Formation and Crystallographic Study of a (σ-Phenyl)molybdenum Porphyrin Complex: Mo(TPP)(σ-C_6H_5)(Cl)

Jocelyne Colin*[1] and Bernard Chevrier[1]

Laboratoire de Cristallochimie et Chimie Structurale (E.R.A. 08), Institut Le Bel,
67070 Strasbourg Cedex, France

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The (σ-phenyl)molybdenum porphyrin complex Mo(TPP)(σ-C_6H_5)(Cl) has been obtained by photodecomposition of Mo(TPP)$(CO)_2$ in chlorinated benzene solution. Its structure was determined by a single-crystal X-ray diffraction study. It forms monoclinic crystals of space group $P2_1/n$ with four molecules in a cell of dimensions $a = 14.778$ (6) Å, $b = 23.513$ (9) Å, $c = 13.163$ (5) Å, and $\beta = 101.70$ (4)°. The structure was solved by standard Patterson and Fourier methods and refined by full-matrix least-squares techniques to $R = 0.054$ for 529 parameters and 4467 observed reflections. The Mo–C(σ-phenyl) bond length is 2.241 (4) Å, and the phenyl ligand is in staggered conformation with respect to the pyrrole nitrogens in the solid state. This study suggests the existence of a very reactive transient Mo(TPP) species.

Introduction

The study of the homogeneous activation of C–H bonds by transition-metal complexes has allowed to characterize many species with σ metal–carbon bonds.[2] Synthetic methods for the formation of such bonds in various metalloporphyrins have been developed either in view of the chemistry of coenzyme vitamin B_{12}[3] or in view of models of metabolic reduction of polyhalogenated compounds by cytochrome P-450.[4] The reagents currently used are Grignard reagents,[5a–d] alkyl halides,[5c,6] alkyl- (or aryl-) lithium,[5c,6b,7] diazoalkanes,[8] methyl radicals,[9] and olefins or acetylenes[10] whereas the direct metalation of arene is reported only for rhodium porphyrins.[11,12]

As part of our continuing synthetic and structural studies on molybdenum porphyrins, we recently showed that Mo(Por)$(Cl)_2$[13] is an excellent precursor of low-valent complexes. So, we isolated a cis-dicarbonyl 16-electron compound Mo(Por)$(CO)_2$ which undergoes substitution and addition reactions.[14] We wish to describe now its products of photodecomposition. On the basis of an X-ray structural analysis, one of them was identified as Mo(TPP)(σ-C_6H_5)(Cl). Structural aspects of (σ-phenyl)-metalloporphyrins are still poorly documented. Expect the recent description of the pentacoordinate species Fe(TPP)(σ-C_6H_5),[15] only the structure determination of the rhodium analogue of our complex Rh(TPP)(σ-C_6H_5)(Cl) has been briefly reported.[11]

Results and Discussion

Formation of Mo(TPP)(σ-C_6H_5)(Cl). In a recent paper, we described the synthesis and geometry of Mo(Por)$(CO)_2$.[14] We emphasized that this compound must be kept in darkness. During an attempt of crystallization, this condition was not respected. Moreover, mesitylene was replaced by technical benzene. On the basis of different experiments with other complexes, we are convinced that this solvent contained chlorinated impurities. After several weeks, a few long crystalline needles appeared. Their IR spectrum revealed the disappearance of the carbonyl vibration bands. According to the structural results described later, additional ring substitution bands at 695k and 712 cm^{-1} were assigned to the σ-phenyl ligand. An intense band at 300 cm^{-1} was ascribed to the Mo–Cl stretching vibration by referring to the values of 330 and 280 cm^{-1} found, respectively, in $MoCl_2$ (TPP)[16] and [Mo(TPP)Cl]$_2$O.[17] Unfortunately, we were not able to es-

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(1) Present address: Institut de Biologie Moléculaire et Cellulaire, 67084 Strasbourg Cedex, France.

