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$P(OC_6H_3Bu^t_2\text{-}2,4)_2N(Me)CON(Me)PPh_2$: the facile route to an unsymmetrically substituted bisphosphinourea

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The phosphinourea derivative $PPh_2N(Me)CON(Me)H$ **1a** and the phosphoramidite derivative $P(OC_6H_3Bu^t_2\text{-}2,4)_2N(Me)CON(Me)H$ **1b** and their conversion to the unsymmetrically substituted urea phosphinophosphoramidite $P(OC_6H_3Bu^t_2\text{-}2,4)_2N(Me)CON(Me)PPh_2$ **2b** are described. These ligands were reacted with $[Mo(CO)_4(NCMe)_2]$ to the *cis* complexes *cis*-$[Mo(CO)_4\{P(OC_6H_3Bu^t_2\text{-}2,4)_2N(Me)CON(Me)H\}_2]$ **3b** and *cis*-$[Mo(CO)_4\{P(OC_6H_3Bu^t_2\text{-}2,4)_2N(Me)CON(Me)PPh_2\}_2]$ **4b**, respectively. The structure of **3b** and **4b** was determined by multinuclear NMR spectroscopy.

Introduction

Recently phosphino derivatives of urea[1] and thiourea[2] have found renewed interest as ligands for transition metals. In particular, reports on symmetrically substituted diphosphinoureas have dominated this area of research.[3–5] This is undoubtedly due to the facile synthesis of the dialkylbisphosphinoureas from the respective dialkylureas and chlorodiarylphosphines in toluene or dichloromethane with triethylamine as auxiliary base. Examples for monophosphinourea derivatives remain rare and comprise the *N*-phosphino-*N′*-silyl urea[4a] and thiourea[6] compounds developed by Schmutzler and $NHPPh_2C(S)NH_2$[7] isolated by Woollins *et al.* in very moderate yield as well as some *N*-phosphinocarboxylic acid amides[8] and related biuret derivatives.[9]

In most instances the substitution of protons or trimethylsilyl groups from ureas or trimethylsilyl ureas with chlorophosphines leads to diphosphine substituted ureas. If the urea component is in excess a mixture of mono- and diphosphinoureas is obtained. A noteable exception is $Bu^tPhPNMeCONMeSiMe_3$ reported by Schmutzler.[4a] A general route to monophosphinoureas and subsequently to unsymmetrically substituted bisphosphinoureas was lacking.

Here we report on a general route for the synthesis of unsymmetrically substituted bisphosphinoureas utilising the monophosphino compound recently published in a preliminary communication.[10]

Experimental

All experiments were carried out under purified dry argon. Solvents were dried with sodium and freshly distilled under argon. The ligand $PPh_2N(Me)CON(Me)H$ **1a** was prepared as described in ref. 10. NMR spectra were measured with ARX 300 (Bruker), standards: ^1H NMR (300.1 MHz): trace amounts of protonated solvent, $CDCl_3$, ^{13}C NMR (75.5 MHz): internal solvent, 31P NMR (121.5 MHz): external standard 85% H_3PO_4. The mass spectra were recorded with a single focussing sector field mass spectrometer AMD40 (Intectra). Elemental analyses were carried out with an elemental analyzer LECO Model CHNS-932 with standard combustion conditions and handling of the samples at air. Melting points were determined in sealed capillaries under argon and are uncorrected.

$P(OC_6H_3Bu^t_2\text{-}2,4)_2N(Me)CON(Me)H$, 1b

823 mg (9.34 mmol) *N*,*N′*-dimethyl urea were dissolved in 30 ml thf and 2 ml (27.5 mmol) NEt_3 added. To this solution 5.25 g (9.34 mmol) $ClP(OC_6H_3Bu^t_2\text{-}2,4)_2$(hexane) dissolved in 10 ml thf were added dropwise. Immediately a white precipitate ($HNEt_3Cl$) began to form. The mixture was stirred for a further 4 h and then filtrated. The filtrate was concentrated under reduced pressure and 20 ml hexane added to precipitate the product. The white product was filtered off and dried, yield 4.8 g (97%). Melting point 81 °C.

