New Piano Stool *cis*-Bis(organohydrazido) Complexes of Molybdenum. X-ray Structure of [(η^5-C₅H₅)Mo(NNPh₂)₂(PPh₃)]⁺CF₃SO₃⁻

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A two-step procedure for the synthesis of cationic organometallic complexes containing the robust *cis*-{Mo(NNRPh)₂}²⁺ core (R = Me, Ph) is reported. The reaction of silver triflate, AgOTf (OTf⁻ = CF₃SO₃⁻), with an equimolar amount of [Mo(NNMePh)₂Cl₂(PPh₃)₂] (**1**) or [Mo(NNPh₂)₂Cl₂(PPh₃)] (**2**) (in the presence of 1 equiv of PPh₃) in CH₂Cl₂/CH₃CN yields ionic intermediates formulated as [Mo(NNRPh)₂Cl(PPh₃)₂]⁺OTf⁻ (R = Me, [**3**]⁺OTf⁻; R = Ph, [**4**]⁺OTf⁻), which give ionic products formulated as [(η^5-C₅H₅)Mo(NNRPh)₂(PPh₃)]⁺OTf⁻ (R = Me, [**5**]⁺OTf⁻; R = Ph, [**6**]⁺OTf⁻) upon reaction with excess NaCp in THF. These compounds have been characterized by IR, UV−visible, and NMR spectroscopy and cyclic voltammetry. The molecular structure of [**6**]⁺OTf⁻ has also been determined by X-ray diffraction.

Introduction

A number of coordination complexes containing the *cis*-{M(NNRR′)₂}²⁺ functional unit with two η^1-bonded hydrazido ligands (R, R′ = alkyl, aryl) have been characterized, particularly when M = Mo,[1−16] Re,[17−19]

W,[4,6,18] V,[20] Nb,[20] and Ta.[20] However, to the best of our knowledge, organometallic compounds containing such a unit have not been reported.[21] To date, only two types of related binuclear compounds containing either two equivalent (μ-η^1),[22,23] or nonequivalent (μ-η^1 and μ-η^2),[24−26] NNR₂ ligands have been described.

We have recently reported the synthesis of molybdenum complexes of general formula [Mo(NNRPh)₂Cl₂-(PMe$_x$Ph$_{3−x}$)$_n$] (R = Me, Ph; x = 0, 1, 2; n = 1, 2),[11] from molybdenum complexes containing both the NNRPh and NHNRPh ligands.[27] Now, in view of the reactivity of [Mo(NNMe₂)₂Cl(PPh₃)₂]⁺ toward various nucleophiles,[4] we have investigated the potential of [Mo-(NNMePh)₂Cl₂(PPh₃)₂] (**1**) and [Mo(NNPh₂)₂Cl₂(PPh₃)] (**2**) in the synthesis of organometallic compounds con-

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taining the *cis*-{Mo(NNRPh)$_2$}$^{2+}$ unit (R = Me, Ph). In this context, we will now report on (i) the synthesis and characterization of two new bis(organohydrazido)molybdenum complexes, [Mo(NNRPh)$_2$Cl(PPh$_3$)$_2$]$^+$OTf$^-$ (R = Me, [**3**]$^+$OTf$^-$; Ph, [**4**]$^+$OTf$^-$), and the first two members of a new class of organometallics compounds, formulated as [(η^5-C$_5$H$_5$)Mo(NNRPh)$_2$(PPh$_3$)]$^+$OTf$^-$ (R = Me, [**5**]$^+$OTf$^-$; R = Ph, [**6**]$^+$OTf$^-$) and (ii) their full spectroscopic characterizations, including the crystal and molecular structure of [**6**]$^+$OTf$^-$.

Results and Discussion

The syntheses of the organometallic compounds [**5**]$^+$OTf$^-$ and [**6**]$^+$OTf$^-$ have been conveniently achieved from the neutral complexes **1** and **2**, in a two-step procedure.

