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The Monophosphino Urea Derivative $PPh_2NMeC(O)NMeH$: A Hemilabile Ligand Switching between P,O- and P,N-Coordination

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Treatment of *N*,*N*′-dimethyl urea with $ClPPh_2$ and NEt_3 as auxiliary base in thf affords the title compound $PPh_2NMeC(O)NMeH$ (**1**) in high yield. The monophosphino urea derivative **1** constitutes the first isolated and fully characterized representative of this class with a NH functional group. Evidence for a solvent effect in the synthesis of **1** is given and the X-ray crystal structure determined. The reaction of **1** with $[Mo(CO)_4(NCMe)_2]$ and the hemilabile character of the ligand **1** in the obtained P,O-chelate complex *cis*-$[Mo(CO)_4(\eta^2\text{-}PPh_2NMeC(O)NMeH)]$ (**2**) are described. Furthermore, synthesis of the known bisphosphino urea derivative $CO(NMePPh_2)_2$ (**3**) starting from **1** is reported.

Recently, Woollins described the synthesis of **3** from *N*,*N*′-dimethyl urea and $ClPPh_2$ in CH_2Cl_2 in the presence of NEt_3 as auxiliary base.[1] He observed the transient occurrence of another phosphorus-containing species at the beginning of the reaction claimed to be **1**. As it is logical to assume that **3** is formed from *N*,*N*′-dimethyl urea via **1** as intermediate and we are interested in the synthesis of **1** for the investigation of P,O-chelate complexes of *N*-phosphino amides, we needed to study the reaction in more detail. In the literature only very few monophosphino urea derivatives can be found. They comprise the *N*-phosphino-*N*′-silyl urea[2] and thiourea[3] compounds developed by Schmutzler and $NHPPh_2C(S)NH_2$[4] isolated by Woollins in very moderate yield as well as some *N*-phosphino carboxylic acid amides[5] and related biuret derivatives.[6] We found that by performing the reaction in thf **1** is obtained in near quantitative yield as colorless crystals. Its $^{31}P\{^1H\}$ NMR signal at 45.81 ppm ($CDCl_3$) compares well with the transient compound observed by Woollins. Woollins et al. have postulated the existence of **1** as a reaction intermediate in the synthesis of an oxidized species, but no analytical data were given. The analytical data are in agreement with the proposed formula for **1**.[15] The IR spectrum (KBr tablet) displays the expected bands at 3372 cm^{-1} (vs) for the NH group and at 1650 cm^{-1} (vs) for the carbonyl group, respectively. As the choice of solvent seems to be crucial in the synthesis of **1** (in both CH_2Cl_2 and toluene only mixtures of **1** and **3** were obtained), the X-ray crystal structure of **1** was determined[16] (see Figure 1) in order to investigate the influence of hydrogen bonding so characteristic for *N*-phosphino amides[6,7] and carboxylic acid amides in general.[8] In the solid state the structure of **1** exhibits the NCN group and the phosphorus atom P1 in a crescent

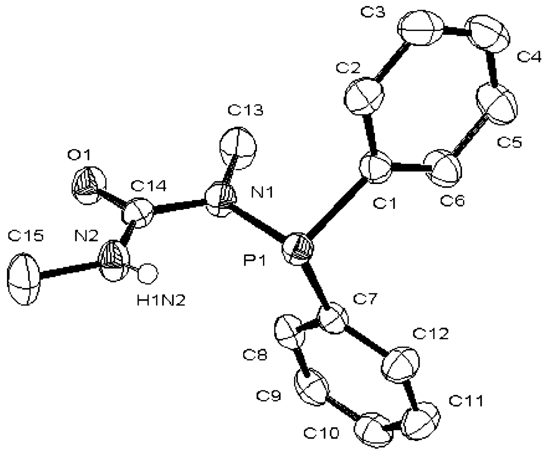

Figure 1. Crystal structure of **1**. Thermal ellipsoids are drawn at 50% probability. H atoms (except for H1n2) have been omitted.

