Functionalised *N*-pyrrolyl phosphines: synthesis and molybdenum chemistry of a new ketophosphine

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The synthesis and X-ray crystal structure of the new keto-functionalised *N*-pyrrolyl phosphine ligand $PPh_2NC_4H_3\{C(O)CH_3\}$-2 **L** is reported. The ligand coordinates to molybdenum(II) as either a uni- or a bi-dentate ligand, and the reversibility of the ketone coordination is demonstrated by the interconversion of the complexes $[MoCl(CO)_2(\mathbf{L}\text{-}\kappa^1P)(\eta^5\text{-}C_5H_5)]$ **1** and $[Mo(\mathbf{L}\text{-}\kappa^2P,O)(CO)_2(\eta^5\text{-}C_5H_5)][BF_4]$ **2** on abstraction or addition of chloride. The X-ray crystal structure of **1** is also reported.

There has recently been an upsurge of interest in *N*-pyrrolyl phosphines[1] due to their strongly electron withdrawing character, and the catalytic implications of this behaviour.[2] While functionalities have been added with a view to enhancing the electronic character,[3] very little use has been made of the pyrrolyl ring as a skeleton for phosphines with additional donor groups.[4] Since functionalised pyrroles are readily available, we reasoned that *N*-pyrrolyl phosphines containing additional functionalities were likely to be easily accessible ligands with interesting properties.

Ketophosphines such as $PPh_2CH_2C(O)Ph$ have attracted considerable interest, most notably from Braunstein and coworkers,[5] for their ability to act as uni- or bi-dentate ligands. Bifunctional ligands containing both hard and soft donor atoms are of interest catalytically, in part through the potential for hemilability,[6] and also for the formation of heterobimetallic compounds.[7] The π-acceptor nature of *N*-pyrrolyl phosphines affords the potential for enhancing the electronic difference between the donor atoms in such a ligand.

The majority of studies with ketophosphines have concentrated on late transition metals, and a search of the Cambridge Structural Database[8] reveals only one example of a Group 6 metal ketophosphine complex, a tungsten complex in which the ketophosphine was formed *in situ*.[9] Very recently, molybdenum half-sandwich compounds of the amidophosphine $PPh_2CH_2C(O)NPh_2$ have been reported,[10] and a preliminary account of molybdenum η^6-arene complexes with β-ketophosphines has appeared.[11] In this paper we report the synthesis of a new ketophosphine, based on 2-acetylpyrrole, and the reactions of this ligand with molybdenum(II) complexes.

Results and discussion

The keto-functionalised *N*-pyrrolyl phosphine $PPh_2NC_4H_3\{C(O)CH_3\}$-2 **L** can be prepared in good yield from the reaction of 2-acetylpyrrole and PPh_2Cl in the presence of base. If NEt_3 is used the reaction is slow, taking 48 h to reach completion. However, use of the stronger base DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) reduces the reaction time to 2 h. As in the case of functionalised aminophosphines,[12] care needs to be taken to exclude water to prevent the formation of $Ph_2PP(O)Ph_2$. Compound **L** was characterised on the basis of multinuclear NMR, IR and a single-crystal X-ray analysis. The molecular structure of **L** is shown in Fig. 1 and selected bond lengths and angles are given in Table 1.

The sum of angles around the nitrogen atom in **L** is 360°, similar to those in tri(*N*-pyrrolyl)phosphine. The P–N distance in **L** is longer than those in tri(*N*-pyrrolyl)phosphine [1.677(8)–1.710(8) Å],[13] and consistent with no double bond character in contrast to aminophosphines of the type PPh_2NHR.[12] The bond lengths observed for **L** suggest a significant structural contribution from an enolate canonical