First Step. Syntheses and Characterizations of the Intermediate Complexes [Mo(NNRPh)$_2$Cl-(PPh$_3$)$_2$]$^+$OTf$^-$ (R = Me, [3]$^+$OTf$^-$; R = Ph, [4]$^+$OTf$^-$). The synthesis of [**3**]$^+$OTf$^-$ was carried out at room temperature by reaction of Ag$^+$OTf$^-$ with an equimolar amount of **1** in CH$_2$Cl$_2$/CH$_3$CN (2:1). In this way, one chloro ligand of **1** is removed, which affords the stable ionic species [Mo(NNPhMe)$_2$Cl(PPh$_3$)$_2$]$^+$OTf$^-$ in high yield (96%, before recrystallization). However, the similar reaction of Ag$^+$OTf$^-$ with **2** gives a complex mixture, from which [**4**]$^+$OTf$^-$ was isolated in low yield through successive recrystallizations. It was assumed that the unstable intermediate [Mo(NNPh$_2$)$_2$Cl(PPh$_3$)]$^+$ transforms partially into the stable pentacoordinated product [Mo(NNPh$_2$)$_2$Cl(PPh$_3$)$_2$]$^+$ ([**4**]$^+$). Consistent with this hypothesis, the yield of [**4**]$^+$OTf$^-$ was significantly increased (91%, before recrystallization) when the reaction was carried out in the presence of an equimolar amount of PPh$_3$. The cationic complexes [**3**]$^+$ and [**4**]$^+$ are similar to [Mo(NNMe$_2$)$_2$Cl(PPh$_3$)$_2$]$^+$, which has been authenticated by X-ray diffraction methods.[4]

The compounds [**3**]$^+$OTf$^-$ and [**4**]$^+$OTf$^-$ were characterized by ^{1}H and ^{31}P NMR, IR, and UV−visible spectroscopy (for further details, see the Experimental Section). The ^{1}H NMR spectra of both complexes show a complex multiplet in the 6.30−7.60 ppm range, corresponding to the phenyl proton resonances of the hydrazido and phosphine ligands. In addition, that of [**3**]$^+$OTf$^-$ shows a unique singlet at 3.51 ppm, indicating the equivalence of the hydrazido methyl groups. The ^{31}P{^{1}H} NMR spectra of [**3**]$^+$OTf$^-$ and of [**4**]$^+$OTf$^-$ show only one signal at 29.52 and 29.72 ppm, respectively, indicating the magnetic equivalence of the phosphorus atoms of both PPh$_3$ ligands, in solution at room temperature. The spectroscopic similarities between [**3**]$^+$ and [**4**]$^+$ and [Mo(NNMe$_2$)$_2$Cl(PPh$_3$)$_2$]$^+$ [4] favor a trigonal-bipyramidal geometry around the metal, in which the two axial bulky phosphines adopt a *trans* arrangement.

The IR spectra of both complexes show a characteristic medium-intensity band at 1588 cm^{-1}, which has been attributed to the ν(NN) vibration.[4,28−30] The characteristic strong bands due to the ν(SO$_3$) and ν(CF$_3$) modes of the triflate anion were observed at 1264 and

1150 cm^{-1} for [**3**]$^+$OTf$^-$ and 1273 and 1155 cm^{-1} for [**4**]$^+$OTf$^-$.[31,32] These data indicate unambiguously that the triflate anions are not coordinated.[32]

The electronic spectra of [**3**]$^+$OTf$^-$ and [**4**]$^+$OTf$^-$ show two bands of similar intensities at 354 and 380 nm and at 358 and 404 nm, respectively. In addition, both spectra show a shoulder at *ca.* 270 nm. Absorption in the 260−360 nm region has been attributed to the {Mo(NNRPh)$_2$}$^{2+}$ chromophore.[33]

Second Step. Syntheses of the Organometallic Compounds [CpMo(NNRPh)$_2$(PPh$_3$)]$^+$OTf$^-$ (R = Me, [5]$^+$OTf$^-$; R = Ph, [6]$^+$OTf$^-$). These syntheses were performed at room temperature in THF by reaction of [**3**]$^+$OTf$^-$ and [**4**]$^+$OTf$^-$, respectively, with NaCp in excess. These reactions involve the displacement of the chloro and of one phosphine ligands by a cyclopentadienyl ring. The compounds [**5**]$^+$OTf$^-$ and [**6**]$^+$OTf$^-$ were isolated as air-stable solids in 34% and 39% yields, respectively. Orange crystals of [**6**]$^+$OTf$^-$ were obtained from CH$_2$Cl$_2$ solutions carefully layered with *n*-hexane.