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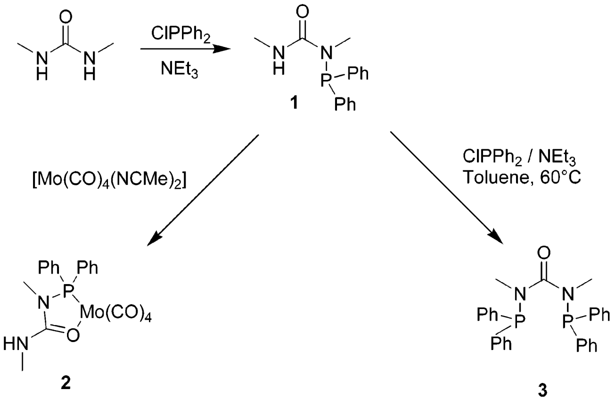
Scheme 1. Stepwise Formation of **1** and **3** and Use of **1** in the Synthesis of **2**

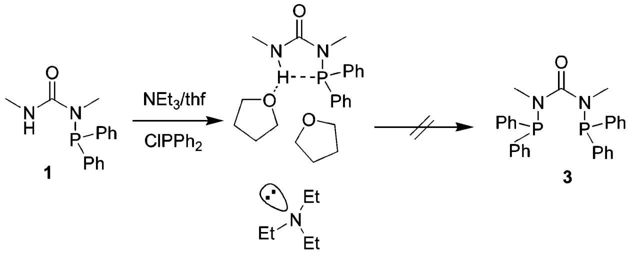


arrangement with the electron lone pair on phosphorus pointing toward the hydrogen atom on N2, suggesting a weak N−H- -P hydrogen bond (P1−H1n2 260.9 pm, N2−H1n2−P1 108.15°). The two nitrogen atoms are in a trigonal planar environment (total bond angles of 359.8° (N1) and 358.9° (N2), respectively), and all bond lengths can be considered to be normal for this type of compound (P1−N1 172.33(13), C14−O1 122.80(17), N1−C14 139.48(18), N2−C14 134.75(18), and N2−H1n2 81.8(2) pm). It is interesting to note that N2−C14 is almost 5 pm shorter than N1−C14, suggesting that the electron lone pair on N1 is to some extent used to strengthen the P−N bond. The exocyclic oxygen atom on C14 is involved in a weak N−H- -O hydrogen bond (O1−H1n2′ 234.3 pm, O1−H1n2′−N2′ 139.90°, sum of van der Waals radii 272 pm[9]) to the NH group of an adjacent molecule. Taking into account the difference in the van der Waals radii for oxygen and phosphorus, it can be concluded that the intermolecular N−H- -O hydrogen bond is of the same magnitude as the intramolecular N−H- -P hydrogen bond. Both are comparatively weak. In graph theory the pattern of these hydrogen bonds can be described as **C (4) [S (5)]**.[10]

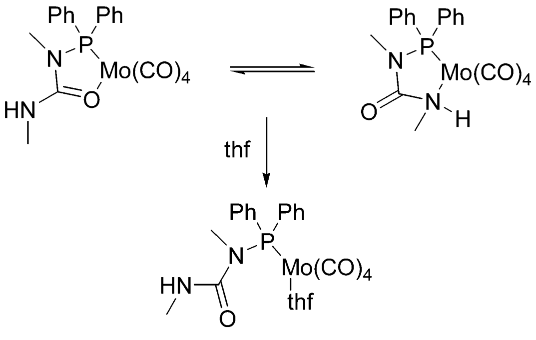
It seems reasonable to assume that these weak hydrogen bonds do not prevail in solution, rendering the NH group susceptible to attack from a chlorophosphine moiety. Breaking of the much stronger hydrogen bonds in *N*,*N′*-dimethyl urea then becomes the rate-determining step, resulting in a preference for **3** over **1**. If only 1 equiv of $ClPPh_2$ is used, this results in the observed mixture of **1** and **3**. However, if thf is used as solvent, **1** is formed exclusively even if the ratio of *N*,*N′*-dimethyl urea to $ClPPh_2$ is 1:2. The likely explanation is the formation of strong hydrogen bonds between the NH group of **1** and the oxygen atom of the solvent effectively protecting H1n2 from attack by the Lewis base NEt_3 and subsequently $ClPPh_2$ (Scheme 2).