NMR: ^1H δ 7.38 (d, $^4J_{HH}$ = 2.5 Hz, 2H, H^3), 7.11 (dd, $^4J_{PH}$ = 2.5 Hz, $^3J_{HH}$ = 8.4 Hz, 2H, H^6), 6.97 (dd, $^4J_{HH}$ = 2.4 Hz, $^3J_{HH}$ = 8.4 Hz, 2H, H^5), 5.57 (m, 1H, NH), 3.09 (d, $^3J_{HH}$ = 3.16 Hz, 3H, N(H)Me), 2.90 (dd, $^3J_{PH}$ = 4.67 Hz, J_{HH} = 0.63 Hz, 3H, N(P)Me), 1.41 (s, 18H, $C(CH_3)_3$), 1.30 (s, 18H, $C(CH_3)_3$). $^{13}C\text{-}\{^1H\}$ δ 158.00 (d, $^2J_{PC}$ = 19.5 Hz, CO), 149.66 (d, J_{PC} = 9.9 Hz, C^1), 145.62 (s, C^4), 138.82 (d, J_{PC} = 3.5 Hz, C^2), 124.60 (s, C^5), 123.72 (s, C^3), 117.51 (d, J_{PC} = 20.3 Hz, C^6), 34.98 (s, NMe), 34.48 (s, NMe), 31.50 (s, $C(CH_3)_3$), 30.06 (s, $C(CH_3)_3$). $^{31}P\text{-}\{^1H\}$ δ 128.77 (s).

EI-MS (*m*/*z*, %): 528.4 (14.85) M^+, 441.2 (21.89) $[P(OAr)_2]^+$, 323 (19.18) $[NHMeCONMePOAr]^+$, 265.9 (58.46) $[NHMeCONMePOC_6H_3 - C_4H_9]^+$, 237.0 (10.90) $[POAr]^+$ and fragmentations thereof. IR (KBr, cm^{-1}): 3366 (m, NH), 1634 (st, CO). Elemental analysis for $C_{31}H_{49}N_2O_3P$ (528.71): calc. C 70.44 H 9.34 N 5.30; found C 70.32 H 9.51 N 5.02.

$P(OC_6H_3Bu^t_2\text{-}2,4)_2N(Me)CON(Me)PPh_2$, 2b

1.36 g (5 mmol) **1a** were dissolved in 20 ml toluene and 2 ml NEt_3 added. To this solution 2.81 g (5 mmol) $ClP(OC_6H_3Bu^t_2\text{-}2,4)_2$(hexane) dissolved in 10 ml toluene was added dropwise. After stirring for 4 h the white precipitate ($HNEt_3Cl$) was filtered off and the filtrate concentrated under reduced pressure. Upon addition of 20 ml hexane the off-white product precipitated. Yield: 2.4 g (68%). Melting point 143 °C.

NMR: ^1H δ 7.42–7.19 (m, 12H, Ph and H^3), 6.92 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{PH}$ = 2.5 Hz, 2H, H^6), 6.75 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HH}$ = 3.3 Hz, 2H, H^5), 3.27 (t, J_{PH} = 0.5 Hz, 3H NMe), 2.68 (t, J_{PH} = 1.3 Hz, 3H, NMe), 1.40 (s, 18H, CMe_3), 1.27 (s, 18H, CMe_3). $^{13}C\text{-}\{^1H\}$ δ 163.15 (dd, $^2J_{PC}$ = 21.13 Hz, $^2J_{PC}$ = 20.38 Hz, CO), 150.28 (d, J_{PC} = 11.1 Hz, C^1), 144.74 (s, C^4), 138.12 (d, J_{PC} = 3.3 Hz, C^2), 134.78 (dd, $^2J_{PC}$ = 15.3 Hz, $^2J_{PC}$ = 8.1 Hz, *i*-Ph), 132.16 (dd, J_{PC} = 19.7 Hz, J_{PC} = 2.3 Hz, *o*-Ph), 129.18 (s, *p*-Ph), 128.23 (d, J_{PC} = 5.9 Hz, *m*-Ph), 124.08 (s, C^5), 123.56 (s, C^3), 117.21 (d, J_{PC} = 23.6 Hz, C^6), 34.89 (s, *C*Me), 34.39 (s, *C*Me), 31.51 (s, C*Me*), 30.25 (s, NMe), 30.00 (s, C*Me*), 29.80 (s, NMe). $^{31}P\text{-}\{^1H\}$ δ 124.61 (d, $^4J_{PP}$ = 182 Hz, PO_2N), 57.56 (d, $^4J_{PP}$ = 182 Hz, PC_2N).

