Syntheses of Molybdenum(II) and Molybdenum(IV) Complexes Bearing Tethered Homoallylic Phosphines†

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Photolysis of [CpMo(CO)$_3$Cl] in the presence of 2-(1-propenyl)phenyldiphenylphosphane (**PP**, cis/trans mixture) yields the complex [CpMo(CO)Cl(PP)], **2**, with an olefin ligand tethered to a phosphorus donor atom. A trans configuration of the substituents at the olefinic unit is thermodynamically preferred, so that the corresponding complex **2^t** can be isolated in isomerically pure form under certain conditions. However, the cis-olefin complex **2^c** has been characterized in its mixture with **2^t**, too. Treatment of **2^t** with HNMe$_2$ leads to the intramolecular elimination of HCl under formation of the compound [CpMo(CO)(CH$_2$-CHCHC$_6$H$_4$PPh$_2$)], **3**, bearing a chelating π-allyl/PPh$_2$ ligand. When a CH$_2$Cl$_2$ solution of **3** is photolyzed in the presence of N$_2$O, the CO ligand is replaced by two chloride ligands, i.e., the Mo center is oxidized to the oxidation state +IV. The resulting complex [CpMoCl$_2$(CH$_2$-CHCHC$_6$H$_4$PPh$_2$)], **4**, is one of the rare examples, where a soft allyl ligand is bound to a metal center in a comparatively high oxidation state. However, probably due to the chelate effect, the Mo−allyl bond is remarkably stable. All compounds **2**−**4** have been investigated by means of single-crystal X-ray diffraction, and their crystal structures are discussed.

Introduction

The rate-determining step of the acrolein synthesis via propene oxidation on bismuthmolybdate catalysts is proposed to proceed via surface intermediates with π-allyl ligands coordinated to high-valent Mo$^{V/VI}$ centers.[1] These intermediates are considered to be only very short-lived, as the combination of a “soft” π-allyl ligand with a “hard” molybdenum oxo moiety is naturally unstable, and, moreover, metals in high oxidation states are not capable of stabilizing metal−ligand π-bonds by efficient back-bonding. Thus it is believed that the (π-allyl)−Mo bonds formed initially during the propene oxidation are quickly cleaved again and that the allyl radicals generated thereby are subsequently trapped by Mo^{VI}O functions in close proximity.[1]

This conception stimulates research with the aim of preparing *molecular* high-valent allylmolybdenum compounds. Whereas a fairly large number of η^5-cyclopentadienyl complexes with metals in relatively high oxidation states are known, for the above-mentioned reasons the number of compounds that have an η^3-allyl group coordinated to a high oxidation state metal is limited.[2−4] The latter should become more amenable to isolation if the (π-allyl)−metal bond is stabilized, and stabilization of coordinative bonds is often accomplished making use of the chelate effect. Consequently, we decided to investigate the synthesis and reactions of molybdenum complexes bearing donor-functionalized π-allyl ligands. This goal seemed attractive also for another reason: π-allylmolybdenum complexes are particularly versatile reagents in organic chemistry, since they have been shown to react with both electrophiles and nucleophiles, depending on the nature of the other ligands on the complex.[5] This also recently lead Krafft, Abboud, and Procter to synthesize organomolybdenum compounds with π-allyl ligands tethered to chelating N or S atoms, as it was anticipated that these complexes would undergo selective reactions due to the influence of the chelating heteroatom.[6] Their preparation involved heating of donor-functionalized allylic acetates in the presence of the sodium salt of β-dicarbonyl compounds and Mo(CO)$_6$.

We report here the syntheses of molybdenum complexes with (π-allyl)/PPh$_2$ chelating ligands—obtained from the corresponding tethered olefin complexes, which had to prepared first—and their behavior under oxidative conditions.

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† Dedicated to Prof. Dr. A. J. Downs on the occasion of his 65th birthday.

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(1) Grasselli, R. K.; Burrington, J. D. *Ind. Engl. Chem. Prod. Res. Dev.* **1984**, *23*, 394. Belgacem, J.; Kress, J.; Osborn, J. A. *J. Mol. Catal.* **1994**, *86*, 267. Ono, T.; Numata, H.; Ogata, N. *J. Mol. Catal.* **1996**, *105*, 31. Kinne, M.; Heidenreich, A.; Rademann, K. *Angew. Chem.* **1998**, *110*, 2637; *Angew. Chem., Int. Ed.* **1998**, *37*, 2509.

(2) Faller, J. W.; Ma, Y. *Organometallics* **1986**, *5*, 1949.

(3) Mo(η^3-allyl)$_3$R compounds (R = negatively charged organic or inorganic ligand): Wilke, G.; Bogdanovic, B.; Hardt, P.; Heimbach, P.; Kerm, W.; Kroner, M.; Oberkirch, W.; Tanaka, K.; Steinrucke, E.; Walter, W.; Zimmermann, H. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 151. Benn, R.; Holle, S.; Jolly, P. W.; Mynott, R.; Romão, C. C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 555. Jolly, P. W.; Krüger, C.; Romao, C. C.; Romao, M. J. *Organometallics* **1984**, *3*, 936. Andell, O.; Goddard, R.; Holle, S.; Jolly, P. W.; Krüger, C.; Tsay, Y. H. *Polyhedron* **1989**, *8*, 203.

