# Structure and Metal Coordination of the Diphosphine 2,2'-Bis((diphenylphosphino)methyl)-1,1'-binaphthyl (NAPHOS)

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The crystal structure of the diphosphine 2,2'-bis((diphenylphosphino)methyl)-1,1'-binaphthyl (1, NAPHOS) has been determined by means of an X-ray diffraction study. The compound crystallizes in the triclinic space group  $P\overline{1}$  with a = 10.568(1) Å, b = 10.737(1) Å, c = 15.986(1) Å,  $\alpha = 81.63(1)^{\circ}$ ,  $\beta = 86.42(1)^{\circ}$ ,  $\gamma = 81.47(1)^{\circ}$ , V = 1773 Å<sup>3</sup>, and Z = 2. The metal complex  $Mo(CO)_4(NAPHOS)$  (4) crystallizes in the space group  $P2_1/c$  with a = 11.064-(3) Å, b = 15.931(2) Å, c = 28.462(8) Å,  $\beta = 100.67(1)^\circ$ , V = 4930 Å<sup>3</sup>, and Z = 4. Molecular mechanics (MM) calculations for both Mo(CO)<sub>4</sub>(NAPHOS) (4) and Mo(CO)<sub>4</sub>(BISBI) (5) show an excellent match with the experimentally determined structures. A molecular dynamics (MD) simulation is demonstrated to be an efficient tool to sample over the accessible conformational space in order to cope with the "global minimum problem". The dynamic behavior of these compounds in solution is also explainable on this basis.

#### Introduction

Tertiary phosphines represent the major class of ligands used in homogeneous catalysis to stabilize metal centers in low formal oxidation states. Chelating ligands such as diphosphines often show improved activities and selectivities for a given catalytic reaction.<sup>1</sup> Recent developments in the field of hydroformylation clearly show that the activity of rhodium catalysts is improved by orders of magnitude upon replacement of multidentate for monodentate phosphines as ligands.<sup>2</sup> Moreover, the selectivity for linear aldehydes is improved by enlargement of the ligand's "bite angle".<sup>3</sup> In our ongoing work on water-soluble catalysts<sup>4</sup> and hydroformylation<sup>5</sup> we became interested in diphosphines with large bite angles, with NAPHOS (1) and BISBI (2) being typical examples. They both exhibit high activity and n/iso selectivity in the rhodium-catalyzed hydroformylation,<sup>3</sup> especially as sulfonated derivatives in two-phase processes.6

As an experimental basis of further investigations in this field we present in this paper the crystal structures



of the free and metal-coordinated ligand NAPHOS. Mo- $(CO)_4(NAPHOS)$  (4) is the first structurally characterized complex of NAPHOS and can be compared with several similar complexes of diphosphine ligands. Thus, it serves as a model to study the coordination behavior of NAPHOS.

In order to predict the coordination chemistry and the behavior of phosphines in catalytic systems, it is necessary to quantify their steric requirements, their conformational flexibility, and their electronic properties. These correlations are based mainly on experimental results such as the so-called "cone angle" and "electronic factor", as defined by Tolman for monodentate phosphines.<sup>7</sup> Recently, the determination of steric requirements of phosphines was extended by means of MM calculations,<sup>8</sup> since their structure cannot be considered to be rigid. This approach accounts for deformations upon coordination and dynamic effects in a quantitative way. For diphosphines Casey et al. introduced the socalled "natural bite angle", which is also determined by MM calculations;<sup>9</sup> it gives an estimate of the bidentate ligands' steric requirements.

The consideration of the coordination mode of ligands alone describes the behavior in catalysis only insuf-

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ficiently. For example, the correlation of the natural bite angle of ligands  $R_2P-X-PR_2$  with the n/iso selectivity in the (Rh<sup>I</sup>-catalyzed) hydroformylation of 1-hexene is limited to diphosphines with equal substituents R at phosphorus. More reliable strategies to estimate the selectivity of a given ligand in a catalytic cycle should include ligand-ligand interactions in the transition state(s). Since the structures of the latter are not known with certainty, reasonable model structures must be used. This approach has been successful, for example, in modeling the isospecific polymerization of propylene by means of substituted ansa-metallocenes.<sup>10</sup>

Recent methodical developments in the area of molecular mechanics calculations have established that this empirical approach can be elaborated to treat transition-metal complexes. Landis et al. introduced a scheme to describe  $\pi$ -bonding<sup>11</sup> and extended the analytical expressions of angular potential energy terms according to angular overlap considerations.<sup>12</sup> The problem of parametrization has been tackled by Rappé et al. in an elegant way: parameters are generated by rules based on atomic values.<sup>13</sup> Nevertheless, "conventional" calculations can also give reasonable insight into the coordination behavior of (organic) ligands.<sup>14</sup>

In this context, empirical force field calculations are demonstrated to be able to predict conformational changes induced upon coordination of diphosphine ligands. This validates the method on experimental results as a useful tool in catalysis-related applications.