EI-MS (*m*/*z*, %): 712 (1) $[M]^+$, 507 (47.77) $[M - OC_6H_3(C_4H_9)_2]^+$, 457 (39.86) $[H_2NP\{OC_6H_3(C_4H_9)_2\}_2]^+$, 443 (85.48) $[HP\{OC_6H_3(C_4H_9)_2\}_2]^+$, 386 (7.03) $[HP\{OC_6H_3(C_4H_9)_2\}_2 - C_4H_9]^+$, 308 (14.58) $[OCN(Me)P(O)OC_6H_3(C_4H_9)_2]^+$, 266

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(54.98) $[NP(O)OC_6H_3(C_4H_9)_2]^+$, 236 (18.92) $[POC_6H_3(C_4H_9)_2]^+$, 191 (51.34) $[HOC_6H_3(C_4H_9)_2]^+$ and fragmentations thereof. IR (KBr, cm^{-1}): 1671 (st, CO). Elemental analysis for $C_{43}H_{58}N_2O_3P_2$ (712.89): calc. C 72.45 H 8.20 N 3.93; found C 72.71 H 8.04 N 3.78.

cis-[Mo(CO)$_4${P(OC$_6$H$_3$Bu$^t_2$-2,4)$_2$N(Me)CON(Me)H}], 3b

528 mg (1.0 mmol) **1b** were dissolved in 20 ml CH_2Cl_2 and 290 mg (1.0 mmol) $[Mo(CO)_4(NCMe)_2]$ added. After stirring for 2 h the solution was concentrated under reduced pressure and 20 ml hexane added. The pale yellow product was filtered off and dried *in vacuo*. Yield: 634 mg (86%).

NMR: ^{1}H δ 7.41 (d, $^4J_{HH}$ = 1.3 Hz, 1H, H^3), 7.18 (d, $^3J_{HH}$ = 8.5 Hz, 1H, H^5), 7.00 (d, $^3J_{HH}$ = 8.4 Hz, 1H, H^6), 5.38 (br, 1H, NH), 3.09 (s, 3H, NMe), 2.91 (s, 3H, NMe), 1.45 (s, 18H, CMe), 1.29 (s, 18H, CMe). ^{13}C-{^{1}H} δ 220.57 (d, $^2J_{PC}$ = 10.1 Hz, C^{a}O), 214.47 (d, $^2J_{PC}$ = 59.8 Hz, C^{b}O), 204.91 (d, $^2J_{PC}$ = 11.5 Hz, C^{c}O), 162.15 (d, $^2J_{PC}$ = 31.7 Hz, ligand CO), 148.42 (s, C^1), 147.03 (s, C^4), 139.21 (d, J_{PC} = 5.5 Hz, C^2), 124.75 (s, C^5), 123.76 (s, C^3), 119.52 (d, J_{PC} = 8.6 Hz, C^6), 35.13 (s, NMe), 34.93 (s, *C*Me), 34.49 (s, *C*Me), 31.37 (s, C*Me*), 30.20 (s, C*Me*), 28.03 (s, NMe). ^{31}P-{^{1}H} δ 172.31 (s).

IR (KBr, cm^{-1}): 3461 (m, NH), 2030 (st, CO), 1929 (st, CO), 1889 (st, CO), 1872 (st, CO), 1610 (st, ligand CO). Elemental analysis for $C_{35}H_{49}MoN_2O_7P$ (736.70): calc. C 57.06 H 6.70 N 3.80; found C 57.34 H 6.55 N 3.63.

cis-[Mo(CO)$_4${P(OC$_6$H$_3$Bu$^t_2$-2,4)$_2$N(Me)CON(Me)PPh$_2$}], 4b

516 mg (0.72 mmol) **2b** were dissolved in 20 ml thf and 210 mg (0.72 mmol) $[Mo(CO)_4(NCMe)_2]$ added. After stirring for 2 h the solution was concentrated under reduced pressure and 20 ml hexane added. The off-white product was filtered off and dried *in vacuo*, yield 537 mg (81%). Melting point 110 °C (dec.).