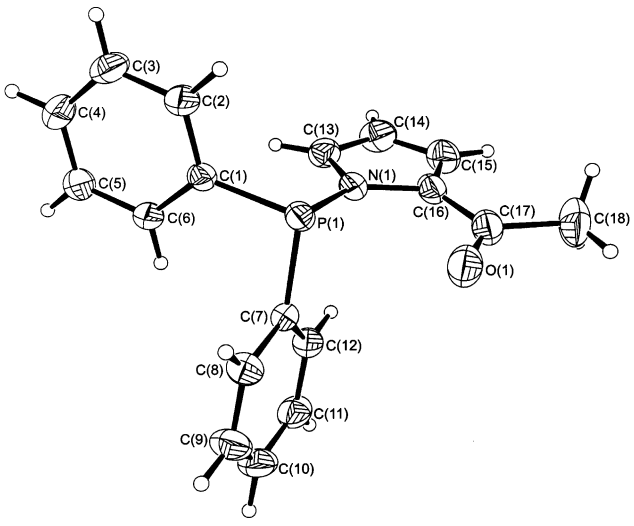

Fig. 1 The molecular structure of **L** with thermal ellipsoids shown at the 30% probability level.

Table 1 Selected bond lengths (Å) and angles (°) for **L**

P(1)–N(1)	1.7637(14)	C(15)–C(16)	1.375(3)
N(1)–C(13)	1.365(2)	C(16)–C(17)	1.441(3)
N(1)–C(16)	1.388(2)	C(17)–C(18)	1.504(3)
C(13)–C(14)	1.358(3)	C(17)–O(1)	1.216(2)
C(14)–C(15)	1.380(3)		
C(13)–N(1)–C(16)	107.45(15)	N(1)–C(16)–C(17)	122.14(17)
C(13)–N(1)–P(1)	126.74(12)	O(1)–C(17)–C(16)	121.11(18)
C(16)–N(1)–P(1)	125.48(12)		

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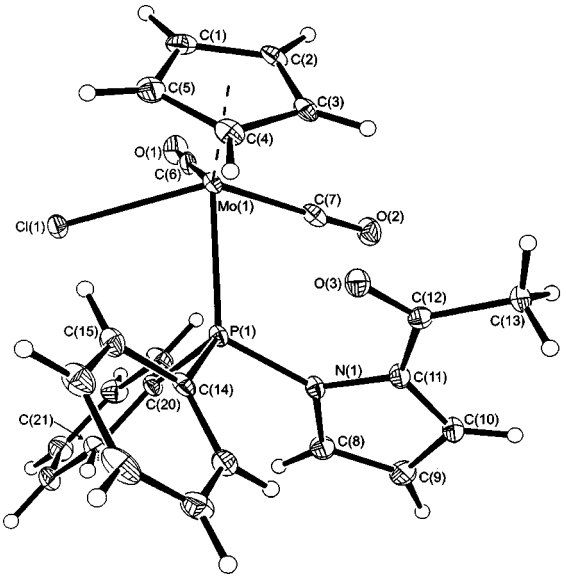


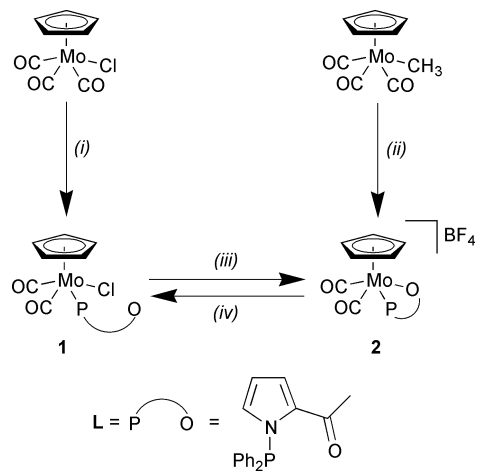
Fig. 2 The molecular structure of complex **1** with thermal ellipsoids shown at the 30% probability level.

form, thus C(16)–C(17) is very short for a C–C single bond, and C(15)–C(16) is significantly longer than C(13)–C(14). The low value of the carbonyl stretching frequency [ν(CO) = 1643 cm^{-1}] is also consistent with this, as is the fact that the carbonyl group lies approximately in the plane of the pyrrole ring.