Reaction of **1** with $[Mo(CO)_4(NCMe)_2]$ in thf results in the P,O-chelate complex **2**.[17] The P,O-chelate structure was assigned on the strength of the IR spectrum (KBr tablet)

Scheme 2. Protection of the NH Group in **1** from Proton Abstraction by thf



Scheme 3. Lability of P,O-Coordination Mode



displaying the characteristic *ν*(CO) pattern of the cis-Mo(CO)$_4$ unit and a *ν*(CO) band (1603 cm^{-1} compared to 1650 cm^{-1} for **1**) in agreement with a *N*-phosphino urea ligand bonded to a group 6 metal via its oxygen atom.[2,5b] The NH band appears at 3422 cm^{-1} (compared to 3372 cm^{-1} in **1**) in the solid state. In solution (CH_2Cl_2) another band appears at 3473 cm^{-1} for NH, indicating a different coordination behavior of the ligand toward the metal. In the CO region a second band at 1678 cm^{-1} appears besides that at 1605 cm^{-1}, supporting the changes in the NH region of the IR spectrum. No ^{13}C NMR spectrum of **2** was obtained due to low solubility in noncoordinating solvents. In the ^1H NMR spectrum the signals for the phenyl and methyl groups are very broad. In the aromatic region the broad signals are unresolved, but in the methyl region two groups can be clearly distinguished. The resonance at 3.04 ppm can be assigned to one methyl group after integration, whereas the resonance at 2.81 ppm contains three methyl groups. This is in line with expectations, if the existence of two isomers for **2** is assumed in solution with dynamic behavior between the two. The two isomers would differ in the chelate mode of the ligand, P,O- and P,N-chelation. Unfortunately, no NH peak was observed, probably due to further line broadening of the already broad signal in **1**. The $^{31}P\{^1H\}$ NMR spectrum ($CDCl_3$) of **2** exhibits two singlets at 135.63 and 125.80 ppm in an approximately 1:1 ratio, respectively, suggesting a P,O- and a P,N-bonding mode in solution (Scheme 3). The chemical shift is in agreement with a P,O-chelate bonding mode.[2] The P,O- and P,N-chelates are both five-membered ring systems and should therefore experience a downfield shift relative to the $Mo(CO)_4$ complex of **3**, a six-membered ring.[11] Assignment of the two phosphorus signals of **2** in

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solution to the P,O- and P,N-chelates is no easy task, as the actual chemical shift value of five-membered rings involving phosphorus bound to a transition metal is largely governed by geometrical constraints rather than straightforward electronic effects. Thus, we tentatively assign the signal at δ 135.63 ppm to the P,N-chelate and the signal at δ 125.80 to the P,O-chelate on the grounds that the sterically more demanding NHMe group results in a larger distortion of the ring and thus downfield shift than the smaller carbonyl oxygen. Rapid dynamic behavior involving the carbonyl oxygen of related *N*-phosphino amides has been observed in the $^{31}P\{^1H\}$ NMR spectrum of the palladium complexes published by Braunstein et al.[5b] They exhibit an upfield shift of $\Delta\delta = 20.3$ from P,O- to P-coordination similar to that observed for **2**. Addition of thf to a solution of **2** in $CDCl_3$ results in a solitary singlet at $\delta = 104.36$ ppm, indicative of the displacement of the carbonyl oxygen of the ligand by thf (Scheme 3). The chemical shift value of $\delta = 104.36$ ppm is in the vicinity of that displayed by *cis*-P,P-[Mo(CO)$_4$(**3**)][1] ($\delta = 102.03$ ppm). The solid-state structure of **1** suggests a P,N-chelate complex for **2**. However, rotation around the N1−C14 bond in **1** would result in a P,O-bonding mode. Such rotations are frequently observed in amides,[12−17] and in **1** the N1−C14 bond is already elongated by 5 pm, thus making rotation more facile.

Taking into acount the nature of the NH group in **1** and its ability to form hydrogen bonds with solvents such as thf, it becomes apparent that solvents such as CH_2Cl_2 and toluene, incapable of forming hydrogen bonds, are a good choice for the synthesis of **3** from **1** or directly from *N*,*N′*-dialkyl ureas. For the synthesis of **3** we used **1** in toluene at 60 °C for 1 h. The analytical data were as described in ref 1.