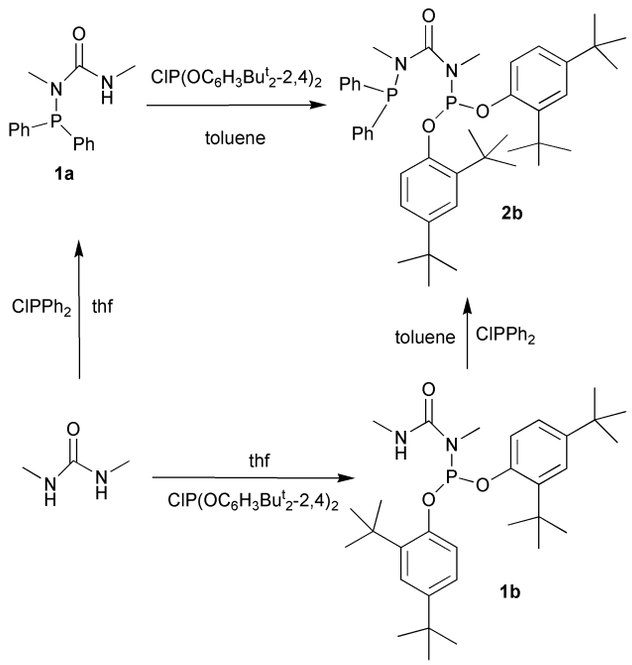
NMR: ^{1}H δ 7.68–7.21 (m, 12H, Ph and H^3), 7.16 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HH}$ = 2.5 Hz, 2H, H^5 major), 6.96 (d, $^3J_{HH}$ = 8.5 Hz, H^5 minor), 6.83 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{PH}$ = 2.6 Hz, 2H, H^6 major), 6.79 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{PH}$ = 2.4 Hz, H^6 minor), 3.15 (d, $^3J_{PH}$ = 3.8 Hz, minor, Me), 3.10 (d, $^3J_{PH}$ = 3.3 Hz, Me), 2.94 (d, $^3J_{PH}$ = 4.0 Hz, Me), 2.89 (d, $^3J_{PH}$ = 4.6 Hz, minor, Me), 1.45 (s, 9H, ^{t}Bu), 1.44 (s, minor, ^{t}Bu), 1.33 (s, 9H, ^{t}Bu), 1.30 (s, 9H, ^{t}Bu), 1.26 (s, minor, ^{t}Bu), 1.22 (s, 9H, ^{t}Bu). ^{13}C-{^{1}H} δ 211.85 (dd, $^2J_{PC}$ = 27.5 Hz, $^2J_{PC}$ = 13.1 Hz, *trans*-CO), 211.09 (dd, $^2J_{PC}$ = 43.0 Hz, $^2J_{PC}$ = 9.6 Hz, *trans*-CO), 206.6 (dd, $^2J_{PC}$ = 11.3 Hz, $^2J_{PC}$ = 9.1 Hz, *cis*-CO), 159.69 (t, $^2J_{PC}$ = 11.8 Hz, ligand CO), 147.86 (s, C^1), 146.09 (s, C^4), 138.97 (d, J_{PC} = 5.5 Hz, C^2), 136.56 (dd, J_{PC} = 36.6 Hz, J_{PC} = 2.5 Hz, *i*-Ph), 130.75 (d, J_{PC} = 13.6 Hz, *o*-Ph), 130.27 (s, *p*-Ph), 128.67 (d, J_{PC} = 9.4 Hz, *m*-Ph), 124.53 (s, C^5), 123.20 (s, C^3), 118.78 (d, J_{PC} = 8.0 Hz, C^6), 38.89 (s, NMe), 34.87 (s, *C*Me), 34.23 (s, *C*Me), 32.06 (s, NMe), 31.24 (s, C*Me*), 30.10 (s, C*Me*). ^{31}P-{^{1}H} δ 155.83 (d, $^2J_{PP}$ = 34 Hz, PO_2N, minor), 149.0 (d, $^2J_{PP}$ = 32 Hz, PO_2N), 103.8 (d, 2J_{PP} = 32 Hz, PC_2N), 101.72 (d, $^2J_{PP}$ = 34 Hz, PC_2N, minor).