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(13) Abbreviations used: Por means porphinato dianion, TPP is the dianion of *meso*-tetraphenylporphyrin, and TTP is *meso-tetra-p*-tolylporphyrin.

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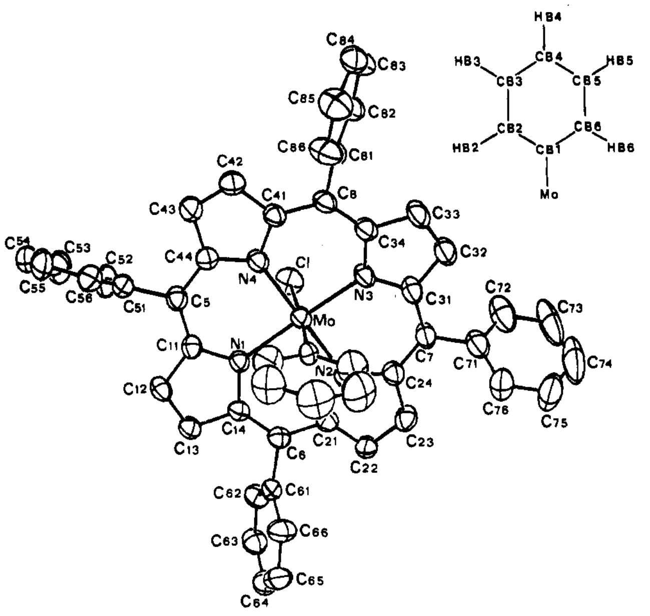

Figure 1. ORTEP drawing of $Mo(TPP)(\sigma\text{-}C_6H_5)(Cl)$. The numbering of phenyl carbon atoms is given at right for clarity.

tablish a more pertinent procedure to synthesize this σ-phenyl complex. Consequently, its other physical properties, particularly its magnetic behavior, were not studied.

The reaction was repeated with purified benzene in hopes of synthesizing $Mo(TPP)(\sigma\text{-}C_6H_5)(H)$. No σ-phenyl complex could be detected. During the decomposition reaction, the alterations of the UV–visible spectrum remain minor. More informative are the IR spectrum changes which show the disappearance of the CO bands and the concomitant appearance of a strong absorption at 850 cm^{-1} in the Mo–O–Mo region.[17] The final product, that might be a μ-oxo dimer has not yet been completely identified. It seems that these conditions lead to a process of oxidation of an hypothetical transient "Mo(TPP)" species in preference to an oxidative addition of a molecule of benzene on the metal. On the other hand, neither addition of traces of HCl to the benzene solution nor simultaneous irradiation with Hg vapor lamp yielded the title compound. Addition of various organomagnesien or phenyllithium on $Mo(TPP)(Cl_2)$ failed as well.

Crystallographic Structure of $Mo(TPP)(\sigma\text{-}C_6H_5)(Cl)$. A view of the molecule with the atom numbering scheme is shown in Figure 1. Some relevant distances and angles are selected in Table III. The four pyrrole nitrogens are coplanar ((4N) plane). The molybdenum atom lies 0.089 Å out of this plane toward the chlorine ligand. This displacement is weak but significant. A similar trend is also seen in $Fe(TPP)(N_3)(py)$ with a displacement of 0.031 Å of the iron atom toward the azido ligand.[19] In $Rh(TPP)(C_6H_5)(Cl)$, the metal atom is said to be in the plane without numerical indications.[11] The four Mo–N bond lengths average to 2.070 (3) Å. This is the expected value for such a geometry. We found 2.074 (6) Å in $Mo(TTP)(Cl_2)$,[16] 2.070 (5) Å in $Mo(TTP)(N_2Ph)_2$,[18] and 2.071 (3) Å in $Mo(TTP)(py)_2$.[14] The molybdenum atom lies 0.125 Å out of the 24-atom-core mean plane. Thus, there is almost no doming of the core. However, the macrocycle is not planar as is shown in Figure 2. There is a S_4 ruffling, with angles between adjacent pyrrole rings ranging from 8.5 to 14.2°. In the bis(pyridine) derivative, we observed only 5.2°.