The ^{1}H NMR spectra of [**5**]$^+$OTf$^-$ and [**6**]$^+$OTf$^-$ show a complex multiplet in the 6.80−7.80 ppm range, corresponding to the phenyl proton resonances of the hydrazido and phosphine ligands, and a singlet characteristic of the Cp ligand at 6.10 and 5.67 ppm, respectively. In addition, that of [**5**]$^+$OTf$^-$ exhibits a unique methyl proton resonance at 3.66 ppm, which indicates the equivalence of both hydrazido ligands. The ^{13}C NMR spectra of both compounds show also a characteristic singlet for the carbons of the Cp ligand at 102.6 and 103.0 ppm, respectively. On the other hand, the ^{31}P{^{1}H} NMR spectra show the expected singlet for the PPh$_3$ ligand at 51.93 and 49.65 ppm, respectively.

The IR spectra exhibit a characteristic medium-intensity band at 1589 cm^{-1} due to the ν(NN) vibration.[4,28−30] The characteristic strong bands due to the ν(SO$_3$) and ν(CF$_3$) modes of the triflate counterions[31,32] were observed at 1271 and 1150 cm^{-1}, respectively, which indicates that they are not coordinated.[32] The X-ray crystal structure of [**6**]$^+$OTf$^-$ supports unambiguously this conclusion (*vide infra*).

The electronic spectra of [**5**]$^+$OTf$^-$ and [**6**]$^+$OTf$^-$ exhibit three bands at 284, 316, and 388 nm and at 290, 322, and 384 nm, respectively. The bands in the 280−330 nm region have been attributed to the {Mo(NNRPh)$_2$}$^{2+}$ chromophore.[33]

Cyclic voltammetry studies were carried out in CH$_3$-CN at a platinum electrode at scan rates varying from 10 to 500 mV s^{-1}. The electrochemical behavior of [**5**]$^+$OTf$^-$ and [**6**]$^+$ OTf$^-$ is similar to that of compounds **1** and **2** and other related complexes.[11] Both complexes show a reduction peak at −1.70 and −1.64 V, respectively, and an oxidation peak at +0.86 and +1.01 V vs SCE, respectively. In the range of scan rates studied both processes appear to be irreversible. The number of electrons transferred was estimated to be 1 by comparison to the ferrocene oxidation under the same experimental conditions.

X-ray Structure of [CpMo(NNPh$_2$)$_2$(PPh$_3$)]$^+$OTf$^-$ ([6]$^+$OTf$^-$). Crystallographic data for [**6**]$^+$OTf$^-$ are