IR (KBr, cm^{-1}): 2038 (w, Mo–CO), 1970 (st, Mo–CO), 1931 (st, Mo–CO), 1900 (st, Mo–CO), 1857 (m, Mo–CO), 1650 (m, ligand CO), 1605 (w, ligand CO). Elemental analysis for $C_{47}H_{58}MoN_2O_7P_2$ (920.87): calc. C 61.30 H 6.35 N 3.04; found C 61.17 H 6.15 N 3.38.

Results and discussion

The reaction between dimethyl urea and a chlorophosphine or chlorophosphite leads to the respective monophosphorus substituted urea in high yields, if the reaction is carried out in thf. If toluene is used as the solvent the reaction is usually carried to the disubstituted product, likewise in high yield (Scheme 1).

The choice of solvent is crucial as the monosubstituted product was only obtained as sole product in thf, whereas in toluene or dichloromethane a mixture of the mono- and disubstituted products was obtained when the reactants were present in a 1 : 1 ratio.



Scheme 1 The synthesis of **2b**.

The monophosphinourea derivatives **1a**,**b** (**1a**: PPh_2, **1b**: P{$OC_6H_3(C_4H_9)_2$-2,4}) can be converted into the diphosphinoureas **2a**,**b** (**2a**: PPh_2, PPh_2; **2b**: PPh_2, P{$OC_6H_3(C_4H_9)_2$-2,4) by reaction with the appropriate chlorophosphine or chlorophosphite, respectively. The reaction follows eqn. (2). However, as already observed by Schmutzler and Gruber,[6] we could not isolate the product, if a chlorodialkylphosphine such as ClP^iPr_2 was used.

Compound **2a** is known from the literature[1] and compounds **1a**,[10] **1b**, and **2b** were fully characterised by multinuclear NMR, IR, EI-MS, and elemental analysis.

In the attempted reaction of *N*,*N*′-dimethylurea with two equivalents of $ClP(OC_6H_3Bu^t_2\text{-}2,4)_2$ in toluene the desired product $\{P(OC_6H_3Bu^t_2\text{-}2,4)_2NMe\}_2CO$ **2c** was not obtained. Instead a mixture of **1b** and unreacted $ClP(OC_6H_3Bu^t_2\text{-}2,4)_2$ was recovered from the reaction mixture. The likely explanation is that the bulky phosphite ligand is sterically too demanding for the formation of the bisphosphoramidite urea derivative. From an electronic point of view, the compound **1b** should be more reactive than **1a** since the electron withdrawing phenoxy groups weaken the intramolecular N–H–P hydrogen bond and thus make the N–H proton more accessible to attack by an incoming chlorophosphite.

The ^{31}P-{^{1}H} NMR spectra of **1a** and **1b** show the expected singlets at 45.8 and 128.8 ppm, respectively. The difference in chemical shift between **1a** and **1b** reflects the difference between phosphine and phosphoramidite. The CO resonances of **1a** and **1b** are observed at 160.7 and 158.0 ppm with coupling constants of 20.1 and 19.5 Hz, respectively. The relevant bands in the IR spectrum of **1a** and **1b** are very similar as well. The NH band is observed at 3372 cm^{-1} for **1a** and at 3366 cm^{-1} for **1b** with the values for the CO band being 1650 cm^{-1} for **1a** and 1634 cm^{-1} for **1b**. However, the ^{1}H NMR spectrum reveals a significant difference in the resonance for the NH proton. The signal is observed at 6.36 ppm for **1a** and 5.57 ppm for **1b**, a difference of $\Delta\delta$ = 0.79 ppm. Although one would expect that the introduction of a phosphite as opposed to a phosphine has a significant influence not only on the phosphorus centre, but also on the carbonyl and amino groups, the spectroscopic evidence for such an electronic influence is at best unclear.