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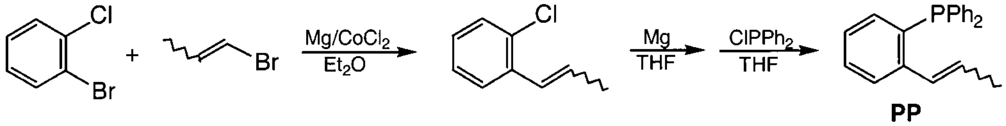
Scheme 1



Results and Discussion

2-(1-Propenyl)phenyldiphenylphosphane, **PP**, appeared to be a suitable potential ligand to start with in the above-mentioned investigation. A particularly attractive feature of **PP** is the fact that the two donor functions (olefinic double bond and phosphorus atom) are connected by a C_2 unit incorporated into an aryl ring. This makes the system more rigid, defining a certain bite angle and enforcing the chelate effect in comparison to aliphatic C_2 units. Moreover, the methyl group at the olefinic donor function offered the opportunity of converting this moiety into the desirable allyl ligand via proton abstraction. **PP** was synthesized in a modified way following the route published by Interrante et al.:[7,8] starting from 1-bromo-2-chlorobenzene, 1-chloro-2-(1-propenyl)benzene was prepared in a Grignard reaction and then treated with magnesium. Subsequent reaction with $ClPPh_2$ (compare Scheme 1) gave pure **PP** in 25% yield after chromatography with a cis/trans ratio **PP**^{c}/**PP**^{t} of typically 1:3.3. As reportedly[8] transition metals can catalyze cis/trans isomerizations, no effort was made to separate the individual isomers **PP**^{c} and **PP**^{t}: the mixture was used directly for subsequent reactions with molybdenum complexes such as $[CpMo(CO)_3Cl]$, **1**.[9] **1** appeared to be the ideal starting material, since it contains (i) CO ligands, which could be imagined to be easily replaced by **PP** in a substitution reaction, (ii) a Cl ligand, which could allow a subsequent deprotonation to proceed in the form of an HCl elimination, and (iii) a cyclopentadienyl ligand stabilizing high as well as low oxidation states. Photolysis of a diluted, equimolar solution of **1** and **PP** in toluene indeed yielded the desired product [CpMo(CO)Cl(PP^{t})], **2**^{t}, in 95% yield after purification with the aid of adsorption chromatography (Scheme 2). **2**^{t} was characterized by means of IR and NMR spectroscopy (^{1}H, ^{31}P, ^{1}H{^{31}P}, ^{13}C, HSQC), MS spectrometry, and elemental analyses. Single crystals were investigated in an X-ray diffraction study, and the result is shown in Figure 1 (selected bond lengths and angles are listed in Table 1). The η^5-C_5H_5 ring, the Cl ligand, and one CO ligand are still coordinated to the molybdenum atom in **2**^{t}, while two of the CO ligands have been replaced by **PP**. The latter is seen to act as a bidentate ligand, bonding to the metal through both the phosphorus atom and the *o*-propenyl substituent (coordinated as a η^2-olefin). The resulting geometry can be described as a four-legged piano stool. The olefinic Mo−C distances are significantly different from each other [Mo−C(26) amounts to 2.283(3) and Mo−C(25) to 2.321(3) Å] and much shorter than those observed[10] in the complex [Mo(CO)$_4$PP^{t}], where the olefin moiety is located in trans position to a strongly π-accepting carbonyl ligand. The configuration of the substituents at the olefinic double bond is *E*, so that the distance between the C atom of

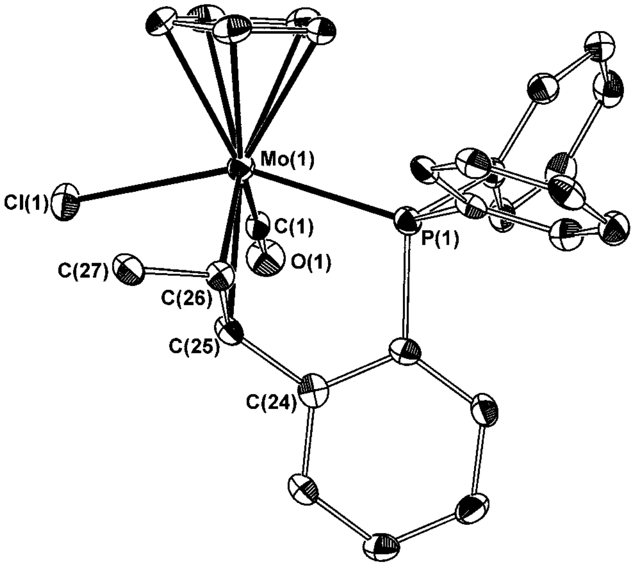


Figure 1. Molecular structure of **2**^{t} with partial atom-labeling scheme. Hydrogen atoms have been omitted for clarity, and thermal ellipsoids are drawn at the 30% level.

Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 2^{t}

Mo(1)−C(1)	1.962(3)	Mo(1)−C(26)	2.283(3)
Mo(1)−P(1)	2.4827(9)	C(24)−C(25)	1.482(4)
Mo(1)−Cl(1)	2.5597(8)	C(25)−C(26)	1.413(4)
Mo(1)−C(25)	2.321(3)	C(26)−C(27)	1.508(3)
Cl(1)−Mo(1)−C(1)	82.19(7)	C(26)−Mo(1)−C(1)	114.8(1)
C(1)−Mo(1)−P(1)	84.44(8)	P(1)−Mo(1)−C(26)	79.26(7)
P(1)−Mo(1)−C(25)	75.37(7)	C(26)−Mo(1)−Cl(1)	84.06(7)
C(25)−Mo(1)−C(26)	35.73(9)	P(1)−Mo(1)−Cl(1)	151.85(2)
C(25)−Mo(1)−Cl(1)	77.83(7)	C(27)−C(26)−C(25)	123.1(2)
C(25)−Mo(1)−C(1)	79.1(2)	C(26)−C(25)−C(24)	123.7(2)

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(6) Krafft, M. E.; Procter M. J.; Abboud, K. A. *Organometallics* **1999**, *18*, 1122.

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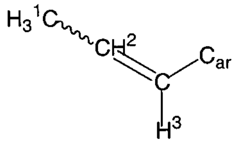
(9) *Synthetic Methods of Organometallic and Inorganic Chemistry*; Herrmann, W. A., Ed.; Transition metals, Part 2; Thieme Verlag: Stuttgart, 1997; Vol. 8.

(10) Luth, H.; Truter, M. R.; Robson, A. *J. Chem. Soc. A* **1969**, *1*, 28.