#### **Results and Discussion**

A. Crystal Structure of the Diphosphine NA-PHOS. NAPHOS (1) was first described in 1977 by Kumada et al.<sup>15</sup> Single crystals were grown from a CH<sub>2</sub>-Cl<sub>2</sub>/*n*-hexane solution (1/3 v/v). The compound crystallizes in the triclinic space group  $P\overline{1}$  with a = 10.568(1)Å, b = 10.737(1) Å, c = 15.986(1) Å,  $\alpha = 81.63(1)^{\circ}$ ,  $\beta =$ 86.42(1)°,  $\gamma = 81.47(1)^{\circ}$ , V = 1773 Å<sup>3</sup>, and Z = 2. Figure 1 shows a PLATON plot of NAPHOS (1). The coordination geometry of phosphorus is as expected for sp<sup>3</sup> hybridization including an electron lone pair, with the sum of bond angles C-P-C amounting to 301.6° and 304.9°. The bond distances are in the normal range of P-C(aliphatic) and P-C(aromatic) single bonds (Table 1). Although the interplanar angle of the binaphthyl structure is almost the same as in one of the two

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**Figure 1.** PLATON view of NAPHOS (1) with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table 1.	Selected Bond Lengths (Å) and Angles (deg) fo	r
	NAPHOS (1)	

the second se		
1.859(1)	P2-C6	1.868(1)
1.820(2)	P2-C30	1.821(1)
1.824(2)	P2-C40	1.844(1)
97.89(7)	C6-P2-C30	103.41(7)
102.96(7)	C6-P2-C40	99.94(7)
100.78(8)	C30-P2-C40	101.51(7)
	1.859(1) 1.820(2) 1.824(2) 97.89(7) 102.96(7) 100.78(8)	1.859(1)         P2-C6           1.820(2)         P2-C30           1.824(2)         P2-C40           97.89(7)         C6-P2-C30           102.96(7)         C6-P2-C40           100.78(8)         C30-P2-C40

Scheme 1. Preparation of Mo(CO)<sub>4</sub>(NAPHOS) (4) and Mo(CO)<sub>4</sub>(BISBI) (5) from the Norbornadiene Complex 3



crystallographically observed structures of BISBI (2) (76.8 vs 77.0°) the (nonbonding) distance of the two P atoms is somewhat longer than in 2 (7.01 vs 6.86 Å).<sup>16</sup> This result is due to the conformationally flexible Ar-CH<sub>2</sub>-P chain (Ar = aryl). In the solid state the two phosphine fragments of 1 adopt different rotational conformations. The lone pair of atom P2 is almost *parallel* to the  $C_2$  axis of the binaphthyl moiety, whereas that of P1 is *perpendicular* to this axis, pointing away from the molecule.

**B.** Synthesis and Crystal Structure of  $Mo(CO)_4$ -(NAPHOS). If NAPHOS is treated with the norbornadiene complex 3 (as a traditional source of  $Mo(CO)_4$ fragments) in refluxing toluene, the complex  $Mo(CO)_4$ -(NAPHOS) (4) forms as a yellow, air-stable solid (61% yield) according to Scheme 1.

Single crystals of 4 were grown from an NMR sample  $(CDCl_3)$  at room temperature. Figure 2 shows a PLA-TON plot, and Table 2 gives selected bond lengths and angles. The Mo atom is the center of an octahedral coordination sphere with a *cis* arrangement of the phosphorus atoms. The P-Mo-P bite angle in 4 amounts to  $100.0(1)^\circ$ ; the P-Mo bond lengths average 2.559 Å. The corresponding values for Mo(CO)<sub>4</sub>(BISBI) (5) are  $103.54(2)^\circ$  and 2.566 Å, respectively. The leastsquares planes of the two naphthyl systems C50-C59 and C60-C69 are tilted toward each other by 94.3° (obtuse angle), whereas the corresponding interplanar

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Figure 2. PLATON view of Mo(CO)<sub>4</sub>(NAPHOS) (4) with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Ma(CO) (NAPHOS) (4)

	110(00)4(11)		
P1-C5	1.883(7)	Mo-Pl	2.570(2)
P1-C10	1.820(7)	Mo-P2	2.547(2)
P1-C20	1.827(7)	Mo-C1	1.976(8)
P2-C6	1.844(7)	Mo-C2	1.986(8)
P2-C30	1.830(7)	Mo-C3	2.037(7)
P2-C40	1.855(7)	Mo-C4	2.035(8)
C5-P1-C10	99.2(3)	P1-Mo-P2	100.0(1)
C5-P1-C20	99.7(3)	C3-Mo-C4	171.4(3)
C10-P1-C20	103.5(3)	P1-Mo-C1	172.2(2)
C6-P2-C30	102.4(3)	P1-Mo-C2	89.5(2)
C6-P2-C40	100.0(3)	P1-Mo-C3	88.1(2)
C30-P2-C40	101.6(3)	P1-Mo-C4	89.7(2)
		P2-Mo-C2	170.5(2)
Mo-P1-C5	126.2(2)	P2-Mo-C1	86.2(2)
Mo-PI-C10	118.8(2)	P2-Mo-C3	94.5(2)
Mo-P1-C20	106.1(2)	P2-Mo-C4	94.0(2)
Mo-P2-C6	121.9(2)	C1-Mo-C2	84.3(3)
Mo-P2-C30	112.3(3)	C1-Mo-C3	96.2(3)
Mo-P2-C40	115.9(2)	C1-Mo-C4	85.0(3)
		C2-Mo-C3	86.4(3)
		C2-Mo-C4	85.2(2)

angle of the biphenyl system of 5 is 117.7°. The average metal-carbon distance (1.981 Å) of the carbonyl groups trans to phosphorus (C1 and C2) shows the expected shortening as compared with the (average) metalcarbon bond length of 2.036 Å for the apical positions C3 and C4. The average phosphorus-phenyl carbon distance of 1.833 Å and the average C-P-C angle of 102.6° show no significant difference from the values for NAPHOS (1) at 1.827 Å and 101.1°, respectively. This is in full accord with the result of a systematic structure analysis of triphenylphosphine fragments by Orpen et al., which confirmed that there is no structural deformation upon coordination on low-valent metals.<sup>17</sup> This allows the utilization of parameters derived for free phosphines in empirical force field calculations on metal-coordinated phosphines.