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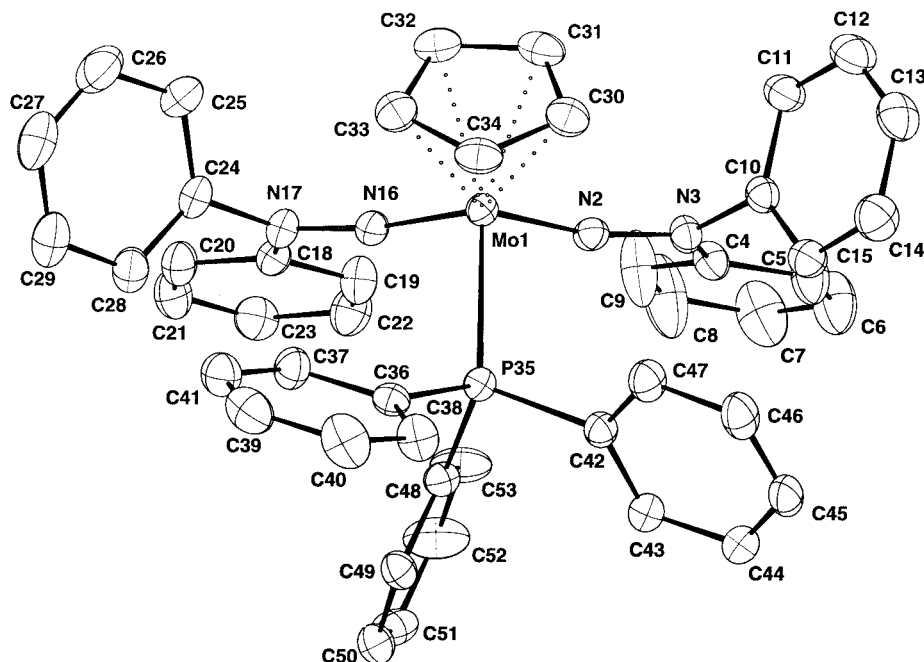
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Figure 1. CAMERON plot of [**6**]$^+$ with the atom-labeling scheme. The hydrogen atoms and the OTf$^-$ anion have been omitted for clarity.

Table 1. Crystallographic Data for Compound [6]$^+$OTf$^-$

formula	[(η^5-C$_5$H$_5$)Mo(NNPh$_2$)$_2$(PPh$_3$)]$^+$CF$_3$SO$_3^-$
fw	936.81
space group	$P\bar{1}$
a, Å	12.414(2)
b, Å	14.105(7)
c, Å	14.304(2)
α, deg	81.73(3)
β, deg	66.10(1)
γ, deg	78.94(3)
V, Å^3	2241
Z	2
T, °C	20
λ, Å	0.710 69
μ(Mo Kα), cm^{-1}	1.39
ρ_{calcd}, g cm^{-3}	4.2
2θ range, deg	2–50
octants collected	−13 to +14; −16 to +16; 0−16
scan width, deg	0.8 + 0.345 tan θ
diffractometer	Enraf-Nonius CAD4F
no. of unique rflns	7865
no. of rflns with $I > 3\sigma(I)$	5829
abs cor	DIFABS
no. of variables	550
R^a	0.053
$R_w{}^b$ (w = 1.0)	0.056

^{a} $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

Table 2. Selected Interatomic Distances (Å) for [6]$^+$OTf$^-$

Mo(1)−N(2)	1.816(4)	Mo(1)−N(16)	1.797(4)
N(2)−N(3)	1.309(6)	N(16)−N(17)	1.312(6)
N(3)−C(4)	1.416(7)	N(3)−C(10)	1.450(7)
N(17)−C(18)	1.423(7)	N(17)−C(24)	1.444(7)
Mo(1)−C(30)	2.382(4)	Mo(1)−C(31)	2.370(6)
Mo(1)−C(32)	2.342(6)	Mo(1)−C(33)	2.338(6)
Mo(1)−C(34)	2.361(6)	Mo(1)−P(35)	2.476(1)
P(35)−C(42)	1.828(5)	P(35)−C(36)	1.818(5)
P(35)−C(48)	1.817(5)	C(30)−C(31)	1.406(9)
C(31)−C(32)	1.382(9)	C(32)−C(33)	1.427(9)
C(33)−C(34)	1.406(9)	C(30)−C(34)	1.399(9)