Table 2. ^{1}H and ^{13}C NMR Data Recorded for $\mathbf{2^t}$ and $\mathbf{2^c}$ (200 MHz)

	$\mathbf{2^t}$ ^{1}H ($CDCl_3$)	$\mathbf{2^t}$ ^{13}C (CD_2Cl_2)	$\mathbf{2^c}$ ^{1}H (CD_2Cl_2)	$\mathbf{2^c}$ ^{13}C (CD_2Cl_2)
$CH^1{}_3$	2.15 (d) $^3J_{H1-H2} = 5.80$ Hz	21.91	1.69 (d) $^3J_{H1-H2} = 6.49$ Hz	21.58
CH^2	4.27 (m)	66.40	4.29 (m)	66.04
CH^3	4.76 (dd) $^3J_{H2-H3} = 12.21$ Hz $^4J_{P-H3} = 4.00$ Hz	93.30	4.89 (dd) $^3J_{H2-H3} = 10.58$ Hz $^4J_{P-H3} = 3.07$ Hz	90.44
Cp	5.08 (d) $^3J_{P-HCp} = 2.60$ Hz	95.00	5.11 (d) $^3J_{P-HCp} = 3.41$ Hz	94.60
Ar	7.6−6.9 (m)	159−126	7.6−6.9 (m)	158−127

the methyl group (C(27)) and the Cl atom amounts to only 3.252 Å, providing an ideal basis for the intramolecular HCl elimination planned in the subsequent step. This close contact might also explain the noncoplanarity of the $CH_3-C{=}C-C_{ar}$ unit (compare Figure 1; the torsion angle of C(27)−C(26)−C(25)−C(24) amounts to −138.6°). It can thus be concluded that the $H^3-C-C-H^2$ moiety is also forced out of coplanarity, and this goes along with the coupling constant $^3J_{H2-H3}$ of only 12.21 Hz observed in the ^{1}H NMR spectrum (Table 2), which can be considered[11] as being quite small for two protons in an *E*-configuration on an olefinic bond. In the NMR spectra of bulk samples dissolved in $CDCl_3$ there was no sign of the corresponding *Z*-isomer $\mathbf{2^c}$, although an isomeric mixture ($\mathbf{PP^c}$/$\mathbf{PP^t}$ = 1:3.3) of the **PP** ligand had been employed. This finding is thus in accordance with the observation of Interrante et al., that first of all metal centers can bring about the *Z*/*E* isomerization of **PP** and that second in the case of the **PP** ligand the trans complexes are thermodynamically favored.[8] It was anticipated that it might be possible to observe $\mathbf{2^c}$ if the proportion of $\mathbf{PP^c}$ with respect to $\mathbf{PP^t}$ is raised prior to the reaction, as this prolongs the time required for a complete conversion of $\mathbf{2^c}$ formed initially to give $\mathbf{2^t}$. Having found that the $\mathbf{PP^c}$/$\mathbf{PP^t}$ ratio of 1:3.3 can be increased via photolysis, experiments were performed where a solution of the **PP** ligand in toluene was prephotolyzed for 1 h in the presence of catalytical amounts of **1** before applying the procedure as described above for the preparation of $\mathbf{2^t}$. Indeed a mixture of isomers $\mathbf{2^t}$ and $\mathbf{2^c}$ was isolated then, from which the $\mathbf{2^c}$ isomer could be obtained in crystalline form. Its molecular structure is shown in Figure 2, and selected bond lengths and angles can be found in Table 3. The geometrical arrangement of the ligands around the Mo center is principally very similar to that of $\mathbf{2^t}$, and the atom distances within $\mathbf{2^c}$ are comparable, too. Naturally, the angle C(26)−Mo−P, 87.0(2)°, is somewhat larger (as compared to the corresponding angle in $\mathbf{2^t}$ [79.26(7)°]), while the Cl−Mo−C(26) angle is smaller (78.1(2)° vs 84.06(7)° in $\mathbf{2^t}$) due to the varying steric requirements of the methyl group at the olefinic donor function in the individual configurations. The C(27)−C(26)−C(25)−C(24) moiety is almost coplanar (the torsion angle amounts to only −10.4°), and consequently $^3J_{H2-H3}$, 10.58 Hz, is quite normal[11] for two protons in a *Z*-configuration on an olefinic bond.

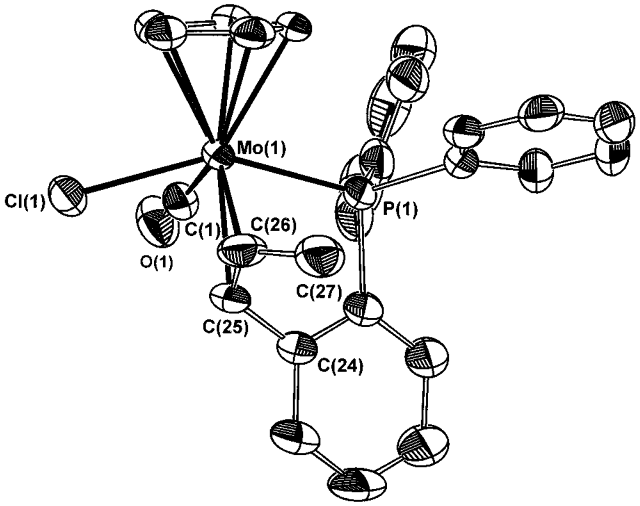


Figure 2. Molecular structure of $\mathbf{2^c}$ with partial atom-labeling scheme. Hydrogen atoms have been omitted for clarity, and thermal ellipsoids are drawn at the 30% level.

Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for $\mathbf{2^c}$

Mo(1)−C(1)	1.996(5)	Mo(1)−C(26)	2.302(4)
Mo(1)−P(1)	2.484(2)	C(24)−C(25)	1.484(6)
Mo(1)−Cl(1)	2.570(1)	C(25)−C(26)	1.411(6)
Mo(1)−C(25)	2.321(4)	C(26)−C(27)	1.484(6)
Cl(1)−Mo(1)−C(1)	82.0(2)	C(25)−Mo(1)−C(1)	82.4(2)
C(1)−Mo(1)−P(1)	83.1(2)	C(25)−Mo(1)−C(26)	35.6(3)
P(1)−Mo(1)−Cl(1)	150.95(3)	C(26)−Mo(1)−Cl(1)	78.1(2)
P(1)−Mo(1)−C(25)	76.6(2)	C(26)−Mo(1)−C(1)	117.5(2)
P(1)−Mo(1)−C(26)	87.0(2)	C(24)−C(25)−C(26)	124.6(4)
C(25)−Mo(1)−Cl(1)	76.8(2)	C(25)−C(26)−C(27)	122.8(5)