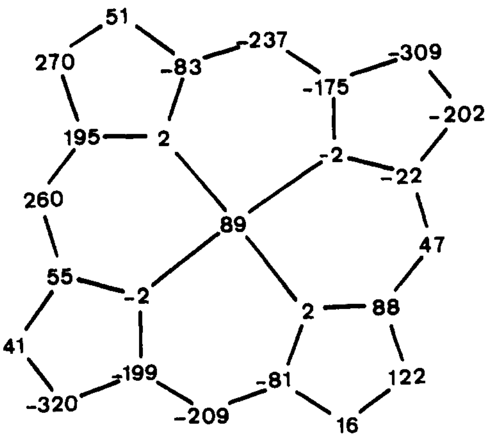

Figure 2. Formal diagram of the porphinato core having the same orientation as Figure 1. Each atom symbol has been replaced by its perpendicular displacement, in units of 0.001 Å, from the (4N) plane.

Table I. Summary of Data Collection and Processing Parameters

formula	$MoC_{53}H_{36}N_4Cl$
mol wt	860.3
space group	$P2_1/n$
cell constants	
a, Å	14.778 (6)
b, Å	23.513 (9)
c, Å	13.163 (5)
β, deg	101.70 (4)
V, Å^3	4479 (6)
Z	4
D(calcd), g cm^{-3}	1.276
cryst dimens, mm	0.37 × 0.22 × 0.17
radiatn (Cu $K\alpha$) λ, Å	1.5418
μ, cm^{-1}	33.67
$F(000)$	1764
data collectn method	θ-2θ scan
scan mode	flying step scan (step width 0.06)
ω scan speed, deg min^{-1}	1.2
scan range, deg	$1.3 + 0.14 \tan\theta$
θ limits	4–57
measd reflctns	6374
obsd reflctns $I > 4\sigma(I)$	4467
absorption correction	
grid size	8 × 8 × 8
transmissn in percent, min	28.5
max	49.6
no. of parameters refined	529
p value	0.08
final $R = \Sigma \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert / \Sigma F_o$	0.054
final $R_\omega = [\Sigma\omega(\lvert F_o\rvert - \lvert F_c\rvert)^2/\Sigma\omega\lvert F_o\rvert^2]^{1/2}$	0.082
goodness-of-fit	1.85

The Mo–Cl bond length of 2.382 (1) Å is within the range of values normally observed for Mo^{IV} complexes.[16,17,20] However, it is slightly longer than the average 2.311 (11) Å distance found in $Mo(TTP)(Cl)_2$. Two reasons may explain this relative lengthening: (i) the trans effect of the phenyl ligand;[21] (ii) a weak hydrogen bond between the chlorine ligand of one molecule and the phenyl ligand HB_3 hydrogen of a neighboring molecule lying at 2.865 Å. The normal packing distance is $\simeq 3$ Å, the sum of the van der Waals radii for hydrogen (1.20 Å) and chlorine (1.80 Å). This feature is shown on a stereoscopic view of the