Table 3. Selected Bond Angles (deg) for [6]$^+$OTf$^-$

N(2)−Mo(1)−N(16)	106.9(2)	N(2)−Mo(1)−C(30)	97.1(2)
N(16)−Mo(1)−C(30)	149.7(2)	N(2)−Mo(1)−C(31)	93.8(2)
N(16)−Mo(1)−C(31)	123.6(2)	N(2)−Mo(1)−C(32)	121.3(2)
N(16)−Mo(1)−C(32)	93.8(2)	N(2)−Mo(1)−C(33)	151.2(2)
N(16)−Mo(1)−C(33)	94.0(2)	N(2)−Mo(1)−C(34)	128.2(2)
N(16)−Mo(1)−C(34)	124.8(2)	N(2)−Mo(1)−P(35)	92.4(1)
N(16)−Mo(1)−P(35)	93.9(1)	C(30)−Mo(1)−P(35)	103.5(2)
C(31)−Mo(1)−P(35)	137.9(2)	C(32)−Mo(1)−P(35)	141.2(2)
C(33)−Mo(1)−P(35)	106.0(2)	C(34)−Mo(1)−P(35)	86.9(2)
C(30)−Mo(1)−C(31)	34.4(2)	C(31)−Mo(1)−C(32)	34.1(2)
C(32)−Mo(1)−C(33)	35.5(2)	C(33)−Mo(1)−C(34)	34.8(2)
Mo(1)−P(35)−C(36)	112.2(2)	C(36)−P(35)−C(48)	104.6(2)
Mo(1)−P(35)−C(48)	114.7(2)	C(36)−P(35)−C(42)	105.7(2)
Mo(1)−P(35)−C(42)	114.9(2)	C(42)−P(35)−C(48)	103.7(2)
Mo(1)−N(2)−N(3)	158.9(4)	N(2)−N(3)−C(4)	120.3(5)
N(2)−N(3)−C(10)	118.2(4)	C(4)−N(3)−C(10)	121.1(4)
Mo(1)−N(16)−N(17)	168.1(4)	N(16)−N(17)−C(18)	119.9(4)
N(16)−N(17)−C(24)	118.5(4)	C(18)−N(17)−C(24)	121.6(4)
C(30)−C(33)−C(32)	108.6(6)	C(31)−C(32)−C(33)	108.1(6)
C(32)−C(33)−C(34)	107.0(6)	C(33)−C(34)−C(30)	108.3(6)
C(31)−C(30)−C(34)	107.9(6)		

given in Table 1, and selected bond distances and angles are listed in Tables 2 and 3, respectively. A CAMERON plot of [**6**]$^+$ is shown in Figure 1. The crystal structure consists of discrete ions with two formula units in the unit cell. The cation is approximately octahedrally coordinated by the η^5-C$_5$H$_5$ ligand, the two η^1-bonded hydrazido ligands, and the phosphine ligand. It has the familiar distorted-piano-stool geometry found previously for [CpMo(NNC$_6$H$_4$Me-*p*)(NNC$_6$H$_4$F-*p*)(PPh$_3$)].[34,35] The short Mo−N (1.816(4) and 1.797(4) Å) and N−N dis-

tances (1.309(6) and 1.312(6) Å) and the near-planarity of the Mo−N−N−C$_2$ moieties (maximum deviation from the mean planes 0.057 Å) indicate extensive electronic delocalization throughout the MoNNPh$_2$ systems. These parameters are similar for most of the complexes containing the *cis*-{Mo(NNRR')$_2$}$^{2+}$ unit.[36] The departure from linearity of the Mo−N−N grouping (Mo−N−N = 158.9(4) and 168.1(4)°) is similar to that observed in

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[Mo(NNMePh)$_2$Cl$_2$(PPh$_3$)$_2$][11] and possibly arises from intramolecular nonbonding contact interactions. On the other hand, the origin of the slight asymmetry observed in the bonding mode of the cyclopentadienyl ligand is not clear. Indeed, both the longest (Mo(1)−C(30) = 2.382(6) Å) and the shortest (Mo(1)−C(33) = 2.338(6) Å) Mo−C bonds are approximately *trans* to the hydrazido ligands.

