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FULL PAPER

A convenient method for selective substitutions at the backbone of a co-ordinated imidazolylphosphine P–N ligand. Single crystal X-ray analyses of $[Mo(CO)_4(MeImCH_2PPh_2)]$ and its ethyl substituted derivative $[Mo(CO)_4(MeImCHEtPPh_2)]$†

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The complex $[Mo(CO)_4(PN)]$ **1** was synthesized by refluxing $[Mo(CO)_6]$, with 2-(diphenylphosphinomethyl)-1-methylimidazole (PN) in ethanol in the presence of $NaBH_4$. The co-ordinated PN is selectively deprotonated to afford a carbanion $[Mo(CO)_4(MeImCHPPh_2)]^-$ **1a** when **1** is treated with strong bases such as methyllithium or n-butyllithium at room temperature. The carbanion **1a** readily reacted with deuterium oxide, methyl iodide, ethyl iodide, allyl bromide, and trimethylsilyl chloride to give $[Mo(CO)_4(MeImCHRPPh_2)]$ (R = D **2**, Me **3**, Et **4**, $CH_2{=}CHCH_2$ **5** or $SiMe_3$ **6**). Treatment of **1a** with chlorodiphenylphosphine and benzoyl chloride gave the corresponding derivatives $[Mo(CO)_4\{MeImCH(PPh_2)_2\}]\cdot 0.5H_2O$ **7** and $[Mo(CO)_4\{MeImCH(COPh)PPh_2\}]\cdot H_2O$ **8** respectively, both containing an additional free donor site. However, slow addition of acetyl chloride to a tetrahydrofuran solution of **1a** gave the O-acetyl enolate derivative $[Mo(CO)_4\{MeImC{=}CMe(OCOMe)PPh_2\}]\cdot 0.5H_2O$ **9** instead of an acetyl derivative. The ^1H and ^{31}P NMR spectra indicated the presence of two geometric isomers (*Z* and *E*) for complex **9**. All of these complexes were fully characterized by IR, ^1H and ^{31}P NMR. The molecular structures of complex **1** and its ethyl substituted derivative **4** have also been studied by single crystal X-ray analyses.

Introduction

Complexes of bidentate P–N or P–O ligands containing hard and soft donor atoms show interesting properties in co-ordination chemistry and catalysis.[1] These ligands are hemilabile in their metal complexes due to the presence of hard and soft donor sites. Therefore the ligand bite can be opened easily by other ligands or solvent molecules. This is the special characteristic for the complexes which might have applications in homogeneous catalysis in C–C bond forming reactions such as oligomerization of olefines,[2] copolymerization of CO/ethylene[3] and telomerization of butadiene.[4] The incorporation of a chiral center into such ligands allows enantioselectivity in catalytic transformation mediated by complexes of these ligands.[5] Enantiopure ferrocenyl P–N ligands have been successfully used in various catalytic reactions including allylic alkylations, allylic aminations, hydroborations and Grignard cross-coupling reactions.[6] Recently we have reported the synthesis of two new bidentate P–N ligands containing an imidazolyl N-donor and their co-ordination behaviors toward some first row transition metal ions.[7]

It is well established that, on co-ordination of tertiary phosphines, the hydrogen of a CH in the α position to the co-ordinated phosphorus becomes much more acidic and can easily be deprotonated by strong bases. These co-ordinated carbanions cleanly react with various electrophiles to give selectively substituted derivatives in high yields.[8] Some of these derivatives show interesting properties and give unexpected products with other reagents. Treatment of $[W(CO)_4\{Ph_2PCH(COPh)PPh_2]$ with hydrazine hydrate causes a 4- to 7-membered chelate ring expansion to give the complex $[W(CO)_4\{Ph_2PNHN{=}C(Ph)CH_2PPh_2\}]$.[9] The "free" phosphine ligands which have an active hydrogen might be deprotonated by strong bases but selective substitutions are not achieved always. For example, the free anion $[Ph_2PCHPPh_2]^-$, which is an ambidentate nucleophile, can be attacked at carbon or phosphorus atoms; Ph_2PCl attacks it mainly at carbon whereas the aliphatic analogues, R_2PCl, attack it predominantly at phosphorus.[10] We anticipated that it is also possible to modify the P–N ligands conveniently when they co-ordinated.