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Table II. Positional Parameters and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
Mo	0.39381 (3)	0.20190 (2)	0.15931 (3)	3.81 (1)	C63	0.6642 (5)	−0.0392 (3)	0.0798 (5)	5.3 (2)
N1	0.4541 (3)	0.1356 (2)	0.2524 (3)	3.51 (9)	C64	0.7559 (5)	−0.0238 (3)	0.0928 (5)	5.9 (2)
C11	0.4364 (4)	0.1208 (2)	0.3472 (4)	3.7 (1)	C65	0.7838 (5)	0.0298 (3)	0.1258 (6)	6.4 (2)
C12	0.4972 (4)	0.0755 (2)	0.3888 (4)	4.1 (1)	C66	0.7187 (5)	0.0694 (3)	0.1431 (6)	5.5 (2)
C13	0.5508 (4)	0.0637 (2)	0.3200 (4)	3.9 (1)	C7	0.4112 (5)	0.2545 (2)	−0.0836 (4)	4.7 (1)
C14	0.5229 (4)	0.1000 (2)	0.2324 (4)	3.4 (1)	C71	0.4216 (5)	0.2770 (3)	−0.1858 (5)	6.0 (2)
N2	0.4665 (3)	0.1791 (2)	0.0465 (3)	3.9 (1)	C72	0.3464 (7)	0.2822 (3)	−0.2672 (6)	7.7 (2)
C21	0.5282 (4)	0.1336 (2)	0.0529 (4)	3.7 (1)	C73	0.357 (1)	0.3032 (4)	−0.3615 (6)	11.3 (3)
C22	0.5560 (4)	0.1289 (2)	−0.0437 (4)	4.1 (1)	C74	0.439 (1)	0.3166 (4)	−0.3791 (7)	13.9 (4)
C23	0.5143 (4)	0.1710 (3)	−0.1060 (4)	4.7 (1)	C75	0.5151 (8)	0.3106 (4)	−0.3012 (8)	12.7 (3)
C24	0.4591 (4)	0.2038 (2)	−0.0503 (4)	4.2 (1)	C76	0.5079 (7)	0.2916 (4)	−0.2028 (7)	9.0 (2)
N3	0.3435 (3)	0.2727 (2)	0.0714 (3)	3.9 (1)	C8	0.2667 (4)	0.3194 (2)	0.1995 (5)	4.2 (1)
C31	0.3593 (5)	0.2867 (2)	−0.0254 (4)	4.4 (1)	C81	0.2206 (4)	0.3733 (2)	0.2245 (4)	4.4 (1)
C32	0.3181 (5)	0.3414 (3)	−0.0543 (5)	5.5 (2)	C82	0.1318 (4)	0.3879 (3)	0.1767 (5)	5.0 (1)
C33	0.2796 (5)	0.3602 (3)	0.0247 (5)	5.5 (2)	C83	0.0940 (5)	0.4376 (3)	0.2010 (6)	5.8 (2)
C34	0.2948 (4)	0.3167 (2)	0.1049 (4)	4.3 (1)	C84	0.1408 (5)	0.4736 (3)	0.2727 (5)	5.7 (2)
N4	0.3309 (3)	0.2288 (2)	0.2770 (3)	3.8 (1)	C85	0.2271 (6)	0.4595 (3)	0.3215 (6)	6.6 (2)
C41	0.2794 (4)	0.2773 (2)	0.2767 (4)	3.9 (1)	C86	0.2671 (5)	0.4090 (3)	0.2975 (6)	6.4 (2)
C42	0.2385 (5)	0.2770 (3)	0.3653 (5)	5.2 (1)	CB1	0.5169 (4)	0.2542 (2)	0.2316 (4)	3.1 (1)
C43	0.2625 (5)	0.2273 (3)	0.4170 (5)	5.1 (1)	CB2	0.5527 (6)	0.2512 (3)	0.3327 (6)	6.7 (2)
C44	0.3234 (4)	0.1976 (2)	0.3633 (4)	4.0 (1)	CB3	0.6276 (6)	0.2811 (4)	0.3820 (7)	8.0 (2)
C5	0.3699 (4)	0.1469 (2)	0.3939 (4)	3.9 (1)	CB4	0.6666 (6)	0.3170 (4)	0.3243 (8)	8.6 (3)
C51	0.3448 (4)	0.1165 (3)	0.4858 (5)	4.4 (1)	CB5	0.6329 (7)	0.3208 (4)	0.2206 (8)	9.0 (3)
C52	0.2942 (5)	0.0666 (3)	0.4672 (5)	5.9 (2)	CB6	0.5565 (6)	0.2893 (3)	0.1777 (6)	7.0 (2)
C53	0.2652 (6)	0.0392 (3)	0.5478 (6)	6.8 (2)	Cl	0.2626 (1)	0.14461 (7)	0.0911 (1)	5.59 (4)
C54	0.2879 (5)	0.0608 (3)	0.6459 (5)	6.2 (2)	CS1	0.034 (2)	0.042 (1)	0.030 (2)	10.9 (6)*
C55	0.3394 (5)	0.1090 (3)	0.6649 (5)	6.2 (2)	CS2	−0.005 (2)	−0.041 (1)	0.066 (2)	13.3 (8)*
C56	0.3691 (5)	0.1368 (3)	0.5861 (5)	5.2 (2)	CS3	0.044 (2)	0.013 (1)	0.120 (2)	14.1 (9)*
C6	0.5553 (4)	0.0986 (2)	0.1399 (4)	3.6 (1)	CS4	0.011 (3)	0.023 (2)	0.361 (3)	23 (1)*
C61	0.6266 (4)	0.0548 (2)	0.1289 (4)	3.7 (1)	CS5	0.006 (2)	−0.033 (1)	0.434 (3)	18 (1)*
C62	0.6007 (4)	−0.0003 (3)	0.1003 (5)	4.5 (1)	CS6	0.502 (2)	0.453 (1)	−0.043 (2)	15.0 (9)*