The asymmetric unit of 4 contains two additional disordered molecules of CDCl<sub>3</sub>. The occupation factor of one molecule with a disordered carbon atom is 1.0, the other  $CDCl_3$  position is 76% occupied. Due to packing effects in the solid state and the presence of solvent molecules, a detailed comparison of 4 and 5 concerning the conformation of the phenyl rings is not possible.

The molecular symmetry of **4** in the solid state is  $C_1$ . The two inequivalent phosphorus atoms should therefore give rise to two separate signals in the  ${}^{31}P{}^{1}H$ NMR spectra. However, only a singlet is observed, even at temperatures as low as -80 °C. The solid-state <sup>31</sup>P CP/MAS NMR spectrum shows two signals with a line separation of 2.67 ppm, being in full accord with the  $C_1$ symmetry seen in the crystal structure.

At room temperature the <sup>1</sup>H NMR shows the expected coupling of the diastereotopic methylene protons. This double doublet is further complicated by coupling to the phosphorus nuclei: because of the different magnitudes of the  ${}^{2}J(PH)$  coupling constants, only one doublet is split up into a tripletlike pattern. The  ${}^{13}C{}^{1}H$  NMR spectrum exhibits one broad signal for the methylene carbons and one multiplet each (due to coupling with phosphorus) for the trans and for the cis carbonyls. The rather complex aromatic regions of the  ${}^{1}H$  and  ${}^{13}C{}^{1}H$ NMR spectra have been elucidated by 2D <sup>1</sup>H-<sup>13</sup>C correlated NMR experiments with inverse detection (<sup>1</sup>H-<sup>13</sup>C HMBC<sup>18</sup> and <sup>1</sup>H-<sup>13</sup>C HMQC<sup>19</sup>). All carbon and hydrogen resonances of the naphthyl systems could thus be assigned unambiguously under the assumption of  $C_2$ symmetry. The remaining <sup>1</sup>H-<sup>13</sup>C cross-peaks in the HMBC spectrum are the six expected couplings in the two diastereotopic but freely rotating phenyl systems. <sup>1</sup>H and <sup>13</sup>C NMR spectra hence support  $C_2$  symmetry for the molecule under the given conditions of observation.

There are two possible explanations for this phenomenon: (i) the diphosphine ligand changes the coordination mode in solution or (ii) a dynamic process faster than the NMR time scale equilibrates inequivalent positions. For the latter possibility, the signals in the <sup>31</sup>P{<sup>1</sup>H} NMR should split at sufficiently low temperatures; this is not seen, however, down to -80 °C.

C. Molecular Mechanics Calculations on Mo-(CO)<sub>4</sub>(NAPHOS) and Mo(CO)<sub>4</sub>(BISBI). The commercially available force field cff91 of BIOSYM<sup>20</sup> utilizes a potential energy expression similar to that of MM2.<sup>21</sup> A set of "cross-terms" is parametrized for pure hydrocarbon interactions:

$$E = \sum E_{\text{bond}} + \sum E_{\text{angle}} + \sum E_{\text{torsion}} + \sum E_{\text{out of plane}} + \sum E_{\text{nonbonded}} + \sum E_{\text{electrostatic}} + (\sum E_{\text{cross}})$$
$$E_{\text{bond}} = k_2(r - r_0)^2 + k_3(r - r_0)^3 + k_4(r - r_0)^4$$
$$E_{\text{angle}} = h_2(\varphi - \varphi_0)^2 + h_3(\varphi - \varphi_0)^3 + h_4(\varphi - \varphi_0)^4$$

$$\begin{split} E_{\text{torsion}} &= V_1 \{ 1 + \cos[\phi - \phi_0] \} + \\ & V_2 \{ 1 + \cos[2(\phi - \phi_0)] \} + V_3 \{ 1 + \cos[3(\phi - \phi_0)] \} \end{split}$$

$$E_{\text{out of plane}} = k_{\chi} (\chi - \chi_0)^2$$
$$E_{\text{nonbonded}} = \epsilon_{ij} \left[ 2 \left( \frac{r_{\text{vdW},ij}}{r} \right)^9 - 3 \left( \frac{r_{\text{vdW},ij}}{r} \right)^6 \right]$$

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$$\begin{aligned} r_{\mathrm{vdW},ij} &= \sqrt[6]{\frac{r_{\mathrm{vdW},i}^{\ \ 6} + r_{\mathrm{vdW},j}^{\ \ 6}}{2}} \\ \epsilon_{ij} &= 2 \sqrt{\epsilon_i \epsilon_j} \bigg[ \frac{(r_{\mathrm{vdW},i})^3 (r_{\mathrm{vdW},j})^3}{r_{\mathrm{vdW},i}^{\ \ 6} + r_{\mathrm{vdW},j}^{\ \ 6}} \bigg] \\ E_{\mathrm{electrostatic}} &= \frac{1}{4\pi\epsilon} \frac{q_1 q_2}{r} \end{aligned}$$

We extended the force field by a set of parameters for phosphines adapted from the values published for MM2<sup>22</sup> to reproduce structure and vibrational frequencies of model compounds (aryl and alkyl phosphines) in the given framework of cff91. These parameters are given in Table 5.23

Because of the conventional force field used in this study with its lack of metal-ligand interaction parameters and the inability to treat octahedral coordination,<sup>12a</sup> we introduced some simplifications in our model of complexes 4 and 5. On the other hand, we incorporated only parameters already known from a general analysis of the given class of compounds and did not use any specific data from the crystal structure analysis of 4 and 5.