Here we report a convenient method for selective substitutions at the backbone of the ligand 2-(diphenylphosphinomethyl)-1-methylimidazole (PN) (Chart 1) in its molybdenum(0) complex. In the complex $[Mo(CO)_4(PN)]$ **1** the PN ligand is selectively deprotonated at its backbone methylene carbon by the action of n-butyllithium or methyllithium at room temperature to give the carbanion $[Mo(CO)_4(MeImCHPPh_2)]^-$ **1a**. The co-ordinated carbanion **1a** can react with various electrophiles to give selectively substituted derivatives in high yields. Such modification of the PN ligand is significant because we can tune the electronic and steric properties of the ligands by choosing an appropriate substituent and can design the ligands which are suitable for catalysis. The substituted derivatives synthesized from complex **1** are summarized in Scheme 1. The single crystal structures of the parent complex **1** and its ethyl substituted derivative $[Mo(CO)_4(MeImCHEtPPh_2)]$ **4** are also discussed.

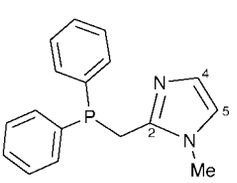


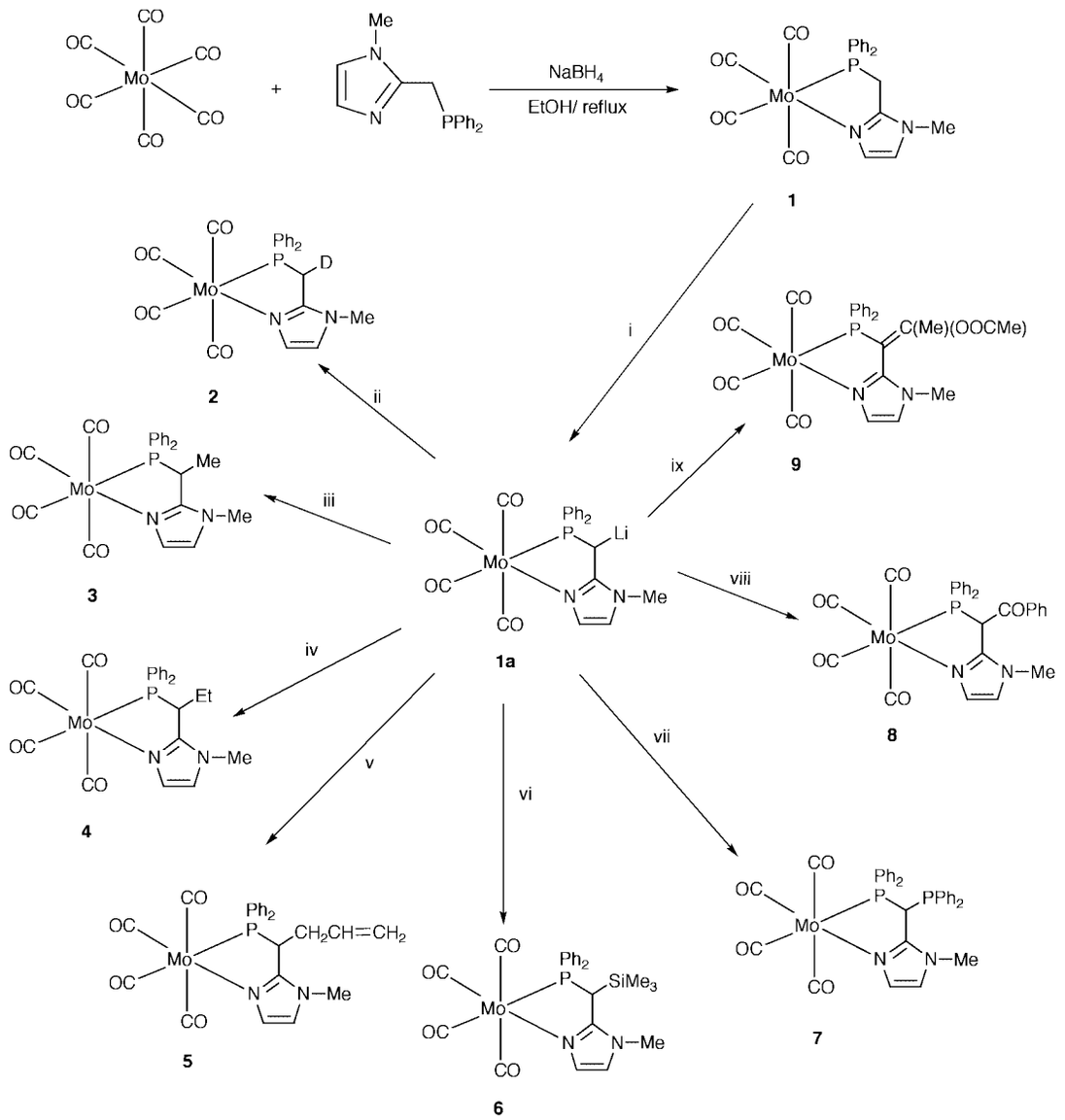
Chart 1

Results and discussion

Synthesis and characterization of complexes

All spectroscopic data for the complexes are given in Table 1. Treatment of $[Mo(CO)_6]$ with an equimolar amount of the

† *Supplementary data available*: rotatable 3-D crystal structure diagram in CHIME format. See http://www.rsc.org/suppdata/dt/1999/3499/



Scheme 1 (i) MeLi or nBuLi/THF or $(Et)_2O$; (ii) D_2O; (iii) MeI; (iv) EtI; (v) $BrCH_2CH{=}CH_2$; (vi) Me_3SiCl; (vii) PPh_2Cl; (viii) PhCOCl; (ix) MeCOCl.

ligand hydrobromide PN·HBr and triethylamine in boiling ethanol in the presence of $NaBH_4$[11] gave the tetracarbonyl complex **1** in 85% yield. This complex was characterized by elemental analysis, NMR and IR spectroscopy. The ν(CO) bands are characteristic for a $[(OC)_4Mo]$ entity[12] (Table1). The co-ordination of the phosphorus atom is evident from its ^{31}P NMR. The resonance was observed at δ 45.88 in contrast to that of the "free" ligand (δ −15.54). The co-ordination of the imidazolyl nitrogen atom is evident from the significant downfield chemical shift of the H^4 proton resonance in the ^1H NMR compared to the corresponding signal of the "free" ligand.