Reaction of **1a**,**b** with $ClPPh_2$ or $ClP(OC_6H_3Bu^t_2\text{-}2,4)_2$ in toluene with triethylamine as auxilliary base yields the bisphos-

phinourea derivatives **2a**,**b**. For compound **2b** both routes *via* **1a** or **1b** are equally viable.

The ^{31}P-{^{1}H} NMR spectra for **2a**,**b** show a small downfield chemical shift for the PPh_2 group with respect to the monophosphino derivatives **1a**,**b**, but not for the $P(OC_6H_3Bu^t_2\text{-}2,4)_2$ group. The signal for the PPh_2 group in **1a** of 45.8 ppm is shifted to 54.6 ppm in **2a** and 57.6 ppm in **2b**. The signal for $P(OC_6H_3Bu^t_2\text{-}2,4)_2$ is shifted very slightly upfield from 128.8 ppm in **1b** to 124.6 ppm in **2b**. A similar small downfield shift for the PPh_2 group is observed in related urea [4a] and thiourea [5,7] derivatives. Thus the very small upfield shift of $\Delta\delta = -4.2$ for the $P(OC_6H_3Bu^t_2\text{-}2,4)_2$ group came as a surprise. The ^{13}C-{^{1}H} NMR spectra shows the signal for the carbonyl carbon as the expected doublet of doublets at 163.2 ppm. The PC coupling constants are almost identical. The chemical shift is 5.2 ppm downfield from that of **1b** and 2.5 ppm downfield from **1a**.[10] Apparently the phosphoramidite substituent exerts a smaller influence on the chemical shift value of the carbonyl carbon than does the phosphine substituent as can also be seen by direct comparison of **1a** and **1b**. In the IR spectrum the ν(CO) band is observed at 1646 cm^{-1} for **2a** and 1671 cm^{-1} for **2b**. Again, no significant change is observed in the IR spectrum for the CO band between **1a** and **2a**, but a small alteration between **1a** or **1b** and **2b** was noted due to the influence of the phosphite substituent $P(OC_6H_3Bu^t_2\text{-}2,4)_2$.

If a second phosphorus group is introduced, the question arises which conformation is adopted by the bisphosphinourea derivatives **2a**,**b**. There are four conformations possible (see Fig. 1).

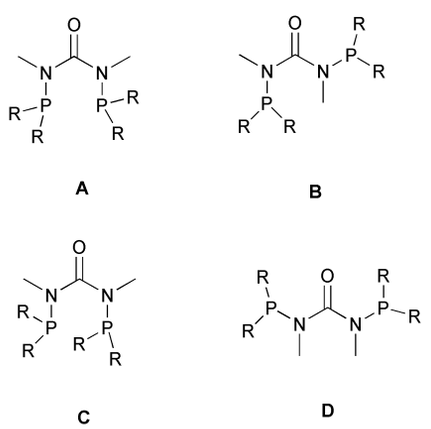


Fig. 1 Possible conformations of **2**.

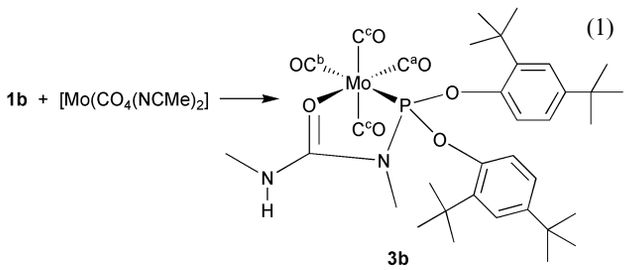
There is no crystal structure available for either of the compounds **2a** or **2b**. However the thiourea analog of **2a** [2] adopts conformation **A** as does the closely related compound {Bu^t-PhPN(Me)}$_2$CO.[4a] Compound **2a** is symmetrically substituted and has equivalent phosphorus atoms. Compound **2b**, however, is unsymmetrically substituted with inequivalent phosphorus atoms. Thus, the ^{31}P-{^{1}H} NMR spectrum of **2b** shows two signals for phosphorus at 124.6 and 57.6 ppm with a coupling constant of 182 Hz. This large coupling constant is conclusive evidence for conformation **A** in solution. Comparison with the two available solid state structures indicates that it is also the prevalent structure in the solid state. Conformation **B** is realised in the $Mo(CO)_4$ complexes of the monophosphinourea derivatives **1a**,**b** and conformation **D** is observed in the dinuclear complex $[(AuCl)PPh_2N(Et)CON(Et)PPh_2(AuCl)]$.[1]