(1) The carbonyl ligands were placed in octahedral positions with bond lengths typical for such complexes  $(M_0-C, 2.00 \text{ Å}; C-O, 1.14 \text{ Å}^{24}).$ 

(2) The resulting  $Mo(CO)_4$  fragment was kept invariable in all calculations.

(3) The phosphine-to-molybdenum interactions were described as follows: (i) the Mo-P distance was restrained to 2.55 Å, which quantity results from the X-ray structure analysis; (ii) the phosphorus atoms were forced into a tetrahedral geometry to ensure that the lone pairs point toward the metal atom. No P-Mo-P or  $P-Mo-C_{CO}$  bending interactions hold the phosphine fragments in octahedral sites with respect to the carbonyls. Therefore, the description is reminiscent of the "point on a sphere model" often referred to in coordination chemistry. In this model only nonbonding interactions determine the details of coordination geometry around the metal atom.<sup>25</sup>

(4) Electrostatic interactions were excluded in all calculations.

Since the *nine*-membered rings in the structures of **4** and 5 should allow for a plethora of conformations, we used a simple "simulated annealing" sequence known from structure determinations of biopolymers.<sup>26</sup> For both compounds a molecular dynamics (MD) simulation at high temperature (1000 K) for 170 picoseconds (ps) was performed.<sup>27</sup> Every 1 ps a structure was retained which gave a set of perturbed structures out of the accessible conformational space. A subsequent energy minimization resulted in six different conformers in the range of 5 kcal/mol above the global minimum. Figure 3 shows the minimized steric energy vs the duration of

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the MD simulation. The conformation of the ninemembered-ring structure can be described by a total of seven dihedral angles defined by the ring bonds, because two dihedral angles of the binaphthyl moiety vary only slightly around 0°.

A comparison of all calculated conformers shows that some of them adopt the same ring conformation but differ in the orientation of the phenyl rings. Three different types of ring conformations were found for both 4 and 5. The lowest energy conformers of these are a, b, and e for 4 and a, b, and d for 5 (see Figure 4).

Tables 3 and 4 show the dihedral angles of the conformers of 4 and 5. The axial chirality of the biaryl structure excludes a mirror plane. For conformers e of **4** and **d** of **5** the  $C_2$  axis of the ligand is equivalent with the  $C_2$  axis of the metal fragment. These conformers show an overall  $C_2$  symmetry, whereas all others lack any symmetry elements  $(C_1)$ . The  $C_2$ -symmetrical coordination with respect to the P-M-P moiety is also found in the crystal structure of  $Fe(CO)_3(BISBI)$  where the ligand occupies two trans-spanning basal positions in a square pyramid with the very large P-Fe-P angle of 152.0°.9b The tendency of large bite angles in the  $C_2$ symmetric coordination-and vice versa-is also manifested in the systematically large P-M-P angles for these conformers of 4 and 5. These findings support the view that the flexibility introduced by the methylene groups between the phosphine and the biaryl fragments is the source of the ligands' ability to adopt to a wide range of bite angles.

Conformers **a** and **b** are different by rotation of one phosphine fragment around the Mo-P2 bond axis (Figure 5).

Superposition of the X-ray structure with the global minimum structure a shows that both belong to the same type of ring conformation (Figure 6). Especially for compound 5, the experimental and the calculated structures are virtually identical, even with regard to the rotational conformation of the phenyl rings. In the case of the crystal structure, the geometric perturbations by the solvent molecules are to be taken into consideration. The calculated minimum energy structures **a** show the same deviation with respect to the crystal structures: the biaryl moiety is slightly tilted, together with a rotation of the Mo-P1 bond (difference in C5-P1-Mo-P2: 15.7° in **4** and 7.6° in **5**). Obviously there is a steric repulsion between one of the aromatic systems of the biaryl fragment and the axial carbonyl ligand, the latter being severely distorted off the octahedral position in the experimental structure. These differences between experimental and calculated structures thus could be due to the fixation of the carbonyl ligands in the molecular mechanics model.

Since the calculated structure (gas-phase conditions) and the crystal structure (solid state) are closely related, it seems reasonable to assume a  $C_1$  symmetry for both compounds in solution and a dynamic process that equilibrates the chemical environment of the two phosphorus atoms. Due to the rigidity of the biaryl moiety, the methylene carbon atoms remain fixed with a through-space distance of  $\sim 4.4$  A. This reduces the structure to a virtual five-membered ring in an envelope conformation as drawn in Figure 7. The phosphorus atoms are inequivalent as a result of axial (biaryl) chirality.  $P_A$  and  $P_B$  will change their environment by a flip of the molybdenum tetracarbonyl fragment (tip

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<sup>(27)</sup> Since we did not intend a physically meaningful simulation but a simple generation of various starting structures, an equilibration period was not included in the MD calculation.