Although such complexes have been considered for a long time as containing hydrazido(2−) ligands, a recent theoretical investigation of mono- and bis(hydrazido) metal complexes[36] indicates that, taken as a whole, two *cis* formally hydrazido(2−) ligands act as a 10-electron system. Therefore, [**3**]$^+$and [**4**]$^+$ are 16-electron complexes, while [**5**]$^+$ and [**6**]$^+$ fulfill the 18-electron rule. In these compounds, the actual NNR$_2$ oxidation state is likely closer to 1− rather than to 2−.[36] Such a ligand formal charge leads us to consider molybdenum in the IV (d^2) oxidation state.

Concluding Remarks

The two-step procedure described herein provides a convenient method for the preparation, under mild conditions, of [**5**]$^+$OTf$^-$ and [**6**]$^+$OTf$^-$ from **1** and **2**. These compounds represent the first examples of organometallic derivatives that contain the *cis*-{Mo(NNRPh)$_2$}$^{2+}$ moiety (R = Me, Ph), where the organodinitrogen ligands are considered as potential models for NNH$_2$, which is a proven intermediate in the conversion of N$_2$ into NH$_3$ at a mononuclear site.[37] Furthermore, the intermediates [**3**]$^+$OTf$^-$ and [**4**]$^+$OTf$^-$ open a facile synthetic route to a number of coordination or organometallic compounds, depending on the nature of the incoming ligands, and we are currently investigating along this line.

Experimental Section

All manipulations were carried out on a vacuum/nitrogen line using standard Schlenk techniques. Cyclopentadienylsodium (NaCp) 2.0 M in THF, silver triflate (AgOTf$^-$), and tetrabutylammonium hexafluorophosphate (*n*-Bu$_4$N$^+$PF$_6^-$) were purchased from commercial sources and used as received. Reagent grade solvents were dried and distilled under nitrogen by standard methods prior to use. The compounds [Mo(NNMePh)$_2$Cl$_2$(PPh$_3$)$_2$] and [Mo(NNPh$_2$)$_2$Cl$_2$(PPh$_3$)] were prepared as described elsewhere.[11] IR spectra were obtained as KBr disks on a Perkin-Elmer Model 1600 FT-IR spectrophotometer. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded in CDCl$_3$ on a Bruker FT AC/200P spectrometer. ^{1}H and ^{13}C NMR spectra were referenced to Me$_4$Si as an external standard. ^{31}P NMR chemical shifts are reported relative to an external standard of 85% H$_3$PO$_4$. Mass spectra were recorded in a high-resolution ZabSpec TOF VG Analytical spectrometer operating in the FAB$^+$ mode. Ions were produced with the standard Cs$^+$ gun at ca. 8 kV, and 3-nitrobenzyl alcohol (NBA) was used as the matrix. Melting points were determined by using a Kofler apparatus. Cyclic voltammetry studies were carried out with a homemade potentiostat of conventional design, using a standard three-electrode setup with platinum working and auxiliary electrodes and an aqueous saturated calomel electrode (SCE) as the reference. CH$_3$CN solutions

were 1.0 mM in the compound under study and 0.1 M in the supporting electrolyte *n*-Bu$_4$N$^+$PF$_6^-$. Under these experimental conditions the FeCp$_2$/FeCp$_2^+$ couple was located at 0.39 V.