Having isolated and characterized $\mathbf{2^t}$ and $\mathbf{2^c}$, attempts were made to convert the olefinic donor groups into allyl functions via intramolecular HCl elimination. As outlined above, in $\mathbf{2^t}$ the methyl residue of the **PP** ligand and the Cl ligand at the molybdenum center are in an ideal preorientation for such a reaction. Accordingly, isomerically pure $\mathbf{2^t}$ was reacted with $LiN(CH_3)_2$ in thf, yielding the product **3** in 30% yield after purification with the aid of adsorption chromatography. **3** was investigated in detail by NMR spectroscopy (see Table 4) as well as by single-crystal X-ray diffraction (Figure 3, Table 5). Both methods agree in their results (see Scheme 2): The H_3C^1 group of the $\mathbf{PP^t}$ ligand in $\mathbf{2^t}$ has been deprotonated, and the resulting carbanion coordinates now at the metal center instead of the Cl atom; that is, the $\mathbf{PP^t}$ ligand has been converted into a tethered homoallylic phosphine ligand (a process that

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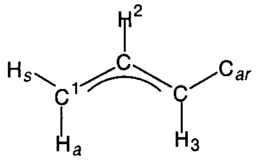
[11] Fribolin, H. *Ein- und Zweidimensionale NMR-Spektroskopie*; VCH: Weinheim, 1988.

Table 4. ^{1}H and ^{13}C NMR Data Recorded for 3 and 4 (200 MHz)

	**3** ^{1}H (CD_2Cl_2)	**3** ^{13}C ($CDCl_3$)	**4** ^{1}H ($CDCl_3$)	**4** ^{13}C (CD_2Cl_2)
C^1H_a	1.36 (d)	26.65	2.54 (d)	71.42
C^1H_s	$^3J_{Ha-H2} = 8.01$ Hz		$^3J_{Ha-H2} = 7.51$ Hz	
	2.04 (d)		4.38 (d)	
	$^3J_{Hs-H2} = 5.40$ Hz		$^3J_{Hs-H2} = 11.26$ Hz	
CH^2	3.79 (m)	85.35	5.28 (m)	69.99
CH^3	3.89 (dd)	65.21	4.74 (dd)	98.46
	$^3J_{H2-H3} = 8.19$ Hz		$^3J_{H2-H3} = 10.24$ Hz	
	$^4J_{P-H3} = 1.71$ Hz		$^4J_{P-H3} = 6.49$ Hz	
Cp	4.66 (s)	89.66	5.39 (d)	97.83
			$^3J_{P-HCp} = 3.07$ Hz	
Ar	7.14 (m)	154−127	7.45 (m)	137−126

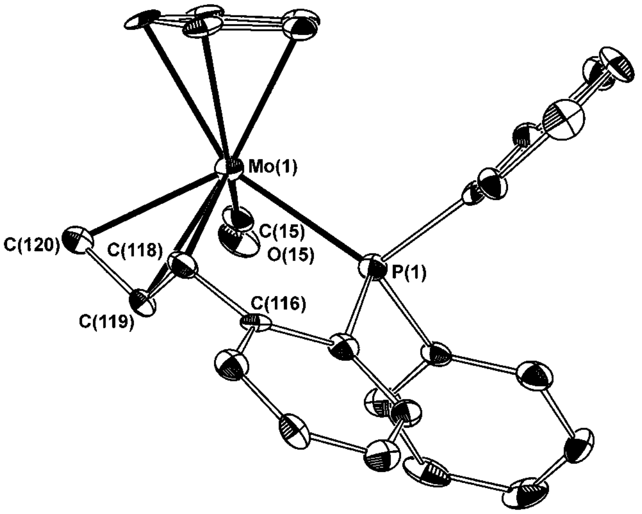


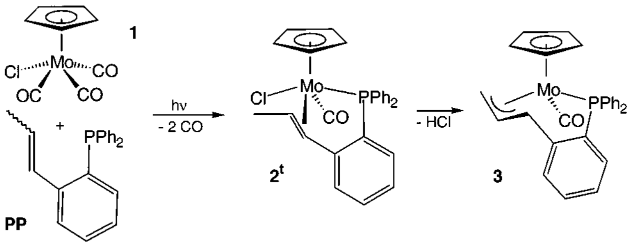
Figure 3. Molecular structure of **3** (one of the two independent molecules) with partial atom-labeling scheme. Hydrogen atoms have been omitted for clarity, and thermal ellipsoids are drawn at the 30% level.

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) for 3

Mo(1)−C(15)	1.932(7)	Mo(1)−C(120)	2.301(6)
Mo(1)−P(1)	2.442(2)	C(116)−C(118)	1.485(7)
Mo(1)−C(118)	2.309(6)	C(118)−C(119)	1.418(8)
Mo(1)−C(119)	2.259(6)	C(119)−C(120)	1.417(8)
C(15)−Mo(1)−P(1)	87.4(2)	P(1)−Mo(1)−C(120)	120.5(3)
C(15)−Mo(1)−C(118)	122.5(2)	C(118)−Mo(1)−C(119)	36.2(2)
C(15)−Mo(1)−C(119)	89.3(2)	C(118)−Mo(1)−C(120)	63.1(2)
C(15)−Mo(1)−C(120)	81.8(2)	C(119)−Mo(1)−C(120)	36.2(2)
P(1)−Mo(1)−C(118)	75.3(2)	C(116)−C(118)−C(119)	120.4(5)
P(1)−Mo(1)−C(119)	85.8(2)	C(118)−C(119)−C(120)	116.5(6)

is accompanied by an increase of the electron density at the metal center, as indicated by a shift of the ν(CO) frequency from 1911 to 1855 cm^{-1} on going from **2^t** to **3**). However, on comparison of the crystal structures of **2^t** and **3**, it becomes obvious that the allyl ligand did not adopt an exo conformation with respect to the P and CO donor functions, as could have been expected considering the preorientation of the $CH_3-C=C-$ moiety in **2^t**. The allyl group is coordinated in an endo orientation instead, which seems to be the thermodynamically preferred geometry. There are two possible mechanisms that can explain this exo−endo switch: Either it proceeds by the so-called $\pi-\sigma-\pi$ mechanism, i.e., via an intermediate containing a η^1-coordinated allyl group (with a Mo−C(118) σ-bond) that can rotate around the C(118)−C(116) axis, or C(120) and C(118) remain bonded in the intermediate while C(119) flips from one side to the other. However, in any case the endo form of **3** seems to represent a thermodynamic sink; on dissolution of **3** there is no sign of the corresponding exo isomer or a fluxional behavior.

