesis of Sandwich Complexes* **1**–**3**. a) *Preparation of Bis(1-4,4a,8a-η-naphthalene)molybdenum(0)* (*[Mo(η^6-$C_{10}H_8$)$_2$]*; **1**). Naphthalene (15 g, 117 mmol) and THF (150 ml) were placed in a 2-l reaction flask. The soln. was degassed by three freeze/pump/thaw cycles and treated at −50° with $MoCl_5$ (4.9 g, 18 mmol). The reaction flask was connected to the rotating soln. metal evaporation apparatus. Upon dissolution of all $MoCl_5$, the mixture was cooled to −110°, and the flask was evacuated to 10^{-3} mbar. Mg (2.15 g, 90 mmol) was evaporated over a period of 2 h from an alumina crucible (2 ml) heatet to *ca.* 500° *via* an embedded resistance heated Mo wire (1.2 mm diameter, 13 A, 3.6 V). The Mg vapor was condensed into a layer of the cold soln. carried over continuously by rotation of the reaction flask. On evaporation of Mg, the deep red-brown soln. turned first green, then gray-brown, brown, and finally black. The flask was filled with Ar, removed from the reactor, and the mixture stirred overnight at −45°. Volatiles were removed *in vacuo*, and the excess of naphthalene was sublimed onto a cold finger. The black residue was extracted with warm toluene, and filtered over *Celite*. The deep brown filtrate was concentrated, then placed at −78° overnight to yield lustrous black crystals of **1** (1.20 g, 19%). The same synthesis, carried out with $MoCl_4 \cdot 2THF$ instead of $MoCl_5$, gave **1** in 15% yield. ^1H-NMR (C_6D_6, 360 MHz): 4.72–4.76 ([*AA'BB'*]*m*, H–C(2,3)); 5.08–5.13 ([*AA'BB'*]*m*, H–C(1,4)); 6.58–6.64 ([*AA'BB'*]*m*, H–C(6,7)); 6.80–6.86 ([*AA'BB'*]*m*, H–C(5,8)). ^{13}C-NMR (C_6D_6, 50.3 MHz): 72.58 (C(1,4)); 78.43 (C(2,3)); 92.63 (C(4a,8a)); 121.53 (C(6,7)); 131.22 (C(5,8)). Anal. calc. for $C_{20}H_{16}Mo$ (352.29): C 68.19, H 4.58; found: C 68.75, H 4.68.

Complex **1** was also obtained *via* metal-vapor synthesis (*vide infra*) in 5% yield. As naphthalene is a solid, flaking off of the matrix on warm up, and occasionally even during cocondensation, proved to be a problem. Yield was further reduced by the low solubility of **1**, making extraction difficult.

b) *Preparation of Bis(1-methylnaphthalene)molybdenum(0)* (*[Mo(η^6-$C_{10}H_7Me$)$_2$]*; **2**) [37] via *Metal-Vapor Synthesis.* A premelted and degassed ingot of Mo (5.7 g) was placed on the 10-mm copper hearth of the electron-beam furnace. The stainless steel bell (300 mm int. diameter) was positioned, and the apparatus was evacuated to $5 \cdot 10^{-6}$ mbar *via* a 160-mm oil diffusion pump backed by a two-stage rotary pump. The bell-shaped, double-walled reaction vessel was then cooled with liq. N_2. Mo was heated with the electron beam, until evaporation started (beam current 180 mA, accelerating potential 5.5 kV). Power was then reduced, and condensation of gaseous 1-methylnaphthalene *via* a heated inlet system was started. After 10 min, power was increased to 1 kW, and over a period of 2 h Mo (0.95 g, 9.9 mmol) and 1-methylnaphthalene (15 g, 106 mmol) were cocondensed onto the cold reactor wall. The furnace and liq. N_2 supply were shut off, and the matrix was allowed to warm up and melt under N_2. The reactor walls were washed with warm toluene (4 × 100 ml) and the reaction mixture was transferred *via* the drain pipe to a *Schlenk* vessel. Workup consisted of filtration, removal of volatiles, short-path distillation of excess ligand, and crystallization from hexane at −30° to give fine black needles of a mixture of isomers of **2** (0.97 g, 24%). ^{1}H-NMR (C_6D_6, 360 MHz): 1.65–2.0 (8 *s*, CH_3); 4.5–5.3 (*m*, coord. arom. H); 6.5–7.1 (*m*, noncoord. arom. H).