The reaction of **L** with $[MoCl(CO)_3(\eta^5\text{-}C_5H_5)]$ in refluxing hexane gave $[MoCl(CO)_2(\mathbf{L}\text{-}\kappa^1P)(\eta^5\text{-}C_5H_5)]$ **1** in good yield. Coordination of the phosphorus atom in **1** is witnessed by the large shift in $\delta(^{31}P)$ from that observed for the free ligand

Table 2 Selected bond lengths (Å) and angles (°) for **1**

Mo(1)–P(1)	2.5176(16)	C(8)–C(9)	1.355(8)
Mo(1)–Cl(1)	2.4991(16)	C(9)–C(10)	1.395(8)
Mo(1)–C(6)	1.961(5)	C(10)–C(11)	1.366(8)
Mo(1)–C(7)	1.969(6)	C(11)–C(12)	1.451(7)
P(1)–N(1)	1.748(4)	C(12)–C(13)	1.495(7)
N(1)–C(8)	1.383(7)	C(12)–O(3)	1.222(6)
N(1)–C(11)	1.407(6)		
C(6)–Mo(1)–C(7)	76.0(2)	C(8)–N(1)–C(11)	106.1(4)
C(6)–Mo(1)–Cl(1)	80.03(15)	C(8)–N(1)–P(1)	125.5(4)
C(7)–Mo(1)–Cl(1)	134.99(15)	C(11)–N(1)–P(1)	128.3(3)
C(6)–Mo(1)–P(1)	111.62(16)	N(1)–C(11)–C(12)	122.2(5)
C(7)–Mo(1)–P(1)	77.86(16)	O(3)–C(12)–C(11)	121.0(5)
Cl(1)–Mo(1)–P(1)	76.42(5)		



Scheme 1 (*i*) L; (*ii*) L, HBF_4; (*iii*) $AgBF_4$; (*iv*) Cl^-.

[$\Delta\delta$ = 56.4 ppm], whereas non-coordination of the carbonyl group is consistent with the small change in ν(CO) from that of **L** [$\Delta\nu$(CO) = +11 cm^{-1}]. The NMR parameters suggest that **1** exists solely as the *cis*-isomer, in a similar manner to $[MoCl(CO)_2(PPh_3)(\eta^5\text{-}C_5H_5)]$.[14] Confirmation of this structure was obtained by a single crystal X-ray structure analysis, and the molecular structure of **1** is shown in Fig. 2, with selected bond lengths and angles given in Table 2. Compound **1** adopts a pseudo-square pyramidal metal geometry, with the *cis* carbonyls, chloride and phosphorus atom forming the base of the pyramid and the cyclopentadienyl ring the apex. The bond lengths and angles within the ketophosphine are generally similar to those in the free ligand, though shortening of the P–N bond on coordination may be significant.

The reaction of **L** with $[Mo(CH_3)(CO)_3(\eta^5\text{-}C_5H_5)]$ and $HBF_4 \cdot OEt_2$ in dichloromethane gave $[Mo(\mathbf{L}\text{-}\kappa^2P,O)(CO)_2(\eta^5\text{-}C_5H_5)][BF_4]$ **2** in good yield. The value of $\delta(^{31}P)$ for **2** is similar to that observed for **1**, though a large decrease in ν(CO) from that of **L** [$\Delta\nu$(CO) = −90 cm^{-1}] is indicative of coordination of the keto oxygen atom. Compounds **1** and **2** can be readily interconverted by the abstraction or addition of chloride. Hence the reaction of **1** with $AgBF_4$ in dichloromethane led to precipitation of AgCl, and coordination of the keto group to give **2**. Furthermore, the reaction of **2** with $[NEt_3Bz]Cl$ in dichloromethane led to the displacement of the keto group by chloride and formation of **1**. These reactions, along with the syntheses of **1** and **2** are summarised in Scheme 1.