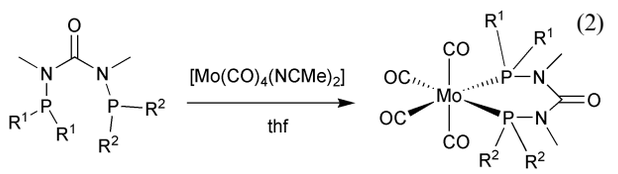
Reaction of the phosphinourea derivatives **1a**,**b** and **2a**,**b** with $[Mo(CO)_4(NCMe)_2]$ renders the P,O- and P,P-chelate complexes *cis*-$[Mo(CO)_4$(**1a**,**b**)] **3a**,**b** [eqn. (1)] and *cis*-$[Mo(CO)_4$(**2a**,**b**)] **4a**,**b** [eqn. (2)], respectively. Complexes **3a** [10] and **4a** [1] are already reported in the literature including an X-ray crystal structure determination for **4a**.

The behaviour of **3b** is similar to that of **3a** in that both

Table 1 Selected IR data

Group/compound	**1a**	**3a**	**1b**	**3b**
NH	3372	3422	3366	3461
CO	1650	1603	1634	1610



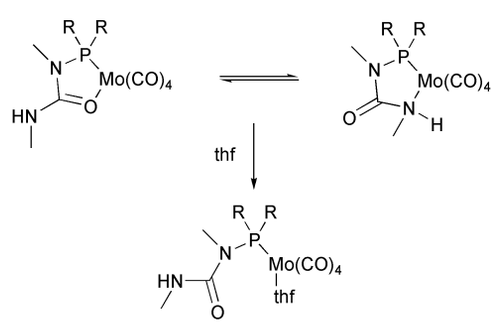


2a: $R^1 = R^2$ = Ph
2b: R^1 = Ph, $R^2 = OC_6H_3Bu^t_2$-2,4

4a: $R^1 = R^2$ = Ph
4b: R^1 = Ph, $R^2 = OC_6H_3Bu^t_2$-2,4

display the characteristic bands for a P,O-chelate in the solid state IR. The IR spectrum of **3a** contains bands at 3461 cm^{-1} for the NH group and at 1610 cm^{-1} for the carbonyl group of the ligand. Both bands are shifted compared to the free ligand in a similar way to those for **1a** and **3a** (Table 1).

In solution **3b** shows far less dynamic behaviour than **3a** (Scheme 2).The ^{31}P-{^{1}H} NMR spectrum of **3b** displays only one signal at 172.4 ppm rather than two as **3a**. The large downfield shift of $\Delta\delta = 43.6$ ppm stems from the additional ring shift common to five member rings.[11] The ^{13}C-{^{1}H} NMR spectrum shows the expected set of signals and a few signals for another isomer. In the carbonyl region the three different signals for the Mo–CO groups are fully resolved and could easily be assigned. The CO ligand *trans* to the ligand CO group is furthest downfield followed by the CO ligand *trans* to phosphorus. The two axial CO groups are assigned to the doublet furthest upfield in full agreement with the respective *trans* influence (O < P < CO). The signal for the carbonyl carbon of the ligand is observed at 162.2 ppm 4.2 ppm downfield from the free ligand.



3a: R = Ph
3b: R = $OC_6H_3Bu^t_2$-2,4

Scheme 2 Dynamic behaviour of **3**.