Scheme 2



In attempts to prepare larger quantities of **2^t** for the subsequent conversion into **3**, it turned out that doubled (or higher) concentrations of **1** and **PP** in the photolysis experiment lead—under otherwise identical conditions—directly to **3** (16%) besides the main product **2^t** (44%). Although one step in the preparation of **3** is saved this way, it is difficult to separate either of the compounds in pure form afterward via adsorption chromatography (this can be achieved most effectively if the mixture already contains one of the compounds in a huge excess).

3 clearly belongs to the envisaged class of compounds, bearing an allyl ligand functionalized by a donor atom, which serves to stabilize the (π-allyl)−Mo bonding via the chelate effect. It is therefore well suited to be employed in reactions with the aim of increasing the oxidation state of Mo as outlined in the Introduction. Treatment of **3** with I_2, Cl_2, O_2, or HOO^{t}Bu under thermal or photolytical conditions gave no tractable products. As there are reports in the literature, where oxidative decarbonylations have been achieved via photolysis using N_2O as the oxidizing agent,[12] a CH_2Cl_2 solution of **3** was photolyzed in the presence of a 7-fold excess of N_2O gas. The course of the reaction was monitored by ^{31}P NMR spectroscopy (Figure 4): The formation of an intermediate **I** with a resonance at 70.4 ppm and of a compound showing a signal at 82.4 ppm close to the one of **3** (possibly its exo isomer?) could be

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[12] Stössel, P.; Mayer, H. A.; Maichle-Mössner, C.; Fawzi, R.; Steinmann, M. *Inorg. Chem.* **1996**, *35*, 5860.

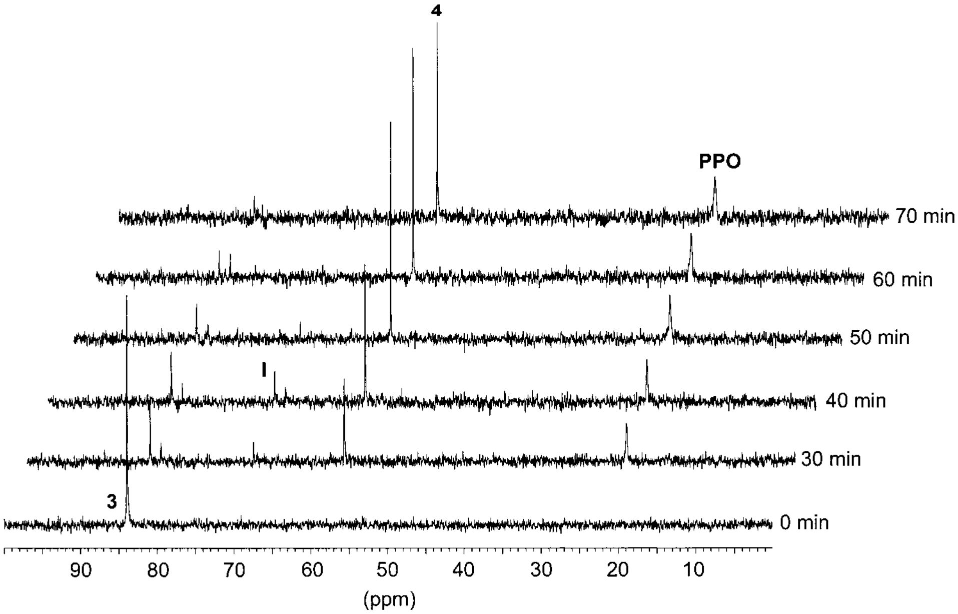

Figure 4. Monitoring of the photolytic reaction of **3** with N_2O in CD_2Cl_2 by means of ^{31}P NMR spectroscopy.

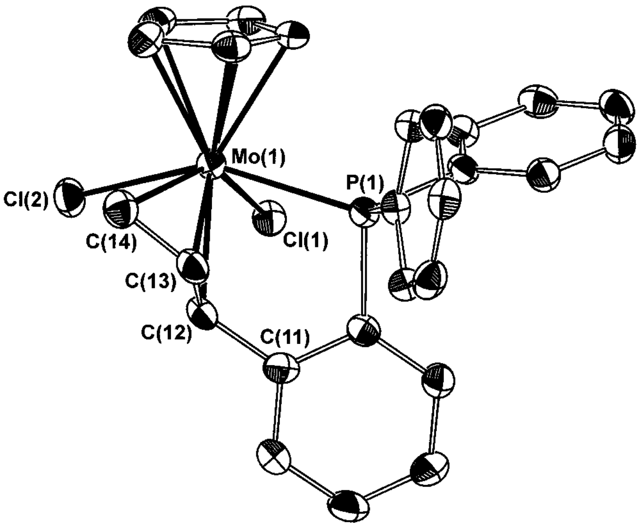

Figure 5. Molecular structure of **4** with partial atom-labeling scheme. Hydrogen atoms have been omitted for clarity, and thermal ellipsoids are drawn at the 30% level.