In summary, we have demonstrated that the pyrrole ring can serve as the skeleton for functionalised phosphines. The new ketophosphine ligand **L** has been prepared and characterised, and shown to coordinate to molybdenum(II) as either a uni- or a bi-dentate ligand. Interconversion of complexes **1** and **2** on abstraction or addition of chloride demonstrates the reversible coordination of the ketone oxygen atom. Despite the contribution from the enolate canonical form, coordinated **L** is not readily deprotonated. This leads to differences in reactivity between compounds of **L** and analogous compounds of $PPh_2CH_2C(O)Ph$. These will be reported at a later date.

Experimental

Reactions were routinely carried out using Schlenk-line techniques under pure dry dinitrogen using dry dioxygen-free solvents unless noted otherwise. Microanalyses (C, H and N) were carried out by Mr Alan Carver (University of Bath Microanalytical Service). Infrared spectra were recorded on a Nicolet 510P spectrometer as KBr pellets or dichloromethane solutions in KBr cells. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a JEOL JNM-EX270 spectrometer operating at 270 MHz referenced to $SiMe_4$ and 109.4 MHz referenced to H_3PO_4, respectively. $^{13}C\{^1H\}$ NMR spectra were recorded on a Varian Mercury 400 spectrometer operating at 100.4 MHz referenced to $SiMe_4$.

Synthesis of L

DBU (1.83 g, 12 mmol) and PPh_2Cl (2.41 g, 11 mmol) were added sequentially with stirring to a solution of 2-acetylpyrrole (1.19 g, 11 mmol) in THF (40 cm^3). The reaction mixture was stirred for 2 h and the solution filtered to remove [DBUH]Cl. The resulting solution was evaporated under reduced pressure to give a white solid, which was washed with hexane and recrystallised from THF–hexane to give block-shaped crystals. Yield 2.34 g (73%) (found: C, 73.4; H, 5.62; N, 4.75; $C_{18}H_{16}NOP$ requires C, 73.7; H, 5.50; N, 4.78%). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 55.8; ^1H NMR ($CDCl_3$) δ 7.40–7.38 (m, 6H, Ar), 7.32–7.27 (m, 4H, Ar), 7.16 (m, 1H, CH), 6.44 (m, 1H, CH), 6.24 (m, 1H, CH), 2.43 (s, 3H, CH_3); $^{13}C\{^1H\}$ NMR

($CDCl_3$) δ 187.4 (s, C=O), 25.7 (s, Me). IR (KBr, cm^{-1}): 1643 [vs, ν(C=O)].

Synthesis of 1

$[MoCl(CO)_3(\eta^5\text{-}C_5H_5)]$ (0.150 g, 0.53 mmol) and **L** (0.149 g, 0.53 mmol) were dissolved in hexane (20 cm^3) and refluxed for 6 h. The crude product was recrystallised from dichloromethane–toluene to give **1** as a dark red powder (0.281 g, 89%) (found: C, 54.9; H, 3.94; N, 2.64; $C_{25}H_{21}ClMoNO_3P$ requires C, 55.0; H, 3.88; N, 2.57%). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 112.2; ^1H NMR ($CDCl_3$) δ 7.72–7.38 (m, 10H, Ar), 7.20 (m, 1H, CH), 6.46 (m, 1H, CH), 6.21 (m, 1H, CH), 5.61 (s, 5H, Cp), 2.31 (s, 3H, Me); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 254.4 (d, MCO, $^2J_{PC} = 31.4$), 242.9 (d, MCO, $^2J_{PC} < 1$ Hz), 185.5 (s, C=O), 96.1 (s, Cp), 26.0 (s, Me). IR (CH_2Cl_2, cm^{-1}): 1970 [vs, ν(CO)], 1888 [vs, ν(CO)], 1654 [s, ν(C=O)].