Complex **2** was also obtained *via* condensation of Mg (1.28 g, 53.4 mmol) into a soln. of $MoCl_5$ (2.9 g, 10.6 mmol), 1-methylnaphthalene (10.0 g, 70.4 mmol) in THF (140 ml) using the procedure as described above for **1**. Yield 1.6 g (26%).

c) *Preparation of Bis(1,4-dimethylnaphthalene)molybdenum(0)* ($[Mo(\eta^6\text{-}C_{10}H_6Me_2)_2]$; **3**). $MoCl_5$ (3.55 g, 12.98 mmol) was added to a cold soln. of freshly distilled 1,4-dimethylnaphthalene (9.0 g, 57.7 mmol) in THF (130 ml). Mg (1.9 g, 80.6 mmol) was condensed into this soln. at −110° over 75 min as described for **1**. After stirring overnight at −45° the mixture was filtered over *Celite*, volatiles were removed *in vacuo*, and excess ligand was removed by short-path distillation. The black residue was taken up in hexane. Filtration gave a deep red-brown soln. from which **3a** (1.18 g, 22%) crystallized on cooling.

Bis(4a–8a-η-1,4-dimethylnaphthalene)molybdenum(0) (**3a**). ^{1}H-NMR (C_6D_6, 360 MHz): 1.95 (*s*, 4 CH_3); 4.79–4.84 ([*AA'BB'*]*m*, H−C(6,7)); 5.25–5.31 ([*AA'BB'*]*m*, H−C(5,8)); 6.62 (*s*, H−C(2,3)). ^{13}C-NMR (C_6D_6, 50.3 MHz): 17.5 (CH_3); 66.5 (C(5,8)); 76.0 (C(6,7)); 91.7 (C(4a,8a)); 119.7 (C(2,3)); 134.2 (C(1,4)). Anal. calc. for $C_{24}H_{24}Mo$ (408.39): C 70.58, H 5.92; found: C 69.70, H 5.85.

Using a *Planar VSP 500* apparatus, Mo (1.85 g, 19.3 mmol) was evaporated in an electron-beam furnace (beam current 220 mA, accelerating potential 5.4 kV) and, over a period of 2 h, cocondensed with 1,4-dimethylnaphthalene (60 g, 0.38 mol) onto a liq. N_2-cooled surface. Workup as described for **2** and crystallization from hexane gave **3** (1.28 g, 16%) as black crystals. ^{1}H-NMR showed this to consist of a mixture **3a**/**3b**/**3c** 1.6:2.4:1. Only small variation of this ratio was observed on repeated recrystallization.

Partial ^{1}H-NMR Data for **3b** *and* **3c** (from isomer mixture): *(4a–8a-η-1,4-dimethylnaphthalene)(1–4,4a,8a-η-1,4-dimethylnaphthalene)molybdenum(0)* (**3b**). ^{1}H-NMR (C_6D_6, 360 MHz): 1.90 (*s*, 2 CH_3); 2.07 (*s*, 2 CH_3); 4.72 ([*AA'BB'*]*m*, H−C(6,7)); 4.86 (*s*, H−C(2',3')); 4.94 ([*AA'BB'*]*m*, H−C(5,8)); 6.75 (*s*, H−C(2,3)); 6.94–7.20 (*m*, 4 H, overlap with **3c**).

Bis(1–4,4a,8a-η-1,4-dimethylnaphthalene)molybdenum(0) (**3c**). ^{1}H-NMR (C_6D_6, 360 MHz): 2.00 (*s*, 2 CH_3); 4.76 (*s*, H−C(2,3)); 6.94–7.20 (*m*, 8 H, overlap with **3b**).

3. *Arene Displacement Reactions.* a) *Reaction of* **2** *and* **3** *with CO.* A soln. of **3a–c** (50 mg, 0.12 mmol) in THF (5 ml) was placed under 4 bar of CO. After 2 h, the dark brown soln. was nealy colorless, and excess CO was vented. Filtration over *Celite* and removal of volatiles at −20° gave a crude oil. Its ^{1}H-NMR only showed 1,4-dimethylnaphthalene. Addition of hexane and cooling to −78° deposited a colorless solid, identified by IR and MS as $Mo(CO)_6$.

In a separate experiment, a soln. of **2** in hexane was stirred under an atmosphere of CO(1 bar). The IR spectra of samples taken after 5, 20, and 60 min showed a single absorption at 1990 cm^{-1}, assigned to $Mo(CO)_6$.

b) *Reactions of* **1** *and* **3** *with PF_3.* PF_3 (2 mmol) was condensed into a pressure-resistant glass tube (40 ml) fitted with an O-ring stopcock and containing a suspension of the sandwich complex **1** (0.116 g, 0.329 mmol) in hexane (20 ml). The mixture was stirred overnight at 35° to yield a bright yellow-orange soln. Excess PF_3 and solvent were pumped off, and naphthalene was sublimed onto a cold finger. The residue was extracted with hexane and filtered through *Celite*. Cooling to −78° precipitated bright yellow **4** (122 mg, 76%).