#### Figure 3.

 Table 3. Relative Steric Energies and Structural Data for the Six Lowest Energy Conformers of Mo(CO)<sub>4</sub>(NAPHOS) (4) in Comparison with the Experimental Values (Crystal Structure)

	conformer						
	a	b	с	d	e	f	exptl
$\Delta E$ (kcal/mol)	0.00	1.32	3.86	3.87	4.02	4.12	
P1-Mo-P2 (deg)	105.0	106.6	106.5	105.5	113.4	102.3	100.0
C50-C51-C61-C60 (deg)	107.2	107.6	108.0	108.6	106.9	97.1	99.0
P2-Mo-P1-C5 (deg)	-66.1	-42.0	-40.7	-39.1	35.9	-57.7	-50.3
Mo-P1-C5-C50 (deg)	101.5	67.2	65.9	58.7	-8.5	104.9	81.2
P1-C5-C50-C51 (deg)	-101.0	-110.1	109.7	-105.0	-81.9	-112.0	-105.0
P1-Mo-P2-C6 (deg)	32.3	73.5	77.2	76.5	35.9	28.7	39.5
Mo-P2-C6-C60 (deg)	54.2	-10.0	-18.4	-12.3	-8.5	55.3	39.5
P2-C6-C60-C61 (deg)	-116.2	-83.5	-77.1	-81.4	-81.9	-120.6	-119.0

of the envelope) to the other side of the ring plane, as indicated by the arrow in Figure 7. This process occurred accidentally in the MD simulation of 4.

This mechanism is supported by the  $C_2$ -symmetric structure of the conformers **e** of **4** and **d** of **5**. They resemble a *twist* conformation of the virtual fivemembered ring. If the activation barrier between **a** and **e** for Mo(CO)<sub>4</sub>(NAPHOS) and **a** and **d** for Mo(CO)<sub>4</sub>-(BISBI) is small, this should be a facile process for both these compounds. It could also explain the equivalence of the two phosphorus atoms on the NMR time scale.

### Conclusion

Our study reveals that the diphosphine ligand NA-PHOS exhibits the same structural flexibility as BISBI. In spite of the higher steric demands of the binaphthyl fragment, NAPHOS is able to coordinate to metals with the relatively small P-M-P angle of only 100.0°. The structural similarities of the molybdenum complexes  $Mo(CO)_4(BISBI)$  and  $Mo(CO)_4(NAPHOS)$  lend support to this assessment. As a matter of fact, NAPHOS-type diphosphines have become outstanding ligands in rhodium-catalyzed CC-coupling reactions.<sup>6,28</sup>

The MM calculations reproduce the experimental structure in terms of a reasonable description of conformational changes induced upon coordination of the ligands, despite the simplified model used in this study. The necessity of a systematic screening of the conformational space to find the global minimum conformation is demonstrated. The high-temperature MD simulation

<sup>(28)</sup> Kohlpaintner, C. W. Ph.D. Thesis, Technische Universität München, München, Germany, 1992.



## Figure 4.

Table 4. Relative Steric Energies and Structural Data for the Six Lowest Energy Conformers of Mo(CO)<sub>4</sub>(BISBI) (5) in Comparison with the Experimental Values (Crystal Structure)

	conformer						
	a	b	с	d	e	f	exptl
$\Delta E$ (kcal/mol)	0.00	1.77	4.41	4.53	4.64	5.00	
P1-Mo-P2 (deg)	106.0	108.5	108.5	116.5	102.9	108.5	103.5
C50-C51-C61-C60 (deg)	110.9	114.0	114.3	114.7	96.6	122.8	117.8
P2-Mo-P1-C5 (deg)	-67.9	-43.1	-41.9	35.6	-57.5	-33.2	-60.3
Mo-P1-C5-C50 (deg)	100.7	66.2	64.6	-6.7	105.4	48.5	87.4
P1-C5-C50-C51 (deg)	-96.9	-104.6	-104.0	-77.9	111.2	-87.9	-93.0
P1-Mo-P2-C6 (deg)	32.5	73.8	77.6	35.6	26.8	74.2	37.0
Mo-P2-C6-C60 (deg)	53.9	-9.1	-17.1	-6.7	57.3	-12.7	44.4
P2-C6-C60-C61 (deg)	-113.0	-79.50	-73.9	-77.9	-119.7	-73.4	-106.2



has proven very efficient to give a sufficiently broad set of starting structures that cover all relevant conformations of ligands of a given size.

The force field predicts conformational changes of the diphosphine geometry resulting from steric interactions

with other ligands. Assuming a reasonable transitionstate model for a reaction step in the catalytic cycle, a complete description of the steric interactions seems possible in the future merely on the basis of theoretical calculations. Work in this field is in progress.

## **Experimental Part**

Computational Details. All molecular mechanics calculations were performed on a Silicon Graphics "Personal Iris" 4D25 with the INSIGHT/DISCOVER program of Biosym Technologies.<sup>29</sup> The "consistent forcefield 1991" cff91<sup>30</sup> was extended by a set of parameters that properly describe tertiary aryl- and alkylphosphines (see Table 5).

The Mo(CO)<sub>4</sub> fragment was fixed in an ideal octahedral geometry with a Mo-C distance of 2.00 Å and a C-O distance

<sup>(29)</sup> InsightII User Guide, Version 2.1; Biosym Technologies: San Diego, CA, 1992. (30) Discover User Guide, Version 2.8; Biosym Technologies: San

Diego, CA, 1992.



5

Figure 6.



Figure 7.