Synthesis of 2

$[Mo(CH_3)(CO)_3(\eta^5\text{-}C_5H_5)]$ (0.133 g, 0.49 mmol) was dissolved in CH_2Cl_2 (10 cm^3), cooled to $-78\,^\circ C$ and $HBF_4 \cdot OEt_2$ (81 μL, 0.49 mmol) added dropwise with stirring. The solution was allowed to warm to room temperature, then cooled back to $-78\,^\circ C$, and **L** (0.148 g, 0.50 mmol) added. The solution was then allowed to warm back to room temperature, stirred at ambient temperature for 16 h, and recrystallised from dichloromethane–toluene to give **2** as a dark red powder (0.250 g, 83%) (found C, 49.2; H, 3.73; N, 2.17; $C_{25}H_{21}BF_4MoNO_3P \cdot 0.25CH_2Cl_2$ requires C, 49.0; H, 3.50; N, 2.27%). $^{31}P\{^1H\}$ NMR ($CDCl_3$) δ 114.6; ^1H NMR ($CDCl_3$) δ 7.67–7.45 (m, 11H, Ar and CH), 7.29 (m, 1H, CH), 6.56 (m, 1H, CH), 5.55 (s, 5H, Cp), 2.59 (s, 3H, Me); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 248.0 (d, MCO, $^2J_{PC} = 30.0$), 240.0 (d, MCO, $^2J_{PC} = 3.2$), 199.3 (d, C=O, $^3J_{PC} = 7$ Hz), 97.7 (s, Cp), 27.8 (s, Me). IR (CH_2Cl_2, cm^{-1}): 1997 [vs, ν(CO)], 1928 [vs, ν(CO)], 1553 [s, ν(C=O)].

Crystallography

Single crystals of **L** and **1** were prepared by recrystallisation from dichloromethane–hexane and dichloromethane–toluene respectively.

L: $C_{18}H_{16}NOP$, $M = 293.29$, monoclinic, $P2_1/a$, $a = 9.501(3)$, $b = 16.156(3)$, $c = 11.009(3)$ Å, $\beta = 112.91(2)^\circ$, $V = 1556.6(7)$ Å^3, $Z = 4$, $T = 293(2)$ K, crystal dimensions $0.50 \times 0.50 \times 0.50$ mm, $\mu = 0.175$ mm^{-1}, 3326 measured reflections, 3036 independent reflections ($R_{int} = 0.0085$), $R1 = 0.0348$, $wR2 = 0.0988$ [$I > 2\sigma(I)$].

1: $C_{25}H_{21}ClMoNO_3P \cdot 0.5CH_2Cl_2$, $M = 588.25$, triclinic, $P\bar{1}$, $a = 9.762(3)$, $b = 10.383(4)$, $c = 14.411(5)$ Å, $\alpha = 110.50(3)$, $\beta = 93.69(3)$, $\gamma = 100.85(3)^\circ$, $V = 1330.2(8)$ Å^3, $Z = 2$, $T = 170(2)$ K, crystal dimensions $0.20 \times 0.20 \times 0.20$ mm, $\mu = 0.780$ mm^{-1}, 5137 measured reflections, 4686 independent reflections ($R_{int} = 0.0242$), $R1 = 0.0492$, $wR2 = 0.1225$ [$I > 2\sigma(I)$].

Data were collected on an Enraf-Nonius CAD4 automatic four-circle diffractometer in the ranges $2.01 < \theta < 25.96^\circ$ (**L**) and $2.13 < \theta < 25.02^\circ$ (**1**) and corrected for Lorentz and polarisation effects. The structure solution and refinement were undertaken using SHELXS-86[15] and SHELXL-97[16] respectively. The plots of the asymmetric units were produced using ORTEX.[17]

CCDC reference numbers 161741 and 161742. See http://www.rsc.org/suppdata/nj/b1/b102193l/ for crystallographic data in CIF or other electronic format.

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References

1 K. G. Moloy and J. L. Petersen, *J. Am. Chem. Soc.*, 1995, **117**, 7696; C. Li, S. Serron, S. P. Nolan and J. L. Petersen, *Organometallics*, 1996, **15**, 4020; S. Serron, S. P. Nolan, Y. A. Abramov, L. Brammer and J. L. Petersen, *Organometallics*, 1998, **17**, 104; V. Rodriguez, B. Donnadieu, S. Sabo-Etienne and B. Chaudret, *Organometallics*, 1998, **17**, 3809; J. Castro, A. Moyano, M. A. Pericàs, A. Riera, M. A. Maestro and J. Mahía, *Organometallics*, 2000, **19**, 1704.