(η^6-Naphthalene)tris(trifluorophosphine)molybdenum(0) ($[Mo(\eta_6\text{-}C_{10}H_8)(PF_3)_3]$; **4**). ^{1}H-NMR ($C_6D_6$, 360 MHz): 4.80–4.88 (*m*, H−C(2,3)); 5.46–5.54 (*m*, H−C(1,4)); 6.70–6.78 ([*AA'BB'*]*m*, H−C(6,7)); 6.86–6.94 ([*AA'BB'*]*m*, H−C(5,8)). ^{31}P-NMR (C_6D_6, 146 MHz): 138 (*qm*, ^1J(P,H) = 1250). ^{19}F-NMR (C_6D_6, 146 MHz): 8 (*dm*, ^1J(P,F) = 1250). Anal. calc. for $C_{10}H_8F_9MoP_3$ (488.02): C 24.61, H 1.65; found: C 24.87, H 1.64.

PF_3 (2.83 mmol) was condensed into a pressure-resistant *Schlenk* tube (100 ml) fitted with an O-ring tap and containing a soln. of the sandwich complex **1** (0.094 g, 0.266 mmol) in toluene (25 ml). The mixture was stirred at 4° for 60 h. Excess PF_3 and solvent were pumped off, and naphthalene was sublimed onto a cold finger. The residue was extracted with hexane and the yellow soln. filtered through *Celite*. Cooling to −78° gave a yellow precipitate (75 mg, 60%) which ^{1}H-NMR showed to consist of a *ca.* 1:1 mixture **4**/**7**.

(η-Toluene)tris(trifluorophosphine)molybdenum (**7**). ^{1}H-NMR (C_6D_6, 360 MHz): 4.45 (*tm*, *J* = 6.5, H−C(4)); 4.58 (*dm*, *J* = 6.5, H−C(2,6)); 4.65 (*tm*, *J* = 6.5, H−C(3,5)).

(4a–8a-η-1,4-Dimethylnaphthalene)tris(trifluorophosphine)molybdenum(0) (**4a**) was prepared by reaction of PF_3 with **3a** in hexane as described for **4a** except that the mixture was stirred at 60° for 12 h. Complex **4a** was isolated as yellow solid in 60% yield. M.p. 165–168° (dec., hexane). ^{1}H-NMR (C_6D_6, 360 MHz): 2.10 (*s*, 2 CH_3); 4.95–5.02 (*m*, H–C(6,7)); 5.74–5.80 (*m*, H–C(5,8)); 6.63 (*s*, H–C(2,3)). ^{19}F-NMR (C_6D_6, 146 MHz): 8 (*dm*, ^1J(P,F) = 1250). MS: The 4 highest mass peaks show the characteristic pattern due to the 7 Mo isotopes. Of these, only the peaks of fragments containing the ^{98}Mo isotope are listed: 518 (28, M^+), 499 (6, $[M-F]^+$), 430 (8, $[M-PF_3]^+$), 342 (30, $[M-2PF_3]^+$), 254 (73, $[M-3PF_3]^+$), 252 (100), 156 (44), 141 (33). Anal. calc. for $C_{12}H_{12}F_9MoP_3$ (516.07): C 27.93, H 2.34; found: C 27.96, H 2.31.

An analogous reaction with a mixture of **3a–c** (1.7:1:2.2; 117 mg, 0.29 mmol) in hexane at 65° for 2 h gave 70 mg (47%) of yellow product shown by ^{1}H-NMR to consist of a mixture **4a**/**4b** 3:1.

(1–4,4a,8a-η-1,4-Dimethylnaphthalene)tris(trifluorophosphine)molybdenum(0) (**4b**). ^{1}H-NMR (C_6D_6, 360 MHz): 2.10 (*s*, 2 CH_3); 5.00 (*s*, H–C(2,3)); 6.90–6.95 (*m*, H–C(5,8)); 7.32–7.37 (*m*, H–C(6,7)).

c) *Reaction of* **1** *with* $P(OMe)_3$. Complex **1** (230 mg, 0.65 mmol) was placed in a *Schlenk* tube and treated with a soln. of $P(OMe)_3$ (1.6 ml, 12.1 mmol) in toluene (20 ml). The mixture was stirred at 4° for 24 h. Volatiles were removed under vacuum. The residue was extracted with hexane and filtered through *Celite*. Slow cooling to −78° of the deep red soln. yielded dark red crystals of **5** (250 mg, 65%).