[7] The H^4 resonance was observed at δ 7.05 whereas, for the "free" ligand it appeared at δ 6.88. Finally the above formulation was confirmed by its single crystal X-ray analysis (see below).

Treatment of a tetrahydrofuran solution of the molybdenum complex **1** with equimolar amount of methyllithium at room temperature gave a bright orange solution. The ^{31}P NMR spectrum showed a singlet phosphorus resonance at δ 33.11. This species can survive for a long time in solution in the absence of air or moisture but reacts rapidly with moisture to regenerate the parent complex. The product is presumably a lithio-derivative $[Mo(CO)_4(MeImCHLiPPh_2)]$ or $Li[Mo(CO)_4(MeImCHPPh_2)]$. When diethyl ether was used as a solvent and n-butyllithium as a base the deprotonation also occurred at the same carbon atom but in this case orange precipitation was formed.

We have studied the action of D_2O on the carbanion **1a** in an attempt to effect monodeuteriation at the backbone carbon atom. An equimolar amount of D_2O was added to a tetrahydofuran solution of this carbanion, generated by adding methyllithium to a tetrahydrofuran solution of **1**. The ^1H NMR spectrum showed a resonance at δ 3.49 with $^2J_{PH} = 7.80$ Hz for the backbone CH. No H–D coupling was observed but the CHD resonance was slightly broader than the resonance of CH_2 in **1**. The ^{31}P NMR spectrum of **2** was almost identical to that of **1**, except that the resonance was shifted by *ca.* 0.25 ppm to lower frequency from that of the undeuteriated complex **1**. The ^{31}P resonance of the deuteriated complex was slightly broader than that of the undeuteriated complex.

Methylation of the carbanion **1a** was successfully achieved by treatment of a THF solution of **1** with an equimolar amount of MeLi followed by addition of methyl iodide. This produced the required methylated complex **3** in 82% yield. The substituted methyl (CH_3) protons were observed at δ 1.07 as a double doublet.