Table 6. Selected Bond Lengths (Å) and Bond Angles (deg) for 4

Mo(1)−Cl(1)	2.477(2)	Mo(1)−C(13)	2.281(3)
Mo(1)−Cl(2)	2.5338(9)	Mo(1)−C(14)	2.363(4)
Mo(1)−P(1)	2.530(2)	C(12)−C(13)	1.414(5)
Mo(1)−C(12)	2.297(3)	C(13)−C(14)	1.406(4)

Cl(1)−Mo(1)−P(1)	77.38(3)	Cl(1)−Mo(1)−C(13)	116.99(9)
P(1)−Mo(1)−C(12)	74.29(9)	C(13)−Mo(1)−C(14)	35.2(2)
Cl(2)−Mo(1)−C(12)	80.91(9)	P(1)−Mo(1)−C(14)	106.26(9)
Cl(1)−Mo(1)−C(12)	82.20(9)	Cl(2)−Mo(1)−C(14)	78.4(2)
C(12)−Mo(1)−C(13)	36.0(2)	Cl(1)−Mo(1)−C(14)	140.9(2)
C(12)−Mo(1)−C(14)	62.5(2)	Cl(2)−Mo(1)−Cl(1)	79.95(3)
P(1)−Mo(1)−C(13)	75.35(8)	C(11)−C(12)−C(13)	121.2(3)
Cl(2)−Mo(1)−C(13)	95.88(9)	C(12)−C(13)−C(14)	117.9(3)

observed in the period of time following the start of the reaction until it had reached completion. The integral of the signal corresponding to **3** constantly decreased, while a signal at 58.6 (designated as compound **4** in Figure 4) constantly gained in intensity. Small amounts of free, oxidized ligand 2-(1-propenyl)phenyldiphenylphosphanoxide, **PPO**, were formed as well. From the resulting red solution a red/brown solid could be isolated, which was purified by adsorption chromatography. Dissolution in CH_2Cl_2 and overlaying with hexane gave red crystals of the product **4**, one of which was subjected to an X-ray structure analysis. The molecular structure of **4** is shown in Figure 5, and selected bond lengths and angles can be found in Table 6. It turned out that indeed the CO ligand present in **3** has been removed oxidatively (CO_2 was detected in the gas phase after the reaction), and two Cl ligands are coordinated at the Mo center in **4** instead (Mo−Cl(1) 2.477(2), Mo−Cl(2) 2.5338(9) Å). In metal allyl compounds the two terminal M−C bond distances are often found to be longer than the $M-C_{meso}$ distance, as this leads to a maximum of orbital overlap[13] (compare for instance in **3** Mo−C(119) 2.259(6) Å with Mo−C(120) 2.301(6) Å and Mo−C(118) 2.309(6) Å). In **4**, however, one of the terminal C atoms (C(12)) shows a distance (2.297(3) Å) almost as short as that of the meso-C(13) atom (2.281(3) Å), while the Mo−C(14) bond length can be considered as long (2.363(4) Å). This reflects the rather unusual bonding situation of the allylic unit in **4**, which can also be found in the related compound [$CpMoBr_2(CO)(\eta^3$-2-bromoallyl)]:[2] in CpMo(allyl) compounds the Cp and allyl ligands are normally oriented symmetrically, i.e., a plane of local symmetry can be drawn through the (η^3-allyl)(η^5-cyclopentadienyl)molybdenum unit, as for instance in **3**. However, probably due to the steric encumberance at the coordination center, the allyl ligand is not allowed to take such a position in **4**, and it therefore rotates out of this plane. Yet again the conversion of **3** to **4** is accompanied by a “formal” flip of the meso carbon atom of the allyl group; that is, a distorted exo conformation of the allyl ligand seems to be thermodynamically favored in the case of **4**. The Mo−P distance of 2.442(2) Å in **3** is elongated to 2.530(2) Å in **4**, probably because in **4** two Cl ligands are competing with the P donor atom with respect to σ-bonding to the metal center.

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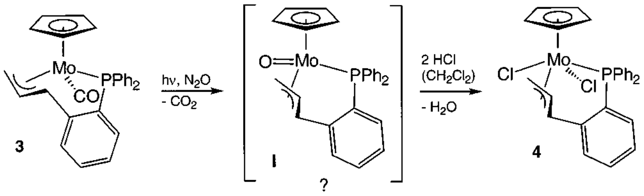
(13) Pruchnik, F. P. *Organometallic Chemistry of the Transition Elements*; Plenum Press: New York, 1990; p 444.

Scheme 3



Undoubtedly the Cl ligands must have their origin in the solvent CH_2Cl_2, which is known to be a source for HCl. However, CH_2Cl_2 is not usually considered an oxidizing reagent. It is therefore more reasonable to assume that the oxidation of Mo^{II} to Mo^{IV} was performed by N_2O, which probably—as planned originally—transferred an oxo atom onto the decarbonylated complex **3** (perhaps the resulting oxo complex (see Scheme 3) is even identical with the intermediate **I**). Formation of **4** can then be imagined by a double addition of HCl to the Mo=O bond under elimination of water.

As mentioned in the Introduction, organometallic complexes that have the combination of soft allyl ligands bound to a metal center of oxidation state IV are rarely encountered.[2–4] With **4** a (π-allyl)molybdenum(IV) complex has been successfully synthesized via a novel method: the oxidation by N_2O in CH_2Cl_2. Previous attempts[2] to prepare similar compounds by chlorination of $[CpMo(CO)_2(\eta^3\text{-}CH_2CRCH_2)]$ (R = Me, Cl, Br) majorly yielded $[CpMo(CO)_2Cl_3]$, and consistently Cl_2 oxidation of **3** did not lead to detectable quantities of **4** in our hands. Probably due to the chelate effect, **4** is remarkably stable, surviving even the contact with silica gel, and it can be handled in air for short periods of time, while the related compound $[CpMoBr_2(CO)(\eta^3\text{-allyl})]$ was reported[2] to be too unstable in solution to allow its isolation. Currently we are investigating the reactivity of **4** especially with respect to a substitution of the Cl ligands by oxo ligands.

Experimental Section

General Procedures. All manipulations were carried out with a vacuum line (at a background pressure $< 10^{-3}$ mbar), or in a glovebox, or by means of Schlenk-type techniques involving the use of a dry argon atmosphere. Microanalyses were performed by the Analytische Laboratorien des Organisch-Chemischen Institutes der Universität Heidelberg using a CHN-Analyser Heraeus (it proved difficult to completely free the samples from CH_2Cl_2 used as the solvent, so that the deviations of the carbon analyses are slightly outside the usual range). The deuterated solvents had been condensed into the NMR tubes before the tubes were flame-sealed. All NMR spectra were recorded using a Bruker Advance-DPX 200 or 300 MHz spectrometer. Infrared (IR) spectra were recorded using samples prepared as KBr pellets using a Bruker FT-IR spectrometer IFS-66. The photolysis source was either a 200 W medium-pressure arc (synthesis of **4**) or a Hg high-pressure arc Hanau TQ 150. The mass spectra were recorded on a Finnigan MAT 8400. The ions were generated by EI (70 eV).