(η⁶-Naphthalene)tris(trimethylphosphite)molybdenum(0) ($[Mo(\eta^6\text{-}C_{10}H_8)\{P(OMe)_3\}_3]$; **5**). ^{1}H-NMR ($C_6D_6$, 360 MHz): 3.30–3.45 (*m*, $P(OMe)_3$); 4.62–4.70 (*m*, H–C(2,3)); 5.14–5.22 (*m*, H–C(1,4)); 6.80–6.88 ([*AA′BB′*]*m*, H–C(6,7)); 7.14–7.22 ([*AA′BB′*]*m*, H–C(5,8)). ^{13}C-NMR (C_6D_6, 90.6 MHz): 50.85 (CH_3O); 76.01 (C(1,4)); 80.18 (C(2,3)); 102.04 (C(4a,8a)); 123.67 (C(6,7)); 129.38 (C(5,8)). ^{31}P-{^{1}H}-NMR ($C_6D_5CD_3$, 146 MHz): 138.3 (*s*). Anal. calc. for $C_{19}H_{35}O_9MoP_3$ (596.34): C 38.27, H 5.92; found: C 38.04, H 6.12.

d) *Reaction of* **1** *with* PMe_3. PMe_3 (*ca.* 0.5 ml, *ca.* 6.5 mmol) was vacuum-transferred into a pressure-resistent *Schlenk* tube equipped with an O-ring tap and containing a suspension of **1** (256 mg, 0.727 mmol) in hexane (25 ml). The mixture was stirred overnight at 35°. The dark-brown soln. was taken to dryness and naphthalene was removed by sublimation. Filtration in hexane and crystallization gave **6** (230 mg, 70%) as black oily solid.

(η⁶-Naphthalene)tris(trimethylphosphine)molybdenum(0) ($[Mo(\eta^6\text{-}C_{10}H_8)(PMe_3)_3]$; **6**). ^{1}H-NMR ($C_6D_6$, 360 MHz): 1.10–1.16 (*m*, $P(CH_3)$); 3.73–3.80 (*m*, H–C(2,3)); 4.34–4.42 (*m*, H–C(1,4)); 6.72–6.80 ([*AA′BB′*]*m*, H–C(6,7)); 7.25–7.33 ([*AA′BB′*]*m*, H–C(5,8)). ^{13}C-NMR (C_6D_6, 50.3 MHz): 26.11 (PMe_3); 68.67 (C(1,4)); 72.64 (C(2,3)); 97.26 (C(4a,8a)); 121.47 (C(6,7)); 129.38 (C(5,8)). ^{31}P-{^{1}H}-NMR (C_6D_6, 81 MHz): 5.02 (*s*). Anal. calc. for $C_{19}H_{35}MoP_3$ (452.35): C 50.45, H 7.80; found: C 51.17, H 7.85.

4. *Reaction of* **5** *and* **6** *with* HBF_4. A 54% soln. of HBF_4 in Et_2O (25 µl, 0.18 mmol) was added dropwise to a cold (−78°) soln. of **1** (107 mg, 0.18 mmol) in CH_2Cl_2 (10 ml). On warming to 0°, the soln. turned orange. After 30 min, the soln. was concentrated. Addition of Et_2O and cooling to −70° yielded precipitated **8** (87 mg, 71%) as an orange solid. Crystals were grown by slow diffusion of Et_2O into a CH_2Cl_2 soln. of **8**.

Hydrido(η⁶-naphthalene)tris(trimethylphosphite)molybdenum Tetrafluoroborate ($[MoH(\eta^6\text{-}C_{10}H_8)\{P(OMe)_3\}_3][BF_4]$; **8**). ^{1}H-NMR ($CD_2Cl_2$, 360 MHz): -8.50 (*q*, ^3J(P,H) = 48, MoH); 3.4–3.9 (*m*, $P(OMe)_3$); 5.46–5.54 (*m*, H–C(2,3)); 6.26–6.34 (*m*, H–C(1,4)); 7.50–7.70 (*m*, H–C(5–8)). ^{31}P-NMR (CD_2Cl_2, 81 MHz): 128,7 (*d*, ^3J(P,H) = 48). Anal. calc. for $C_{19}H_{36}BF_4MoO_9P_3$ (684.16): C 33.35, H 5.30; found: C 33.25, H 5.33.

An analogous experiment with an excess of HBF_4 gave a red oil. Crystallization from CH_2Cl_2/Et_2O yielded a first crop of crystals (yield *ca.* 20%) of **10**.

Tris(dimethylfluorophosphite)hydrido(η⁶-naphthalene)molybdenum Tetrafluoroborate ($[MoH(PF(OMe)_2)_3(\eta^6\text{-}C_{10}H_8)][BF_4]$; **10**). ^{1}H-NMR ($CD_2Cl_2$, 360 MHz): -8.50 (*qq*, ^3J(P,H) = 48, J(H,F) = 6, MoH); 3.5–3.8 (*m*, $P(OMe)_2F$); 5.86–5.94 (*m*, H–C(2,3)); 6.66–6.74 (*m*, H–C(1,4)); 7.60–7.80 (*m*, H–C(5–8)). ^{31}P-NMR (CD_2Cl_2, 146 MHz): 133.6 (*dq*, J(P,H) = 48, J(P,F) = 1160). ^{19}F-NMR (CD_2Cl_2, 94 MHz): -28 (*dd*, ^1J(P,F) = 1160, J(H,F) = 6).