Table 5. cff91 Force Field Parameters for Phosphines<sup>a</sup>

bond	$r_0$ (Å)	$k_2$ (kcal/ (mol·Å <sup>2</sup> ))	k <sub>3</sub> (kcal/ (mol·Å <sup>3</sup> ))	k4 (kcal/ (mol•Å <sup>4</sup> ))
p-c	1.84	205	0	0
р—ср	1.82	205	0	0
······	$arphi_0$	$h_2$ (kcal/	h3 (kcal/	h4 (kcal/
angle	(rad)	(mol·rad <sup>2</sup> ))	(mol•rad <sup>3</sup> ))	(mol•rad <sup>4</sup> ))
cp-p-cp	92.2	39.0	0	0
c-p-c	96.0	45.0	0	0
c-p-cp	92.5	41.0	0	0
p-cp-cp	120.0	27.4	0	0
p-c-cp	110.5	46.6	0	0
p-c-h	111.0	40.0	0	0
	$\phi_0$	$V_2$	$V_3$	$V_4$
torsion angle	(deg)	(kcal/mol)	(kcal/mol)	(kcal/mol)
c-p-cp-cp	0	0.000	0.000	0.200
cp-p-cp-cr	0 0	0.000	0.000	0.170
cp-p-c-h	0	0.025	0.000	0.100
cp-p-c-cp	0	-0.025	0.050	0.150
cp-cp-cp-	0 0	0.000	4.400	0.000
h-cp-cp-p	0	0.000	1.560	0.000
cp-cp-c-p	0	0.122	0.051	-0.223
			k	(kcal/
out of plane		χ <sub>0</sub> (deg)	(n	nol-rad <sup>2</sup> ))
cp-cp-cp-p		0		8.0
nonbond		$r_{\rm vdW}$ (Å)	ε (k	cal/mol)
р		4.2		0.15

<sup>&</sup>quot; The atom types are defined as follows: p, general phosphorus atom; c, sp<sup>3</sup> carbon atom; cp, sp<sup>2</sup> aromatic carbon (six-membered ring); h, hydrogen.

of 1.14 Å. The bond order between molybdenum and the carbonyl carbon atoms was set to zero. Thus, the van der Waals 1,3-interactions around the metal atom are included in the calculation as is done in MMX.<sup>31</sup> The Mo-P distances were constrained to 2.55 Å by a force constant of 1000 kcal/ (mol·Å<sup>2</sup>). The *cff91* atom types c' and o' were used for the carbonyl ligands that are used in the standard *cff91* to describe organic carbonyl functions. Because of the fixation of the carbon and oxygen atoms, only the nonbonding interactions



Table 6.	<b>Force Field</b>	Parameters f	for the	Metal-Phosphine
		Interaction	ı	-

M-P	$r_0 = 2.55 \text{ Å}, k = 1000 \text{ kcal/(mol·Å}^2)$
M-P-C	$\varphi_0 = 109.5^\circ, k = 70 \text{ kcal/(mol rad}^2)$
P-M-P-C	$k = 0 \text{ kcal/(mol \cdot rad^2)}$
M-P-C-C	$k = 0 \text{ kcal/(mol rad}^2)$
$M_{vdW}$	$r_{\rm vdW} = 0$ Å, $\epsilon = 0$ kcal/mol

were active in the calculation. All nonbonding interactions to the metal atom were set to zero. The metal-related parameters are summarized in Table 6.

The standard Verlet integration algorithm<sup>32</sup> of discover 2.8 with a time step of 1 fs was used in the molecular dynamics simulations. The temperature was held at 1000 K. Every 1 ps a structure was retained and minimized with a pseudo-Newton-Raphson minimizer (VA09A) until each degree of freedom had a derivative of less than 0.1 kcal/(mol·Å<sup>2</sup>). The resulting structures were partitioned in groups of equal steric energy and checked for their conformations. One representative was then minimized until each degree of freedom had a derivative of less than 0.001 kcal/(mol·Å<sup>2</sup>).

General Procedures. <sup>1</sup>H NMR spectra and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were measured on a JEOL JMN-GX 400 spectrometer (<sup>13</sup>C NMR, 100.5 MHz). The 2D <sup>1</sup>H-<sup>13</sup>C HMBC and 2D <sup>1</sup>H-<sup>13</sup>C HMQC of Mo(CO)<sub>4</sub>(NAPHOS) (4) were recorded on a Bruker AMX 500 spectrometer (<sup>13</sup>C NMR, 125.8 MHz). Hydrogen and carbon resonances of 4 were assigned by the 2D heteronuclear correlation experiments. Multiplicities and coupling constants are given only when it was possible to derive them from the 1D NMR spectra.

 $^{31}P\{^{1}H\}$  NMR spectra were measured at room temperature and at -80 °C on a JEOL JMN-GX 400 spectrometer (161.8 MHz) and referenced to external H<sub>3</sub>PO<sub>4</sub> (85%). The <sup>31</sup>P CP/ MAS NMR spectra were measured on a Bruker MSL 300 P spectrometer (121.5 MHz) with NH<sub>4</sub>[H<sub>2</sub>PO<sub>4</sub>] as an external standard which was also used to match the Hartmann-Hahn condition. Infrared spectra were obtained on a Nicolet 5-DX FT-IR spectrometer. Mass spectra were determined on a Finnigan MAT-90 instrument. Elemental analyses were performed in the Microanalytical Laboratories of our institute (M. Barth). Air-sensitive materials were manipulated under an inert-gas atmosphere using Schlenk techniques. Solvents were dried in the usual way.