[a] Atoms with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(^4/_3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

crystal packing (Figure 3).

The phenyl ligand is planar and bound to the metal perpendicular to the (4N) plane as indicated by the dihedral angle of 89.3°. The dihedral angle between the plane of the phenyl ring and a plane defined by N1,N3,CB1 is 41°. It is obvious that this nearly perfect staggered conformation along with the ruffling of the core minimizes the steric intramolecular interactions. The shortest observed separations (N1...HB2 = 2.705 Å and N3...HB3 = 2.748 Å) remain at least equal to the sum of the van der Waals radii for hydrogen (1.20 Å) and nitrogen (1.50 Å). The Mo–C(σ-C_6H_5) bond length is 2.241 (4) Å. From Table IV which compares the observed single M–C bond distances in some molybdenum and tungsten complexes in various formal oxidation states, it appears that this value is typical of a single Mo(IV)–C(sp^2) one. Thus the observed orientation of the axial ligand is not prescribed by electronic factors since the phenyl ligand may rotate about the metal–carbon bond. In many cases, as in Mo(TTP)$(py)_2$ and Fe(TPP)(σ-C_6H_5), packing effects were proposed to explain a nonperfect staggered conformation. Here, consequently to the displacement of the metal out of the (4N) plane toward the chlorine ligand, the orientation of the axial ligand must be principally controlled by intramolecular steric factors.

Table III. Selected Stereochemical Parameters

Distances, Å

Mo-N1	2.069 (3)	CB1-CB2	1.330 (7)
Mo-N2	2.072 (3)	CB2-CB3	1.361 (8)
Mo-N3	2.078 (3)	CB3-CB4	1.341 (10)
Mo-N4	2.061 (3)	CB4-CB5	1.357 (10)
Mo-CB1	2.241 (4)	CB5-CB6	1.374 (9)
Mo-C1	2.382 (1)	CB6-CB1	1.302 (7)
HB6···N2	2.919	HB2···N1	2.705
HB6···N3	2.748	HB2···N4	2.917

Angles, deg

N1-Mo-N2	90.35 (13)	N1-Mo-CB1	86.96 (13)
N2-Mo-N3	89.30 (14)	N2-Mo-CB1	87.28 (14)
N3-Mo-N4	90.44 (13)	N3-Mo-CB1	87.99 (14)
N4-Mo-N1	89.50 (13)	N4-Mo-CB1	87.91 (14)
N1-Mo-N3	174.95 (14)	CB1-CB2-CB3	124.7 (6)
N2-Mo-N4	175.19 (14)	CB2-CB3-CB4	117.1 (6)
CB1-Mo-C1	177.08 (10)	CB3-CB4-CB5	120.0 (6)
N1-Mo-C1	90.96 (10)	CB4-CB5-CB6	118.7 (7)
N2-Mo-C1	94.79 (10)	CB5-CB6-CB1	122.8 (6)
N3-Mo-C1	94.09 (11)	CB6-CB1-CB2	116.5 (5)
N4-Mo-C1	90.02 (10)		