Hydrido(η⁶-naphthalene)tris(trimethylphosphine)molybdenum Tetrafluoroborate $[MoH(PMe_3)_3(\eta^6\text{-}C_{10}H_8)][BF_4]$; **9**) was isolated in 43% yield by the same procedure from **5**. ^{1}H-NMR (CD_2Cl_2, 360 MHz): -7.70 (*q*, ^3J(P,H) = 53, MoH); 1.1–1.2 (*m*, PMe_3); 5.11–5.19 (*m*, H–C(2,3)); 5.85–5.93 (*m*, H–C(1,4)); 7.45–7.65 (*m*, H–C(5–8)).

5. *Crystallographic Data for Compounds* **5** *and* **8**. Cell parameters and reflections intensities were measured at r.t. on a *Philips PW1100* diffractometer with monochromated MoK_α radiation (λ = 0.71069 Å). Cell parameters are obtained from refinement of 2θ values ($18 < 2\theta < 33°$) for 30 reflections. Crystals were mounted in capillaries under Ar to prevent degradation. Three reference reflections were measured every 60 min during the data collection and show no variation for **5** ($\Delta I < 2.7\sigma(I)$) and decrease of *ca.* 20% for **8**. All intensities were corrected for this drift. A summary of crystal data, intensity measurement, and structure refinement is given in *Table 2*. The structures were solved by direct methods (MULTAN-80) [70] and refined by least-squares with a local version of

Table 2. *Summary of Crystal Data, Intensity Measurement, and Structure Refinement for Compounds* **5** *and* **8**

	5	**8**		**5**	**8**
Formula	$C_{19}H_{35}O_9P_3Mo$	$C_{19}H_{36}O_9P_3Mo/BF_4$	$((\sin\theta)/\lambda)_{max}$ [Å^{-1}]	0.51	0.49
Mol. wt.	596.5	684.2	Temp. [K]	298	298
Crystal system	monoclinic	monoclinic	No. measured reflections	3015	5825
Space group	$P2_1/n$	$P2_1/c$	No. observed reflections	2337	4273
a [Å]	10.111(2)	19.473(5)	Criterion for observed	$\|F_o\| > 3\sigma(F_o)$	$\|F_o\| > 3\sigma(F_o)$
b [Å]	30.104(7)	12.276(1)	Refinement (on F)	Full matrix	4 blocks
c]Å]	9.662(2)	24.439(6)	No. parameters	289	628
β [°]	118.44(1)	100.27(2)	Weighting scheme	$\omega = 1$	$\omega = 1$
V [Å^3]	2586(1)	5749(9)	Max. and average Δ/σ	0.159, 0.0228	0.938, 0.159
Z	4	8	Max. and min. $\Delta\rho$ [e·Å^{-3}]	0.82, –0.68	1.31, –0.55
$F(000)$	1232	2800			
D_c [g·cm^{-3}]	1.53	1.58	S	2.25	3.94
$\mu(MoK_\alpha)$ [mm^{-1}]	0.719	0.676	$R, \omega R$ [%]	4.2	6.3

the XRAY-76 program [71]. Atomic scattering factors and anomalous dispersion terms are taken from [72]. All coordinates of H-atoms were calculated (the H-atom bonded to Mo of **8** was not observed in the final difference electron-density map). All non-H-atoms were refined with anisotropic displacement parameters excepted for the F-atoms of **8**. Crystallographic data have been deposited with the *Cambridge Crystallographic Data Center*, University Chemical Laboratory, Union Road, Cambridge CB2 1EW, England.

REFERENCES

[1] E. O. Fischer, K. Öfele, H. Essler, W. Fröhlich, J. P. Mortensen, W. Semmlinger, *Chem. Ber.* **1958,** *91,* 2763.

[2] E. L. Muetterties, J. R. Bleeke, E. J. Wucherer, T. A. Albright, *Chem. Rev.* **1982,** *82,* 499.

[3] a) E. P. Kündig, P. L. Timms, *J. Chem. Soc., Chem. Commun.* **1977,** 912; b) E. P. Kündig, P. L. Timms, *J. Chem. Soc., Dalton Trans.* **1980,** 991; c) E. P. Kündig, C. Perret, S. Spichiger, G. Bernardinelli, *J. Organomet. Chem.* **1985,** *286,* 183.

[4] a) C. Elschenbroich, R. Möckel, *Angew. Chem. Int. Ed.* **1977,** *16,* 870; b) C. Elschenbroich, R. Möckel, W. Massa, M. Birkhahn, U. Zenneck, *Chem. Ber.* **1982,** *115,* 334.