**Synthesis and Spectroscopy.** The labeling scheme of NAPHOS shown in Chart 1 has been used.

(1) 2,2'-Bis((diphenylphosphino)methyl)-1,1'-binaphthyl (1) was synthesized according to ref 28; mp 148 °C. Spectroscopic data: <sup>1</sup>H NMR ( $d_6$ -acetone)  $\delta$  3.26 (dd, <sup>2</sup>J(HH) = 14.3 Hz, <sup>2</sup>J(PH) = 1.5 Hz,  $CH_aH_b$ , 2H), 3.36 (d, <sup>2</sup>J(HH) = 14.6 Hz,  $CH_aH_b$ , 2H), 7.01-7.40 (m, 28H); <sup>13</sup>C{<sup>1</sup>H} NMR ( $d_6$ acetone)  $\delta$  35.20 (d, <sup>1</sup>J(PC) = 18.3 Hz, C<sub>11</sub>), 126.24 (s, C<sub>8</sub>), 127.05 (s, C<sub>6</sub>), 127.23 (s, C<sub>7</sub>), 128.55 (s, C<sub>5</sub>), 128.80 (s, C<sub>4</sub>), 128.89-129.34 (m, C<sub>14,14</sub>',C<sub>15,15'</sub> [meta/para]), 129.63 (s, C<sub>3</sub>),

<sup>(31) (</sup>a) Mackie, S. C.; Baird, M. C. Organometallics 1992, 11, 3712.
(b) Polowin, J.; Mackie, S. C.; Baird, M. C. Organometallics 1992, 11, 3724.

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Chart 1. Labeling of the Ligand in the NMR Spectroscopic Results



133.35 (s, C<sub>9</sub>), 133.38 (d,  ${}^{2}J(PC) = 19.8$  Hz, C<sub>13</sub> [ortho]), 133.84 (d,  ${}^{2}J(PC) = 19.8$  Hz, C<sub>13</sub> [ortho]), 133.89 (s, C<sub>10</sub>), 135.67 (s, C<sub>1</sub>), 136.30 (d,  ${}^{2}J(PC) = 10.7$  Hz, C<sub>2</sub>), 139.60 (d,  ${}^{1}J(PC) = 17.3$  Hz, C<sub>12</sub> [ipso]), 139.69 (d,  ${}^{1}J(PC) = 17.3$  Hz, C<sub>12</sub> [ipso]), 139.69 (d,  ${}^{1}J(PC) = 17.3$  Hz, C<sub>12</sub> [ipso]);  ${}^{31}P{}^{1}H{}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  -14.03 (s); IR (KBr, cm<sup>-1</sup>)  $\nu$ (aryl-H) 2923 (st), 2853 (m), 743 (st), 696 (vs),  $\nu$ (C-H) 3070 (m), 1479 (w); MS (EI) *m/e* 651 ([MH]<sup>+</sup>), 466 ([MH - PPh<sub>2</sub>]<sup>+</sup>). Anal. Calcd for C<sub>46</sub>H<sub>36</sub>P<sub>2</sub>: C, 84.90; H, 5.58; P, 9.52. Found: C, 84.52; H, 5.54; P, 9.16.

(2) [2,2'-Bis((diphenylphosphino)methyl)-1,1'-binaphthyl]tetracarbonylmolybdenum (4). A 566 mg (0.87 mmol) amount of 1 in 20 mL of toluene was added dropwise at room temperature to a solution of (bicyclo[2.2.1]hepta-2,5-diene)tetracarbonylmolybdenum (3; 262 mg, 0.87 mmol) in 10 mL of toluene. The solution was then heated for 15 min to reflux and subsequently cooled to ambient temperature. After evaporation of the solvent in vacuo, the resulting solid was dissolved in a minimum amount of methylene chloride and then overlayered with 15 mL of *n*-hexane. Crystallization at -20 °C yielded 453 mg (0.53 mmol) of a yellow, crystalline powder (61% yield); mp 198 °C dec. Spectroscopic data: <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  3.64 (d, <sup>2</sup>J(HH) = 13 Hz, CH<sub>a</sub>H<sub>b</sub>), 3.80 ("tr",  $CH_aH_b$ ), 6.43 (d,  ${}^{3}J(HH) = 8.5 Hz$ , H<sub>3</sub>), 6.86 (d,  ${}^{3}J(HH) = 8.5$ Hz, H<sub>8</sub>), 7.20 (H<sub>7</sub>), 7.31 (H<sub>phenyl</sub>), 7.32 (H<sub>phenyl</sub>), 7.35 (H<sub>phenyl</sub>),  $7.37 (H_{phenyl}), 7.42 (H_6), 7.47 (H_{phenyl}), 7.51 (H_4), 7.56 (H_{phenyl}),$ 7.83 (d,  ${}^{3}J(HH) = 8.5$  Hz, H<sub>5</sub>);  ${}^{13}C{}^{1}H}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  39.55  $(bs, C_{11}), 125.7 (s, C_8), 126.1 (s, C_6), 126.9 (s, C_7), 127.8 (s, C_4),$ 128.3 (C<sub>3</sub>), 128.3 (C<sub>phenyl</sub>), 128.4 (C<sub>5</sub>), 128.5 (C<sub>phenyl</sub>), 129.0  $(C_{phenyl})$ , 130.7 (d, J(PC) = 5 Hz,  $C_{phenyl})$ , 130.8 (d, J(PC) = 5Hz,  $C_{phenyl}$ ), 132.9 (s,  $C_9$ ), 133.0 (s,  $C_{10}$ ), 133.5 (s,  $C_2$ ), 135.8 (s,  $C_1$ ), 135.9 (d, J(PC) = 6 Hz,  $C_{phenyl}$ ), 136.5 ("qua", N = 30.6Hz,  $C_{12/12'}$ , 208.4 (t,  ${}^{2}J(PC) = 9$  Hz, CO [trans]), 214.1 ("qui", N = 18.3 Hz, CO [cis]); <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  30.74 (s); <sup>31</sup>P-CP/MAS NMR  $\delta$  25.00, 27.67; IR (KBr, cm<sup>-1</sup>)  $\nu$ (CO) 2024 (st), 1913 (vst), 1875 (vst), v(aryl-H) 3060 (s), 740 (m), 694 (m),  $\nu$ (C-H) 3070 (m), 1479 (w); MS (EI) *m/e* 804 ([M - 2CO]<sup>++</sup>), 776 ( $[M - 3CO]^{+}$ ), 748 ( $[M - 4CO]^{+}$ ), 541 ( $[NAPHOS]^{+}$ ), 573  $([NAPHOS - Ph]^{+}), 465 ([NAPHOS - PPh_2]^{+}).$  Anal. Calcd for C<sub>50</sub>H<sub>36</sub>MoO<sub>4</sub>P<sub>2</sub>: C, 69.94; H, 4.23; Mo, 11.17; O, 7.45; P, 7.21. Found: C, 69.11; H, 4.26; Mo, 11.33; O, 8.31; P, 7.30.