Investigations into the formation of asymmetric bisphosphino ureas and P,O-chelate complexes to metals other than molybdenum using **1** as starting material are under way.

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Supporting Information Available: X-ray crystallographic files in CIF format. The material is available free of charge via the Internet at http://pubs.acs.org.

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(15) A 7.05 g (80 mmol) portion of *N*,*N′*-dimethyl urea was dissolved in 100 mL of thf and 11.5 mL (80 mmol) of triethylamine added. To this solution was added dropwise 14.35 mL (80 mmol) of chlorodiphenylphosphine in 20 mL of thf, and the resulting mixture stirred for 4 h. Immediately upon addition of $ClPPh_2$ a white precipitate ($HNEt_3$-Cl) formed. The precipitate was filtered off and washed with thf. The filtrate was concentrated under vacuum to 30 mL, and then 30 mL of *n*-hexane was added. **1** (19.2 g, 88%) (mp 132−134 °C) was obtained as a white powder. Crystals suitable for single-crystal X-ray analysis were obtained by recrystallization from thf. ^1H NMR (300.13 MHz, $CDCl_3$): δ 7.42 (m, 10 H, Ph), 6.36 (s, br, 1 H, NH), 2.91 (d,$^3J_{PH} =$ 4.4 Hz, 3 H, CH_3), 2.78 (s, 3 H, CH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 160.7 (d, $^2J_{PC} = 21.1$ Hz, CO); 136.1 (d, $^1J_{PC} = 7.5$ Hz, *i*-Ph); 132.9 (d, $^2J_{PC} = 19.6$ Hz, *o*-Ph); 130.2 (s, *p*-Ph); 129.6 (d, $^3J_{PC} = 6.0$ Hz, *m*-Ph); 32.3 (d, $^2J_{PC} = 8.2$ Hz, PNMe); 28.4 (d, $^4J_{PC} = 3.5$ Hz, HNMe). MS-EI: 272.1 (M^+, 43.43). Anal. Calcd for **1** ($C_{15}H_{17}N_2OP$): C 66.17, H 6.29, N 10.29. Found: C 65.88, H 6.37, N 10.15.

(16) Crystallographic data[13,14] for **1**: $C_{15}H_{17}N_2OP$, $M = 272.28$, monoclinic, space group $P2_1/n$, $a = 833.10(10)$ pm, $b = 998.67(12)$ pm, $c = 1733.3(2)$ pm, $\beta = 99.998(2)°$, $V = 1.4202(3)$ nm^3, $Z = 4$, $\mu = 0.187$ mm^{-1}, $T = 217(2)$ K, 8962 unique reflections ($R_{int} = 0.0430$, R1 = 0.0483, wR2 = 0.1129) and 3370 reflections with $I > 2\sigma(I)$ (R1 = 0.0395, wR2 = 0.1073).

(17) A 1.07 g (3.69 mmol) portion of [Mo(CO)$_4$(NCMe)$_2$] was dissolved in 20 mL of thf. To this solution was added dropwise a solution of 1 g (3.68 mmol) of **1** in 20 mL of thf. The mixture was stirred overnight. Then the solution was concentrated to 10 mL under vacuum, and **2** precipitated as a yellow powder (mp 160−164 °C decomp) in 1.85 g (97%) yield by addition of 20 mL of *n*-hexane. ^1H NMR (300.13 MHz, $CDCl_3$): δ 7.84−7.40 (m, 20 H, Ph), 3.04 (br, 3 H, CH_3), 2.82 (br, 9 H, CH_3), traces of thf observed at 3.75 and 1.87 ppm. IR (KBr): 2021, 1905, 1840, 1804 cm^{-1} (*cis*-Mo(CO)$_4$). MS-EI: 354.3 (M^+ − 4 CO − Me). Anal. Calcd for **2**·0.5thf ($C_{21}H_{21}MoN_2O_{5.5}P$): C 48.85, H 4.10, N 5.43. Found: C 48.92, H 4.25, N 5.78.