[5] a) C. A. L. Mahaffy, P. L. Pauson, *J. Chem. Res. (S)* **1979,** 126; b) C. A. Mahaffy, P. Pauson, *J. Chem. Res. (M)* **1979,** 1738.

[6] I. S. Butler, A. Ismail, *Inorg. Chem.* **1986,** *25,* 3910.

[7] a) A. A. Gonzalez, S. L. Mukerjee, S. J. Chou, Z. Kai, C. D. Hoff, *J. Am. Chem. Soc.* **1988,** *110,* 4419; b) G. J. Kubas, G. Kiss, C. D. Hoff, *Organometallics* **1991,** *10,* 2870.

[8] a) G. Vitulli, P. Pertici, P. Salvadori, *J. Chem. Soc., Dalton Trans.* **1984,** 2255; b) M. A. Bennett, H. Neuman, M. Thomas, X. Wang, P. Pertici, P. Salvadori, G. Vitulli, *Organometallics* **1991,** *10,* 3237.

[9] a) J. A. S. Howell, D. T. Dixon, J. C. Kola, N. F. Ashford, *J. Organomet. Chem.* **1985,** *294,* C1; b) J. A. S. Howell, N. F. Ashford, D. T. Dixon, J. C. Kola, T. A. Albright, S. K. Kang, *Organometallics* **1991,** *10,* 1852.

[10] A. M. McNair, K. R. Mann, *Inorg. Chem.* **1986,** *25,* 2519.

[11] W. Strohmeier, R. Mueller, *Z. Phys. Chem. (München)* **1964,** *40,* 85.

[12] D. L. S. Brown, J. A. Connor, C. D. Demain, M. T. Zafarini-Moattar, *J. Organomet. Chem.* **1977,** *142,* 321.

[13] F. Zingales, A. Chiesa, F. Basolo, *J. Am. Chem. Soc.* **1966,** *88,* 2707.

[14] J. M. O'Connor, C. P. Casey, *Chem. Rev.* **1987,** *87,* 307.

[15] M. Cais, D. Fraenkel, K. Weidenbaum, *Coord. Chem. Rev.* **1975,** *16,* 27.

[16] J. R. Tucker, D. P. Riley, *J. Organomet. Chem.* **1985,** *279,* 49.

[17] a) M. Sodeoka, M. Shibasaki, *J. Org. Chem.* **1985,** *50,* 1147; b) M. Sodeoka, H. Yamada, M. Shibasaki, *J. Am. Chem. Soc.* **1990,** *112,* 4906; c) H. Yamada, M. Sodeoka, M. Shibasaki, *J. Org. Chem.* **1991,** *56,* 4569.

[18] a) E. P. Kündig, G. Bernardinelli, J. Leresche, *J. Chem. Soc., Chem. Commun.* **1991,** 1713; b) E. P. Kündig, D. Amurrio, R. Liu, A. Ripa, *Synlett* **1991,** *2,* 657; c) E. P. Kündig, C. Grivet, E. Wenger, G. Bernardinelli, A. F. Williams, *Helv. Chim. Acta* **1991,** *74,* 2009.

[19] a) M. Uemura, T. Kobayashi, T. Minami, Y. Hayashi, *Tetrahedron Lett.* **1986,** *27,* 2479; b) M. Uemura, T. Kobayashi, K. Isobe, T. Minami, Y. Hayashi, *J. Org. Chem.* **1986,** *51,* 2859; c) M. Uemura, T. Minami, Y. Hayashi, *J. Am. Chem. Soc.* **1987,** *109,* 5277; d) M. Uemura, T. Minami, K. Hirotsu, Y. Hayashi, *J. Org. Chem.* **1989,** *54,* 469.

[20] J. Brocard, J. Lebibi, L. Pelinski, M. Mahmoudi, *Tetrahedron Lett.* **1986,** *27,* 6325.

[21] H.-G. Schmalz, B. Millies, J.W. Bats, G. Dürner, *Angew. Chem. Int. Ed.* **1992,** *31,* 631.

[22] a) B.F. Bush, V.M. Lynch, J.J. Lagowski, *Organometallics* **1987,** *6,* 1267; b) B.F. Bush, J.J. Lagowski, *ibid.* 1988, *7,* 1945.

[23] E.O. Fischer, H.O. Stahl, *Chem. Ber.* **1956,** *89,* 1805.

[24] E.O. Fischer, A. Reckziegel, *Chem. Ber.* **1961,** *94,* 2204.

[25] J.A. Connor, H.A. Skinner, Y. Virmani, *J. Chem. Soc., Faraday Trans. 1* **1973,** 1218.