Preparation of [Mo(NNMePh)$_2$Cl(PPh$_3$)$_2$]$^+$OTf$^-$ ([3]$^+$-OTf$^-$). To a solution of **1** (0.28 g, 0.30 mmol) in CH$_2$Cl$_2$/CH$_3$-CN (2:1, 15 mL) was added AgOTf (0.075 g, 0.30 mmol). The mixture was stirred for 2.0 h at room temperature and filtered through Celite. The solid was washed several times with CH$_2$-Cl$_2$/CH$_3$CN (2:1), and the combined filtrates were evaporated to dryness under vacuum. The residue was stirred in CH$_2$-Cl$_2$/Et$_2$O (1:10, 30 mL) for 1.5 h and then filtered off. The solid was washed with diethyl ether, dried under vacuum, and recrystallized as follows: the crude product was dissolved in CH$_2$Cl$_2$ and then diethyl ether was added with stirring until a brown impurity precipitated. An additional amount of diethyl ether was added to the filtrate. Cooling to −15 °C gave a pale green microcrystalline solid. Further recrystallization was carried out in CH$_2$Cl$_2$, which was layered with *n*-hexane and cooled to −15 °C. Yield before recrystallization: 0.29 g (96%). Mp: 181 °C dec. Anal. Calcd for C$_{51}$H$_{46}$ClF$_3$MoN$_4$-O$_3$P$_2$S: C, 58.6; H, 4.44. Found: C, 58.8; H, 4.60. UV−vis (CH$_2$Cl$_2$; λ_{max}, nm (log ϵ)): 280 sh (4.38); 354 (4.25); 380 sh (4.20). IR (cm^{-1}, KBr): 3056 (w), ν(CH) arom; 2929 (w), ν-(CH) aliph; 1587 (m), ν(NN); 1480 (m, split), ν(CC) arom; 1264 (vs), ν(SO$_3$); 1150 (m), ν(CF$_3$). ^{1}H NMR (CDCl$_3$): δ 3.51 (s, 6H, 2CH_3N); 6.80−7.53 (m, 40H, 8C$_6$H$_5$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 29.52 (s).

Preparation of [Mo(NNPh$_2$)$_2$Cl(PPh$_3$)$_2$]$^+$OTf$^-$ ([4]$^+$OTf$^-$). To a mixture of **2** (0.23 g, 0.30 mmol) and PPh$_3$ (0.076 g, 0.30 mmol) suspended in CH$_2$Cl$_2$/CH$_3$CN (2:1, 15 mL) was added AgOTf (0.075 g, 0.30 mmol). The crude product was isolated as described above for [**3**]$^+$OTf$^-$ and then redissolved in CH$_2$-Cl$_2$. The solution was filtered off, and diethyl ether was added to the filtrate, which was cooled to −15 °C. The resulting crystalline solid was finally dissolved in CH$_2$Cl$_2$ layered with *n*-hexane to afford pure [**4**]$^+$OTf$^-$ as a pale green microcrystalline solid. Yield before recrystallization: 0.30 g (91%). Mp: 190 °C dec. Anal. Calcd for C$_{61}$H$_{50}$ClF$_3$MoN$_4$O$_3$P$_2$S: C, 62.7; H, 4.31; N, 4.79. Found: C, 62.4; H, 3.99; N, 4.76. UV−vis ((CH$_2$Cl$_2$; λ_{max}, nm (log ϵ)): 260 sh (4.69); 358 (4.27); 404 (4.19). IR (cm^{-1}, KBr): 3056 (w), ν(CH) arom; 1588 (m), ν-(NN); 1483 (s), ν(CC); 1272 (vs), ν(SO$_3$); 1150 (m), ν(CF$_3$). ^{1}H NMR (CDCl$_3$): 6.35−7.50 (m, C$_6$H$_5$). ^{31}P{^{1}H} NMR (CDCl$_3$): 29.72 (s). MS (positive Cs-FAB, *m*-nitrobenzylic alcohol): calcd *m/z* for C$_{60}$H$_{50}$ClMoN$_4$P$_2$, C$^+$, 1021.2263; obsd 1021.2265.