Materials. Tetrahydrofuran (thf) and hexane were distilled from potassium and toluene was distilled from sodium metal under Ar. Petroleum ether (40/60) was distilled from P_4O_{10} and CH_2Cl_2 from CaH_2 under an argon atmosphere.

$[CpMo(CO)_3Cl]$, **1**,[9] and **PP**[7, 8] were prepared by published procedures. In the synthesis of **PP** the following modifications were applied: In the preparation of 1-chloro-2-(1-propenyl)benzene the reaction mixture was stirred additionally overnight, and in the subsequent steps all refluxation times were doubled. Hydrolysis was performed with 10% hydrochloric acid, and purification was performed by means of adsorption chromatography after removal of all thf.

Carbonylchlorocyclopentadienyl(2-*trans*-(1-propenyl)phenyldiphenylphosphinomolybdenum(II) (2^t). A 0.62 g (2.05 mmol) sample of **PP** (mixture of isomers) and 0.80 g (2.86 mmol) of **1** are dissolved in 150 mL of toluene, and the solution is photolyzed at −20 °C in a light stream of argon for 3 h. The toluene is removed from the resulting deep red solution, and the solid products are separated by adsorption chromatography (silica; column size 3 × 10 cm). Unreacted **PP** is eluated with 75 mL of petroleum ether (40/60). A yellow band of impurity is removed with 75 mL of a petroleum ether (40/60)/CH_2Cl_2 mixture (2:1). A yellow band containing **3** and a red band containing the main product $\mathbf{2^t}$ in pure form are eluated with 160 mL of a CH_2Cl_2/diethyl ether mixture (24:1). Removal of the volatiles from the red fraction gives 1.03 g (1.96 mmol, 95% yield) of analytically pure $\mathbf{2^t}$. Crystals can be obtained by overlaying a CH_2Cl_2 solution with petroleum ether (40/60). ^{1}H NMR data: see Table 2. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 236.34 (d, $^2J_{P-C} = 13.58$ Hz, 1C, CO), other ^{13}C NMR data see Table 2. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 69.00 (s). IR/KBr [cm^{-1}]: 3075(w), 2849(w), 1911(s), 1437(m), 517(m), 489(m). MS (EI): *m/e* 528 [M^+, 2], 493 [M^+ − Cl, 60], 463 [M^+ − Cp, 71], 302 [$\mathbf{PP}^+$, 99], 287 [$\mathbf{PP}^+$ − Me, 100], 229 [M^+ − **PP**, 4]. Anal. Calcd for $C_{27}H_{24}ClMoOP$: C, 61.55; H, 4.59; Cl, 6.73. Found: C, 60.72; H, 4.95; Cl, 6.87. The analysis fits almost exactly if 0.1 molecule of CH_2Cl_2 per molecule of **2** is considered to be present in the bulk (calcd then: C, 61.05; H, 4.75; Cl, 7.32), as detected NMR spectroscopically; the inclusion of CH_2Cl_2 within crystals of $\mathbf{2^t}$ was also shown by means of X-ray diffraction.

Carbonylchlorocyclopentadienyl(2-*cis*-(1-propenyl)phenyldiphenylphosphinomolybdenum(II) (2^c). A 0.86 g (2.86 mmol) sample of **PP** (mixture of isomers) and 0.06 g (0.23 mmol) of **1** are dissolved in 100 mL of toluene, and the solution is photolyzed at −20 °C in a light stream of argon for 1 h. Another 0.50 g (1.78 mmol) of **1** are dissolved in toluene and added to the reaction mixture, which is subsequently photolyzed for another 3 h. The toluene is removed from the resulting deep red solution, and the solid products are separated by adsorption chromatography (silica; column size 3 × 10 cm). Unreacted **PP** is eluated with 25 mL of petroleum ether (40/60). A yellow band of impurity is removed with 25 mL of a petroleum ether (40/60)/CH_2Cl_2 mixture (2:1). A yellow band containing mainly **3** (but also $\mathbf{2^c}$ and $\mathbf{2^t}$) as well as a red band containing the main product **2** as a mixture of the isomers $\mathbf{2^c}$ and $\mathbf{2^t}$ (in the proportions 1:1.3) are eluated with 175 mL of a CH_2Cl_2/diethyl ether mixture (24:1). $\mathbf{2^c}$ has not been isolated in isomerically pure form in bulk and was thus characterized in its mixture with $\mathbf{2^t}$, whose spectroscopic properties were known (see above). However, overlaying a CH_2Cl_2 solution of this mixture with hexane at 2 °C yielded crystals of both isomers side by side, so that one of those corresponding to $\mathbf{2^c}$ could be subjected to an X-ray diffraction study. ^{1}H NMR and ^{13}C NMR data: see Table 2. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 70.43 (s).

(2-Allylphenyldiphenylphosphino)carbonylcyclopentadienylmolybdenum(II) (3). A 1.40 g (2.66 mmol) sample of $\mathbf{2^t}$ is dissolved in 50 mL of thf, and the solution is added dropwise to a suspension of 0.28 g (5.43 mmol) of $LiNMe_2$ in 25 mL of thf. The solution turns brown immediately. After 12 h of stirring the thf is removed under vacuum. The crude product is purified by means of adsorption chromatography (silica; column size 3 × 19 cm) with a petroleum ether (40/60)/CH_2Cl_2 mixture (3:2) as an eluent. **3** is isolated in 31% yield (0.40 g, 0.82 mmol) as a yellow solid. Crystals can be obtained by overlaying a $CHCl_3$ solution with petroleum ether (40/60) at 4 °C. ^{1}H NMR and ^{13}C NMR data: see Table 4. $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ 83.92 (s). IR/KBr [cm^{-1}]: 3059(w), 2967(w), 2919(w), 1855(s), 1437(m), 541(m), 481(m). MS (EI): *m/e* 493 [M^+, 22], 462 [M^+ − CO, 100]. Anal. Calcd for $C_{27}H_{23}MoOP$: C, 66.13; H, 4.73; P, 6.32. Found: C, 64.47; H, 4.79; P, 6.18.