We have also prepared analogues of complex **3** by alkylating the carbanion of **1a** with ethyl iodide and allyl bromide giving the ethyl derivative **4** and the allyl derivative **5** respectively. Preparative details are in the Experimental section and character-

Table 1 IR and NMR data of complexes

Complex	ν(CO)[a]	^{1}H (δ)[b]	^{31}P (δ)[c]
1	2013, 1909, 1878, 1820	3.51 (d, 2 H, CH_2), 3.69 (s, 3 H, NCH_3), 6.85 (d, 1 H, H^5), 7.05 (d, 1 H, H^4), 7.40–7.54 (m, 10 H, Ph)	45.88
2	2013, 1896, 1880, 1832	3.49 (d, 1 H, CHD), 3.69 (s, 3 H, NCH_3), 6.85 (d, 1 H, H^5), 7.05 (d, 1 H, H^4), 7.41–7.51 (m, 10 H, Ph)	45.63
3	2011, 1911, 1878, 1828	1.07 (q, 3 H, CH_3), 3.77 (s, 3 H, NCH_3), 3.85 (m, 1 H, PCH), 6.85 (d, 1 H, H^5), 7.01 (d, 1 H, H^4), 6.93–7.86 (m, 10 H, Ph)	58.66
4	2013, 1913, 1876, 1822	0.76 (t, 3 H, CH_3), 1.46 (m, 1 H, CH_2), 1.74 (m, 1 H, CH_2), 3.67 (m, 1 H, PCH), 3.79 (s, 3 H, NCH_3), 6.88 (d, 1 H, H^5), 7.08 (d, 1 H, H^4), 6.90–7.85 (m, 10 H, Ph)	59.25
5	2013, 1907, 1872, 1834	2.00 (m, 1 H, CH_2CH), 2.34 (m, 1 H, CH_2CH), 3.66 (s, 3 H, NCH_3), 3.76 (m, 1 H, PCH), 4.80 (m, 2 H, CH=CH_2), 5.42 (m, 1 H, CH=CH_2), 6.77 (d, 1 H, H^5), 7.01 (d, 1 H, H^4), 6.80–7.81 (m, 10 H, Ph)	59.54
6	2011, 1909, 1880, 1826	0.00 (s, 9 H, $SiMe_3$), 3.80 (d, 1 H, PCH), 3.97 (s, 3 H, NCH_3), 7.05 (d, 1 H, H^5), 7.26 (d, 1 H, H^5), 7.01–8.12 (m, 10 H, Ph)	51.92
7	2017, 1909, 1882, 1810	2.91 (s, 3 H, NCH_3), 4.82 (d, 1 H, PCH), 6.51 (s, 1 H, H^5), 6.59 (s, 1 H, H^4), 7.01–7.52 (m, 20 H, Ph)	62.03, 10.48 J_{PP} = 46.45 Hz
8	2015, 1901, 1884, 1836, 1676	3.54 (s, 3 H, NCH_3), 5.83 (d, 1 H, PCH), 6.87 (s, 1 H, H^5), 7.04 (d, 1 H, H^4), 7.02–7.57 (m, 15 H, Ph)	66.69
9	2011, 1907, 1882, 1837, 1760, 1161	1.32 (s, 3 H, =CCH_3), 2.03 (s, 3 H, $COCH_3$), 3.72 (s, 3 H, NCH_3), 6.82 (s, 1 H, H^5), 7.08 (s, 1 H, H^4), 7.40–7.82 (m, 10 H, Ph) (major isomer); 1.22 (s, 3 H, CCH_3), 2.06 (s, 3 H, $COCH_3$), 3.64 (s, 3 H, NCH_3), 6.79 (s, 1 H, H^5), 7.04 (s, 1 H, H^4), 7.40–7.82 (m, 10 H, Ph) (minor isomer)	58.90 (major) 57.11 (minor)