The ^{1}H NMR spectrum shows an almost complete set of signals for the minor isomer.[12] Only the signals for the aromatic protons are hidden underneath those of the major isomer. All signals for the minor isomer are upfield to those of the major one except the NMe group next to phosphorus that is shifted upfield by 0.18 ppm. Thus it appears that although there are two isomers for **3b** in solution the P,N-chelate is only present in very small amounts. The P,O-chelate is dominant. This is

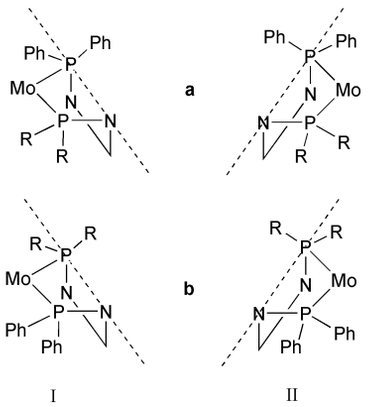


Fig. 2 Conformations of **4**.

in contrast to **3a** that exists in equal amounts as P,O- and P,N-chelates in solution.[10]

The molybdenum complex **4b** exists in two conformations in solution. They are distinguished by slightly different chemical shifts in the ^{31}P-{^{1}H} NMR spectrum. The major conformation displays two doublets at 149.0 and 103.8 ppm ($^{2}J_{PP}$ = 32 Hz) whereas the two doublets of the minor conformation are further apart at 155.8 and 101.7 ppm ($^{2}J_{PP}$ = 34 Hz). For all four signals the observed downfield shift as compared to the free ligand **2b** is consistent with a P,P-chelate coordination. In a P,O-coordination mode only one of the two phosphorus atoms would experience a downfield shift (as it were a five member ring, the downfield shift would indeed be larger than observed[11]), whereas the uncoordinated phosphorus atom would be unchanged. However, the IR spectrum shows a different behaviour. Here two bands for the CO group of the ligand are observed, a stronger one at 1650 cm^{-1} and a much weaker one at 1605 cm^{-1}. As the ratio of the two conformations is approximately 9 : 1 we assume that the difference lies indeed in the folding of the ring rather then the bonding mode of the ligand on the metal.

The structure of **4a** displays a MoP_2N_2C six member ring that is not planar, but tilted by 55° on a 1,4-N–P axis. This axis is formed by an N and P atom occupying opposite positions on the six member ring. In **4a** both 1,4-N–P axis are equivalent (R^1 = R^2 = Ph). In **4b** two such axes are distinguishable, one in which the phosphoramidite phosphorus lies on the axis and another where the phosphine phosphorus is so located (Fig. 2).

The tilting along the 1,4-N–P axis renders the two phosphorus atoms inequivalent irrespective of the substitution pattern. Thus, one would expect to observe two closely spaced doublets even for **4a**. Instead a singlet was reported,[1] presumably due to rapid equilibration on the NMR timescale. For **4a** structures I and II are mirror images of each other. For **4b** that is no longer the case as the substituents on phosphorus are different. However, as the phosphoramidite can occupy either of the two phosphorus positions in either of the two structure types I and II, two pairs of enantiomers result and are observed in a 9 : 1 ratio.

The ^{13}C-{^{1}H} NMR spectrum shows a complete set of signals for the major conformer only. The CO signal for the major conformer is displayed at 159.7 ppm shifted 3.5 ppm upfield from the free ligand. There is at best only a small influence from either the nature of the phosphorus atom or ligation to a metal on the carbonyl carbon judging from the ^{13}C chemical shifts.

An X-ray crystal structure determination for **4b** was performed. Unfortunately, the quality of the single crystals did not permit an internal *R* value below 0.18. Therefore, reliable data on bond lengths and bond angles could not be obtained. However, the positions of the atoms could be determined with sufficient accuracy to allow the structural motif to be elucidated. The compound **4b** is isostructural to **4a** and the phosphine phosphorus of the specimen measured lies on the tilt vector.

Conclusion

Phosphorylation of *N*,*N*′-dimethyl urea is a viable route to monophosphorylated and subsequently unsymmetrically diphosphorylated urea derivatives. Whereas the former have shown hemilabile behaviour in molybdenum carbonyl complexes, the latter constitute a new class of sterically and electronically unsymmetric diphosphine ligands. It is anticipated that both classes of urea based ligands will display a rich and versatile coordination chemistry.

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