Conclusion

This study emphasizes the analogy that we suspected between molybdenum porphyrin and dicyclopentadienylmolybdenum complexes. Several analogue derivatives exist already in these two families despite a difference in the total number of electrons. These are the oxo,[31] dichloro,[32] and acetylene[33] derivatives. The transient

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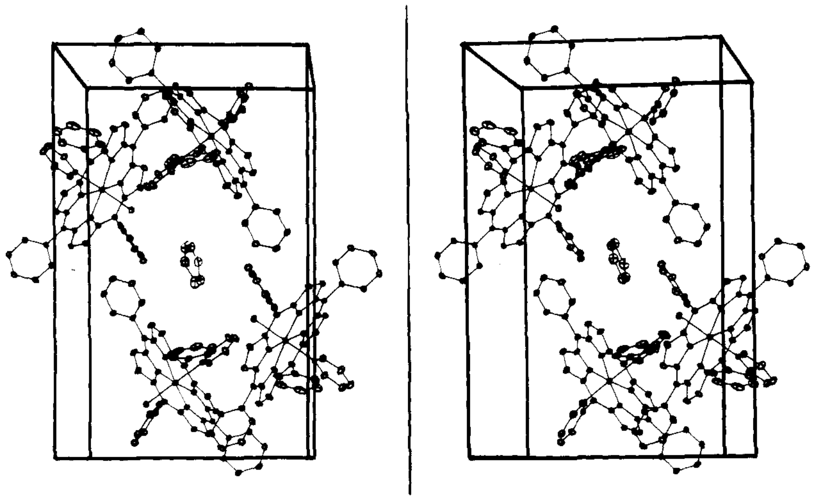

Figure 3. Stereoscopic view of the crystal packing of $Mo(TPP)(\sigma\text{-}C_6H_5)(Cl)$, looking down the *z* axis.

Table IV. Metal–Carbon Bond Lengths in Some Molybdenum and Tungsten Complexes

compd	Bond	d(M–C), Å	ref
$(\eta^5\text{-Cp})Mo(CO)_2(PPh_3)[C(CN)_2C(CN)_2CH_3]$	$Mo^{II}C(CN)_2C(CN)_2CH_3$	2.414 (4)	22
$(\eta^5\text{-Cp})Mo(CO)_3(C_3F_7)$	$Mo^{II}C_3F_7$	2.288 (9)	23
$(\eta^5\text{-Cp})Mo(CO)_3(CH_2COOH)$	$Mo^{II}CH_2COOH$	2.370 (22)	24
$(\eta^5\text{-Cp})Mo(CO)_3(C_2H_5)$	$Mo^{II}C_2H_5$	2.397 (19)	25
$(\eta^5\text{-Cp})W(CO)_3(\sigma\text{-}C_6H_5)$	$W^{II}(\sigma\text{-}C_6H_5)$	2.32	26
$(\eta^7\text{-}C_7H_7)Mo(CO)_2(\sigma\text{-}C_6F_5)$	$Mo^{II}(\sigma\text{-}C_6F_5)$	2.244 (9)	27
$(\eta^5\text{-Cp})_2Mo(NO)(\sigma\text{-Cp})$	$Mo^{III}(\sigma\text{-Cp})$	2.291 (3)	28
$(\eta^5\text{-Cp})_2W[CH_2\text{-}C_6H_3(CH_3)_2]_2$	$W^{IV}CH_2C_6H_3(CH_3)_2$	2.276 (7)	29
$(\eta^5\text{-Cp})WO(PhC{\equiv}CPh)(\sigma\text{-}C_6H_5)$		2.291 (7)	29
$(TPP)Mo(Cl)(\sigma\text{-}C_6H_5)$	$W^{IV}(\sigma\text{-}C_6H_5)$	2.25 (3)	30
	$Mo^{IV}(\sigma\text{-}C_6H_5)$	2.241 (4)	this work