2 A. M. Trzeciak, T. Glowiak, R. Grzybek and J. J. Ziólkowski, *J. Chem. Soc., Dalton Trans.*, 1997, 1831; A. M. Trzeciak, T. Glowiak and J. J. Ziólkowski, *J. Organomet. Chem.*, 1998, **552**, 159.

3 A. Huang, J. E. Marcone, K. L. Mason, W. J. Marshall, K. G. Moloy, S. Serron and S. P. Nolan, *Organometallics*, 1997, **16**, 3377.

4 H. Brunner and H. Weber, *Chem. Ber.*, 1985, **118**, 3380; H. Brunner, W. Li and H. Weber, *J. Organomet. Chem.*, 1985, **288**, 359.

5 S.-E. Bouaoud, P. Braunstein, D. Grandjean, D. Matt and D. Nobel, *Inorg. Chem.*, 1986, **25**, 3765; P. Braunstein, D. Matt, D. Nobel, F. Balegroune, S.-E. Bouaoud, D. Grandjean and J. Fischer, *J. Chem. Soc., Dalton Trans.*, 1988, 353; P. Braunstein, Y. Chauvin, J. Nähring, A. DeCian, J. Fischer, A. Tiripicchio and F. Ugozzoli, *Organometallics*, 1996, **15**, 5551; J. Andrieu, P. Braunstein, F. Naud and R. D. Adams, *J. Organomet. Chem.*, 2000, **601**, 43.

6 A. Bader and E. Lindner, *Coord. Chem. Rev.*, 1991, **108**, 27; C. S. Slone, C. A. Mirkin, G. P. A. Yap, I. A. Guzei and A. L. Rheingold, *J. Am. Chem. Soc.*, 1997, **119**, 10743; P. Braunstein and F. Naud, *Angew. Chem., Int. Ed.*, 2001, **40**, 680.

7 A. D. Burrows, M. F. Mahon and M. T. Palmer, *J. Chem. Soc., Dalton Trans.*, 2000, 3615.

8 D. A. Fletcher, R. F. McMeeking and D. Parkin, *J. Chem. Inf. Comput. Sci.*, 1996, **36**, 746; F. H. Allen and O. Kennard, *Chem. Des. Automat. News*, 1993, **8**, 31.

9 S. Al-Jibori, M. Hall, A. T. Hutton and B. L. Shaw, *J. Chem. Soc., Dalton Trans.*, 1984, 863.

10 J.-M. Camus, D. Morales, J. Andrieu, P. Richard, R. Poli, P. Braunstein and F. Naud, *J. Chem. Soc., Dalton Trans.*, 2000, 2577.

11 N. G. Jones, M. L. H. Green, X. Morise, L. Rees and D. Watkin, *34th Conference on Coordination Chemistry*, Edinburgh, 2000, poster abstract P0453.

12 A. D. Burrows, M. F. Mahon and M. T. Palmer, *J. Chem. Soc., Dalton Trans.*, 2000, 1669.

13 J. L. Atwood, A. H. Cowley, W. E. Hunter and S. K. Mehrota, *Inorg. Chem.*, 1982, **21**, 1354.

14 D. L. Beach, M. Dattilo and K. W. Barnett, *J. Organomet. Chem.*, 1977, **140**, 47; L. J. Todd, J. R. Wilkinson, J. P. Hickey, D. L. Beach and K. W. Barnett, *J. Organomet. Chem.*, 1978, **154**, 151.

15 G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 1990, **46**, 467.

16 G. M. Sheldrick, SHELXL-97, Computer Program for Crystal Structure Refinement, University of Göttingen, 1997.

17 P. McArdle, *J. Appl. Crystallogr.*, 1995, **28**, 65.