Table 7. Crystal Data and Structure Refinement Details for Compounds 2, 3, and 4

	2^t	2^c	3	4
empirical formula	$C_{28}H_{26}Cl_3MoOP$	$C_{29}H_{28}Cl_5MoOP$	$C_{27}H_{23}MoOP$	$C_{26}H_{23}PCl_2Mo$
fw	611.750	696.67	490.360	533.250
cryst color	red	red	yellow	orange
cryst dimens, mm	0.25 × 0.15 × 0.15	0.06 × 0.19 × 0.41	0.20 × 0.05 × 0.03	0.10 × 0.10 × 0.05
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
lattice type	primitive	primitive	primitive	primitive
lattice params				
a, Å	12.672(3)	15.9258(5)	15.173(3)	7.7360(15)
b, Å	6.392(3)	11.1976(3)	15.674(3)	15.106(3)
c, Å	12.885(3)	16.9224(4)	18.031(4)	18.726(4)
β, deg	106.81(3)	102.218(2)	100.34(3)	94.05(3)
V, Å^3	2562.2(9)	2949.43(14)	4218.6(14)	2182.8(7)
space group	$P2(1)/n$	$P2(1)/c$	$P2(1)/c$	$P2(1)/n$
Z	4	4	8	4
D_{calcd}, Mg/cm^3	1.586	1.569	1.544	1.623
F_{000}	1240	1408	2000	1080
temp, K	200	173(2)	200	200
μ(Mo Kα), mm^{-1}	0.908	0.974	0.714	0.931
diffractometer	Nonius Kappa CCD			
radiation	Mo Kα, graphite monochromated (λ = 0.71073 Å)			
detector position	34 mm			
scan type	ω(1°/frame)			
$2\theta_{max}$, deg	52.1	56.6	52.0	55.3
no. of rflns measd				
total	39 785	23 070	58 616	19 902
unique	5060	7179	8306	5021
R_{int}	0.0791	0.036	0.1944	0.0773
corrns	Lorentz−polarization factor			
structure soln	direct-method (SHELXS-97; SHELXL-97)			
refinement	full-matrix least-squares			
no. of observns ($I > 2\sigma(I)$)	3775	5503	4777	3695
no. of variables	319	366	483	363
rfln/param ratio	11.83	15.04	9.89	10.18
residuals				
R	0.0319	0.0477	0.0663	0.0392
R_w	0.0602	0.1189	0.1230	0.0756
R(all)	0.0547	0.0678	0.1404	0.0656
goodness of fit	0.993	1.036	1.033	1.031
final diff map				
max peak, e/Å^3	0.403	1.051	0.905	0.424
min peak, e/Å^3	−0.479	−0.928	−0.872	−0.603

The analysis fits almost exactly if 0.2 molecule of CH_2Cl_2 per molecule of **3** is considered to be present in the bulk (calcd then: C, 64.39; H, 4.65; P, 6.10), as detected NMR spectroscopically.

(2-Allylphenyldiphenylphosphino)dichlorocyclopentadienylmolybdenum(IV) (4). A 0.53 g (1.08 mmol) sample of **3** is transferred into a glass tube equipped with a greaseless high-pressure valve, and 15 mL of CH_2Cl_2 is added. The solution is frozen to −196 °C, the reaction vessel evacuated, and 6.28 mmol of N_2O (measured out manometrically on a high-vacuum line) co-condensed. After annealing the solution is vigorously stirred and photolyzed at room temperature with broad band UV/vis radiation. After a short period of time the color of the solution changes from yellow to red. The course of the reaction can be controlled by means of ^{31}P NMR measurements: the photolysis is stopped when the signal of **3** cannot be detected anymore, typically after 24 h. The dark brown solution is then transferred into a Schlenk tube via cannula, and the solvent is removed in a vacuum. The crude product (ca. 0.32 g (0.6 mmol), 55% yield) is purified by means of adsorption chromatography (silica; column size 3 × 8.5 cm): with 125 mL of a diethyl ether/CH_2Cl_2 mixture (1:24) as an eluent impurities such as **PPO** are removed. An orange band is eluted with 100 mL of acetone. After removal of all volatiles from this fraction the residue is extracted with CH_2Cl_2 and overlayed with hexane. After 5 days at room temperature red crystals of **4** are obtained in 13% isolated yield. ^{1}H NMR and ^{13}C NMR data: see Table 4. ^{31}P{^{1}H} NMR (CD_2Cl_2): δ 59.53 (s). IR/KBr [cm^{-1}]: 2964(m), 2901(w), 1262(s), 1097(vs), 1025(vs), 861(m), 802(vs), 703(w), 474(m). MS (EI): m/e 534 [M$^+$, 2], 499 [M$^+$ − Cl, 65], 459 [M$^+$ − Cl − CH_2═CHCH, 20], 383 [M$^+$ − Cl − CH_2═CHCHC_6H_4, 22], 301 [**PP**$^+$ − H, 20]. Anal. Calcd for $C_{26}H_{23}Cl_2MoP$: C, 58.56; H, 4.35. Found: C, 57.62; H, 4.21. The analysis fits almost exactly if 0.1 molecule of CH_2Cl_2 per molecule of **4** is considered to be present in the bulk (calcd then: C, 57.86; H, 4.31).

Crystal Structure Determinations. Single crystals were grown as described in the Experimental Section. Centered reflections were refined by least-squares calculations to indicate the unit cells. Unit cell and collection parameters for the complexes are listed in Table 7. Diffraction data were collected in the appropriate hemispheres and under the conditions specified also in Table 7. The structures were solved by direct methods and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms belonging to the olefin and allyl donor functions were found and refined isotropically for **2** and **3**, while all other hydrogen atoms were included in the calculated idealized positions and refined isotropically. In the case of **4** all hydrogen atoms were found and refined. In the crystal of complex $\mathbf{2^c}$ there are additionally two noncoordinated molecules of CH_2Cl_2 (one of which is disordered) per molecule of $\mathbf{2^c}$ in the unit cell, while there is one of such in the unit cell of $\mathbf{2^t}$. Two independent molecules of **3** were found in the unit cell, one of which is presented in Figure 3.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft for a scholarship (C.L. (Heisenberg)) and funding as well as the Fonds der Chemischen Industrie for funding.

Supporting Information Available: Listings of X-ray structural data for all complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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