species $(\eta^5\text{-}C_5H_5)_2Mo$ and $(\eta^5\text{-}C_5H_5)_2W$ can be produced by photolysis of their respective monocarbonyl complexes.[34] Moreover, benzene or toluene solutions of $(\eta^5\text{-}C_5H_5)_2W(CO)$ give quantitative yields of the corresponding aryl hydride compounds $(\eta^5\text{-}C_5H_5)W(H)(R)$ when photolyzed in the absence of other substrates.[34] We think that a similar mechanism takes place with molybdenum porphyrins. Probably, the photolysis of $Mo(TPP)(CO)_2$ gives a transient species Mo(TPP) which under severe and not yet defined experimental conditions leads to $Mo(TPP)(\sigma\text{-}C_6H_5)(H)$. If chloride is present in the reaction medium, substitution of the hydride ligand will occur easily.

Experimental Section

All reactions were performed under argon atmosphere. Benzene and pentane were respectively dried over sodium and calcium hydride. $Mo(TPP)(CO)_2$ was prepared as previously reported.[14] Infrared spectra were recorded on a Perkin-Elmer 337 spectrophotometer with Nujol mulls (CsI plates).

$Mo(TPP)(\sigma\text{-}C_6H_5)(Cl)\cdot{}^1/_2C_6H_6$. A 25-mg sample of $Mo(CO)_2(TPP)$ (0.03 mmol) was dissolved in 10 mL of technical benzene. Pentane was slowly added. After several weeks of diffusion at room temperature, microcrystals were obtained. They were washed with pentane and then dried in vacuo: IR 695, 712 cm^{-1} (CC ring), 300 cm^{-1} (MoCl).

X-ray Intensity Data Collection and Structure Solution. A crystal of 0.37 × 0.22 × 0.17 mm was sealed in a Lindemann glass capillary in a drybox. Intensity measurements were carried out with a Philips PW 1100 computer-controlled diffractometer at 20 ± 1 °C. Final lattice parameters were determined from 25 high angle reflections ($20 < \theta < 30°$) carefully centered by using graphite-monochromated Cu Kα radiation. Details of crystal data and a summary of intensity data collection parameters are given in Table I. The space group was defined by systematic absences as $P2_1/n$. The intensities of three standard reflections were measured every 90 min; the deviations were all within counting statistics. The intensity data were corrected by application of standard Lorentz and polarization factors. Absorption effects were corrected by numerical integration method of Busing and Levy.[35]

The structure was solved by heavy-atom method and successive difference Fourier maps using the Enraf-Nonius software package on a PDP 11/60 computer. Hydrogen atoms were introduced at calculated position (C–H = 0.95 Å) with an isotropic thermal parameter of 6 Å^2. The benzene solvate is disordered. It was isotropically refined with an occupancy factor of 0.5 for each carbon atom. Successive full-matrix least-squares refinements with anisotropic thermal parameters for all other non-hydrogen atoms gave final values of $R = 0.054$ and $R_\omega = 0.082$. The unit-weight observation was 1.85 for $p = 0.08$. A final difference Fourier map revealed no other peaks higher than 0.6 e Å^{-3}, with the exception of a 1.5 e Å^{-3} maxima located close to the molybdenum atom.

Table II lists the atomic position parameters for all non-hydrogen atoms.

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Registry No. $Mo(TPP)(\sigma\text{-}C_6H_5)(Cl)\cdot1/2C_6H_6$, 95314-88-8; $Mo(TPP)(\sigma\text{-}C_6H_5)(Cl)$, 95314-87-7; $Mo(CO)_2(TPP)$, 91156-34-2.

Supplementary Material Available: Tables of observed and calculated structure factors, positional parameters of hydrogen atoms, general temperature factors for anisotropically refined atoms, bond parameters, and least-squares planes (31 pages). Ordering information is given on any current masthead page.

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