[26] R. Davies, L.A.P. Kane-Maguire, in 'Comprehensive Organometallic Chemistry', Eds. G. Wilkinson, F.G.A. Stone, and E.W. Abel, Pergamon Press, Oxford, 1982, Vol. 3, pp. 975–1050 (Cr), pp. 1204–1231 (Mo).

[27] a) M.L.H. Green, W.E. Silverthorn, *J. Chem. Soc., Dalton Trans.* **1973,** 301; b) W.E. Silverthorn, *Inorg. Synth.* **1977,** *17,* 54.

[28] M.F. Ernst, D.M. Roddick, *Organometallics* **1990,** *9,* 1586.

[29] E.O. Fischer, C. Elschenbroich, G.G. Kreiter, *J. Organomet. Chem.* **1967,** *7,* 481.

[30] a) J.R. Blackborow, D. Young, 'Metal Vapour Synthesis in Organometallic Chemistry', Springer, Berlin, 1979; b) K.J. Klabunde, 'Chemistry of Free Atoms and Particles', Academic Press, New York, 1980.

[31] a) M.L.H. Green, I. Treurnicht, J.A. Bandy, A. Gourdon, K. Prout, *J. Organomet. Chem.* **1986,** *306,* 145; b) M.L.H. Green, in 'Chemical Uses of Molybdenum, Proceedings of the 4th International Conference', Eds. H.F. Barry and C.H. Mitchell, Climax Molybdenum Co., Ann Arbor, Mich., 1982, pp. 74–78.

[32] S.D. Ittel, F.A. Van Catledge, C.A. Tolman, *Inorg. Chem.* **1985,** *24,* 62.

[33] C. Elschenbroich, J. Koch, J. Schneider, B. Spangenberg, P. Schiess, *J. Organomet. Chem.* **1986,** *317,* 41.

[34] F.G.N. Cloke, K.A.E. Courtney, A.A. Sameh, A.C. Swain, *Polyhedron* **1989,** *8,* 1641.

[35] a) M.P. Andrews, in 'Experimental Organometallic Chemistry', Eds. A.L. Wayda and M.Y. Darensbourg, American Chemical Society, Washington, 1987, pp. 158–189; b) G.A. Ozin, M.P. Andrews, C.G. Francis, H.X. Huber, K. Molnar, *Inorg. Chem.* **1990,** *29,* 1068.

[36] a) F.G.N. Cloke, M.L.H. Green, *J. Chem. Soc., Dalton Trans.* **1981,** 1938; b) M.L.H. Green, D. O'Hare, 'High Energy Processes in Organometallic Chemistry', Ed. K.S. Suslick, American Chemical Society, Washington, 1987, Vol. 33, pp. 260–277.

[37] a) P.N. Hawker, E.P. Kündig, P.L. Timms, *J. Chem. Soc., Chem. Commun.* **1978,** 730; b) P.N. Hawker, P.L. Timms, *J. Chem. Soc., Dalton Trans.* **1983,** 1123.

[38] H. Azizan, R. Luck, R.H. Morris, H. Wong, *J. Organomet. Chem.* **1982,** *238,* C4.

[39] W. Gausing, G. Wilke, *Angew. Chem. Int. Ed.* **1981,** *20,* 186.

[40] H.F. Klein, H.H. Karsch, *Chem. Ber.* **1975,** *108,* 944.

[41] H. Bönnemann, B. Bogdanovich, R. Brinkmann, D.W. He, B. Spliethoff, *Angew. Chem. Int. Ed.* **1983,** *22,* 728.

[42] B. Bogdanovitch, S.T. Liao, M. Schwickardi, P. Sikorsky, B. Spliethoff, *Angew. Chem. Int. Ed.* **1980,** *19,* 818.

[43] a) K.J. Klabunde, H.F. Efner. L. Satek, W.J. Donley, *J. Organomet. Chem.* **1974,** *71,* 309; b) E.P. Kündig, C. Perret, *Helv. Chim. Acta* **1981,** *64,* 2606; c) W. Oppolzer, E.P. Kündig, P.M. Bishop, C. Perret, *Tetrahedron Lett.* **1982,** *23,* 3901.

[44] a) B. Deubzer, H.P. Fritz, C.G. Kreiter, K. Ofele, *J. Organomet. Chem.* **1967,** *7,* 289; b) B. Deubzer, E.O. Fischer, H.P. Fritz, C.G. Kreiter, N. Kriebitzsch, Jr., H.D. Simmons, B.R. Willeford, *Chem. Ber.* **1967,** *100,* 3084.

[45] E.P. Kündig, M. Inage, G. Bernardinelli, *Organometallics* **1991,** *10,* 2921.

[46] H. Schäufele, D. Hu, H. Pritzkow, U. Zenneck, *Organometallics* **1989,** *8,* 396.

[47] J.F. Nixon, *Adv. Inorg. Radiochem.* **1985,** *29,* 42.