Preparation of [CpMo(NNMePh)$_2$(PPh$_3$)]$^+$OTf$^-$ ([5]$^+$-OTf$^-$). To a 0.21 g (0.20 mmol) sample of [**3**]$^+$OTf$^-$ dissolved in 20 mL of THF was added 0.20 mL of NaCp 2.0 M in THF (0.40 mmol). The mixture was stirred vigorously for 45 min at room temperature. Then the solution was evaporated to dryness under vacuum. The residue was extracted three times with 10 mL portions of CH$_2$Cl$_2$, and the extracts were filtered through Celite. The filtrate was concentrated to a final volume of 10 mL and layered with diethyl ether. Orange microcrystals appeared after 1 week at −15 °C. Yield: 0.056 g (34.1%). Mp: 191 °C. Anal. Calcd for C$_{38}$H$_{36}$F$_3$MoN$_4$O$_3$PS: C, 56.2; H, 4.47. Found: C, 55.5; H, 4.50. UV−vis ((CH$_2$Cl$_2$; λ_{max}, nm, (log ϵ)): 284 (4.42); 316 sh (4.30); 388 sh (4.05). IR (cm^{-1}, KBr): 3060 (w), ν(CH) arom; 2931 (w), ν(CH) aliph; 1589 (m), ν(NN); 1471 (m), ν(CC) arom; 1271 (vs), ν(SO$_3$); 1150 (m), ν-(CF$_3$). ^{1}H NMR (CDCl$_3$): δ 3.66 (s, 6 H, 2CH_3); 6.10 (s, 5 H, C$_5$H$_5$); 7.08−7.78 (m, 25 H, 5C$_6$H$_5$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 51.93 (s). ^{13}C NMR (CDCl$_3$): δ 43.41 (s, CH$_3$); 102.6 (br s, C_5H$_5$); 116.3, 125.2, 129.1, 129.2, 129.4, 131.6, 133.0, 133.2 (C_6H$_5$); 140.6 (OTf$^-$).

Preparation of [CpMo(NNPh$_2$)$_2$(PPh$_3$)]$^+$OTf$^-$ ([6]$^+$OTf$^-$). This compound was synthesized according to the procedure described above using 0.36 g (0.20 mmol) of [**4**]$^+$OTf$^-$ and 0.20 mL (0.40 mmol) of NaCp 2.0 M in THF. Suitable single crystals for X-ray diffraction studies were obtained by slow diffusion of *n*-hexane into a CH$_2$Cl$_2$ solution of the crude

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product. Yield: 0.14 g (38.5%). Mp: 210 °C dec. Anal. Calcd for $C_{48}H_{40}F_3MoN_4O_3PS$: C, 61.5; H, 4.30. Found: C, 60.8; H, 4.38. UV−vis ((CH_2Cl_2; λ_{max}, nm (log ϵ)): 290 (4.57); 322 sh (4.36); 384 sh (4.16). IR (cm^{-1}, KBr): 3060 (w), ν(CH) arom; 1589 (m), ν(NN); 1486 (s), ν(CC) arom; 1271 (vs), ν(SO$_3$); 1150 (s), ν(CF$_3$). ^{1}H NMR (CDCl$_3$): δ 5.67 (s, 5H, C$_5$*H*$_5$); 6.80−7.56 (m, 35 H, 7C$_6$*H*$_5$). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 49.65 (s). ^{13}C NMR (CDCl$_3$): δ 103.0 (*C*$_5$H$_5$); 129.4, 129.6, 130.2, 131.1, 131.90, 131.95, 133.1, 133.3 (*C*$_6$H$_5$); 205.3 (OTf$^-$).

X-ray Crystallographic Analysis of [6]$^+$OTf$^-$. X-ray data were recorded on an Enraf-Nonius CAD4F diffractometer using graphite-monochromated Mo Kα radiation. A crystal of [**6**]$^+$OTf$^-$ was mounted on a glass fiber. Lattice parameters and the orientation matrix were obtained from a least-squares fit of the setting angles of 25 accurately centered reflections. Crystal data and data collection parameters are summarized in Table 1. No significant variations were observed in the intensities of two check reflections during data collection. The data were corrected for Lorentz and polarization effects. An empirical absorption correction using DIFABS was applied.[38] All computations were performed using the PC version of CRYSTALS.[39] The structure was solved by direct methods and refined with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included in fixed positions in the last refinements, which gave $R = 0.053$ and

$R_w = 0.056$. Scattering factors and corrections for anomalous dispersion were taken from the literature.[40]

Supporting Information Available: Tables of atomic coordinates, anisotropic thermal parameters, interatomic distances, and bond angles for [**6**]$^+$OTf$^-$ (10 pages). Ordering information is given on any current masthead page.

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