X-ray Crystallography. Crystals of compounds 1 and 4 were grown by standard techniques at room temperature from a  $CH_2Cl_2/n$ -hexane mixture (1/3 v/v) and from a deuteriochloroform solution, respectively. Preliminary examination and data collection were carried out on an Enraf-Nonius CAD4 diffractometer with Cu K $\alpha$  radiation ( $\lambda = 151.18$  pm) for 1 and Mo K $\alpha$  radiation ( $\lambda = 71.07$  pm) for 4. Final cell constants were obtained by least-squares analysis of 25 automatically centered reflections (1, 79.8° <  $2\theta$  < 88.7°; 4, 30.1° <  $2\theta$  < 40.0°). Data were collected by a  $\omega/2\theta$  scan mode for 1 (h, -12)to +12; k, -12 to +12; l, -18 to 0) and with a  $\omega$  scan mode in the case of 4(h, -13 to +13; k, 0 to 18; l, 0 to 33). Orientation control reflections were monitored every 200th reflection, and the intensities of 3 reflections were checked every 3600 s for both crystals. Changes in intensities were not corrected. Crystal data and intensity collection parameters together with details of the refinements are summarized in Table 7.

Table 7. Crystallographic Data, Summary of DataCollection, and Refinement Parameters for NAPHOS (1) and<br/>Mo(CO)4(NAPHOS) (4)

	1	• 4
formula	C <sub>46</sub> H <sub>36</sub> P <sub>2</sub>	C <sub>50</sub> H <sub>36</sub> MoO <sub>4</sub> P <sub>2</sub> plus ca. 1.8 CDCl <sub>3</sub>
fw	650.75	858.72 (without solvent)
cryst syst	triclinic	monoclinic
space group	P1 (No. 2)	$P2_1/c$ (No. 14)
temp, K	293	223
a, Å	10.568(1)	11.064(3)
b, Å	10.737(1)	15.931(2)
с, Å	15.986(2)	28.462(8)
α, deg	81.63(1)	90
$\beta$ , deg	86.42(1)	100.67(1)
γ, deg	81.47(1)	90
Ζ	2	4
V, Å <sup>3</sup>	1773	4930
λ, Å	1.5418 (Cu Ka)	0.7107 (Mo Ka)
$d_{\rm calc},  {\rm g}  {\rm cm}^{-3}$	1.219	1.1577 (without $CDCl_3$ ) <sup>d</sup>
$\mu$ , cm <sup>-1</sup>	13.4	3.6 (without $CDCl_3$ ) <sup>d</sup>
R," %	6	7.1
<b>R</b> <sub>w</sub> , %	$4.8^{b}$	6.7 <sup>c</sup>

<sup>*a*</sup>  $R = \sum(||F_0| - |F_c||)/\sum|F_0|$ . <sup>*b*</sup>  $R_w = [\sum w(|F_0| - |F_c|)^2/\sum w|F_0|^2]^{1/2}$  with weighting scheme  $1/\sigma^2$ . <sup>*c*</sup> Weighting scheme according to ref 33 with five refined parameters: p(1) = 0.736, p(2) = -0.137, p(3) = 0.483, p(4) = -0.112, p(5) = 0.113. <sup>*d*</sup> Solvent molecules in the crystal structure; see text.

The structures were solved by direct methods<sup>34</sup> (1) and Patterson methods<sup>34</sup> (4) followed by subsequent difference Fourier techniques. Full-matrix least-squares refinements were carried out, minimizing  $\Sigma w(|F_o| - |F_c|)^2$ . Hydrogen atoms were included at their calculated positions ( $d_{C-H} = 96$  pm) and were not refined in both cases. Anomalous dispersion was considered. The refinement stopped at shift/error <0.001, and final difference Fourier maps showed no significant features. All calculations were performed on a MicroVax 3100 computer and a DEC Station 5000/25 using the program CRYSTALS<sup>35</sup> and the STRUX-IV<sup>36</sup> system, including the programs PLA-TON,<sup>37</sup> SDP,<sup>38</sup> and SHELXS-86.<sup>34</sup>

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**Supplementary Material Available:** For both 1 and 4, tables of atom positions, anisotropic displacement parameters, and bond distances and angles for all atoms (20 pages). Ordering information is given on any current masthead page.

#### OM940914S

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