[48] T.A. Albright, P. Hofmann, R. Hoffmann, P. Lillya, P.A. Dobosh, *J. Am. Chem. Soc.* **1983,** *105,* 3396.

[49] P.C. Nirchio, D.J. Wink, *Organometallics* **1991,** 10, 336.

[50] E.L. Muetterties, J.R. Bleeke, A.C. Sievert, *J. Organomet. Chem.* **1979,** *178,* 197.

[51] J.W.J. Hull, M.L. Gladfelter, *Organometallics* **1982,** *1,* 264.

[52] T. Kruck, A.Z. Prasch, *Z. Naturforsch., B* **1964,** *19,* 669.

[53] a) M.L.H. Green, L.C. Mitchard, W.E. Silverthorn, *J. Chem. Soc. (A)* **1971,** 2929; b) M.L.H. Green, J. Knight, L.C. Mitchard, G.G. Roberts, W.E. Silverthorn, *J. Chem. Soc. (D)* **1971,** 1619; c) M.L.H. Green, L.C. Mitchard, W.E. Silverthorn, *J. Chem. Soc., Dalton Trans.* **1974,** 1361; d) P.R. Brown, F. Geoffrey,

N. Cloke, M.L.H. Green, N.J. Hazel, *J. Chem. Soc., Dalton Trans.* **1983,** 1075; e) M. Canestrari, M.L.H. Green, A. Izquierdo, *ibid.* **1984,** 2795; f) M.L.H. Grenn, A.K. Hughes, P. Lincoln, J.J. Martin-Polo, P. Mountford, A. Sella, L.-L. Wong, J.A. Bandy, T.W. Banks, K. Prout, D. Watkin, *ibid.* **1992,** 2063.

[54] a) H. Werner, R. Werner, *Angew. Chem.* **1978,** *90,* 721; b) R. Werner, H. Werner, *Chem. Ber.* **1982,** *115,* 3781.

[55] V. Desobry, E.P. Kündig, *Helv. Chim. Acta* **1981,** *64,* 1288.

[56] H. Nakazawa, M. Ohta, K. Miyoshi, H. Yoneda, *Organometallics* **1989,** *8,* 638.

[57] R.H. Morris, J.F. Sawyer, C.T. Schweitzer, A. Sella, *Organometallics* **1989,** *8,* 2099.

[58] J.L. Atwood, W.E. Hunter, E. Carmona-Guzman, G. Wilkinson, *J. Chem. Soc., Dalton Trans.* **1979,** 1519.

[59] a) R.L. Luck, R.H. Morris, J.F. Sawyer, *Organometallics* **1984,** *3,* 247; b) F.A. Cotton, R.L. Luck, R.H. Morris, *ibid.* **1989,** *8,* 1282.

[60] A. Barbati, F. Calderazzo, R. Poli, P.F. Zanazzi, *J. Chem. Soc., Dalton Trans.* **1986,** 2569.

[61] J.W. Hull, W.L. Gladfelter, *Organometallics* **1984,** *3,* 605.

[62] J.O. Albright, S. Datta, B. Dezube, J.K. Kouba, D.S. Marynick, S.S. Wreford, B.M. Foxman, *J. Am. Chem. Soc.* **1979,** *101,* 611.

[63] R.L. Thompson, S. Lee, A.L. Rheingold, N.J. Cooper, *Organometallics* **1991,** *10,* 1657.

[64] V. Kunz, W. Nowacki, *Helv. Chem. Acta* **1967,** *50,* 1052.

[65] P. Müller, G. Bernardinelli, Y. Jacquier, *Helv. Chim. Acta* **1988,** *71,* 1328.

[66] M. Crocker, M. Green, J.A.K. Howard, N.C. Norman, D.M. Thomas, *J. Chem. Soc., Dalton Trans.* **1990,** 2299.

[67] M.B. Hursthouse, D. Lyons, M. Tornton-Pett, G. Wilkinson, *J. Chem. Soc., Chem. Commun.* **1983,** 476.

[68] E.A. Allen, B.J. Brisdon, G.W.A. Fowles, *J. Chem. Soc.* **1964,** 4531.

[69] R.J. Clark, H. Belefant, *Inorg. Synth.* **1989,** *26,* 12.

[70] P. Main, S., S.J. Fiske, S.E. Hull, L. Lessinger, G. Germain, J.-P. Declercq, M.M. Woolfson, 'A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data', Univs. of York, England, and Louvain-la-Neuve, Belgium 1980.

[71] J.M. Stewart, P.A. Machin, C.W. Dickinson, H.L. Amon, H. Heck, H. Flack, The XRAY76 system. Tech Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland, 1976.

[72] International Tables for X-Ray Crystallography, Vol. IV, Kynoch Press, Birmingham, 1974.