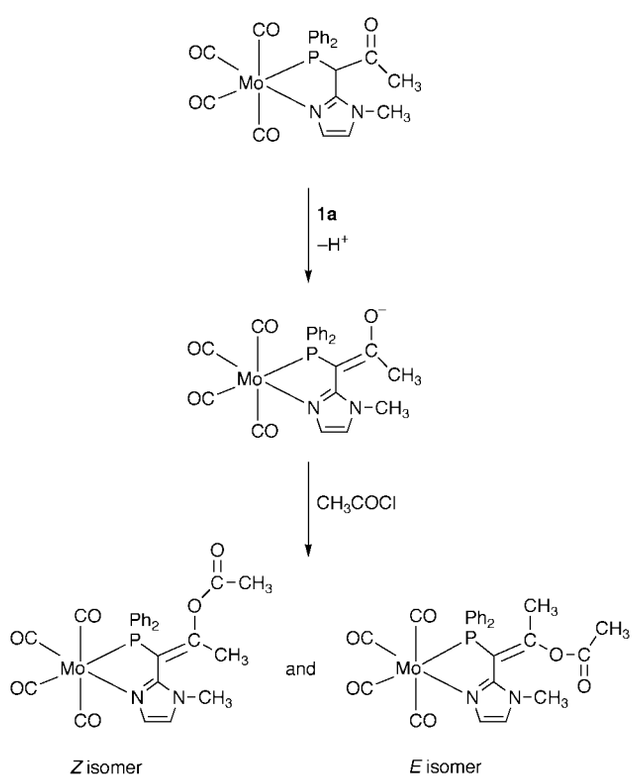
[a] Recorded with the KBr disk method. [b] Recorded at 400 or 300 MHz in $CDCl_3$ at 23 °C, chemical shifts in ppm relative to $SiMe_4$. [c] Recorded at 400 MHz in $CDCl_3$ at 23 °C, chemical shifts in ppm relative to 85% H_3PO_4.

izing data in Table 1. In both complexes **4** and **5** where the substituent is of the type CH_2R the methylene protons are diastereotopic. For the ethyl derivative **4** two kinds of methylene protons (CH_2CH_3) were observed at δ 1.46 and 1.74 as a complex multiplet. The methine proton appeared at δ 3.67 as a multiplet. The ^{31}P NMR spectrum at 23 °C showed only one resonance at δ 59.25 indicating the presence of one conformer. For the allyl derivative **5** the resonances of the diastereotopic methylene (CH_2CH) protons were also observed separately as a complex multiplet. One is centered at δ 2.00 and another at δ 2.34. The backbone methine proton [$CH(CH_2CH{=}CH_2)$] gave a multiple at δ 3.76. The ^{31}P NMR spectrum also showed one resonance at δ 59.54 indicating the presence of one conformer.

We have also prepared the trimethylsilyl derivative **6** by treating complex **1** in diethyl ether with n-butyllithium followed by addition of trimethylsilyl chloride. Details of this preparation and the characterizing data are in the Experimental section and Table 1. However, when the carbanion **1a** was treated with 2-bromopropane we were unable to isolate the desired substitution product. Some impure products were recovered.

It is also possible to attach a variety of functional groups to the backbone carbon atom using this co-ordinated carbanion. When a solution of the carbanion **1a** was treated with chlorodiphenylphosphine the corresponding derivative **7** was obtained. For the preparation of the benzoyl derivative **8** the carbanion **1a** should be reversibly added to benzoyl chloride. Details of these preparations and the characterizing data are in the Experimental section and Table 1. Normal addition of benzoyl chloride to the carbanion **1a** gave a mixture of complexes which we were unable to separate in pure form. Attachment of these additional electron-withdrawing groups into the backbone of the PN caused high deshielding of the backbone methine proton and the corresponding resonances were observed at δ 4.82 and 5.83 respectively. In complex **7** the substituted PPh_2 group is unco-ordinated which is evident from the observation of two non-equivalent phosphorus resonances in the ^{31}P NMR spectrum at δ 62.03 (co-ordinated) and 10.48 (unco-ordinated) respectively, as a doublet with J_{PP} = 46 Hz.

We observed the formation of the O-acetyl enolate derivative **9** in 37% yield instead of an acetyl derivative when acetyl chloride was added slowly to a tetrahydrofuran solution of the carbanion **1a**. Probably this reaction proceeds through an intermediate acetyl derivative. Therefore, slow addition of acetyl chloride to the carbanion **1a** afforded first an acetyl derivative, which readily converted into the enolate ion in the presence of excess of carbanion **1a** in the reaction bulk. This enolate ion reacted with additional acetyl chloride to give complex **9** (Scheme 2). However, we could not prepare a monoacetyl



Scheme 2

derivative in pure form even by reverse addition of **1a** to acetyl chloride.

The IR spectrum of complex **9** showed two additional strong bands at 1760 and 1161 cm^{-1} for ν(C=O) and ν(C–O) respectively. The ^{1}H NMR spectrum showed two sets of proton signals in an intensity ratio of 7:3 indicating the existence of two geometric isomers (*Z* and *E*) (Scheme 2). Two phosphorus resonances are also observed at δ 58.9 and 57.11 for these two isomers. However, we could not separate them.

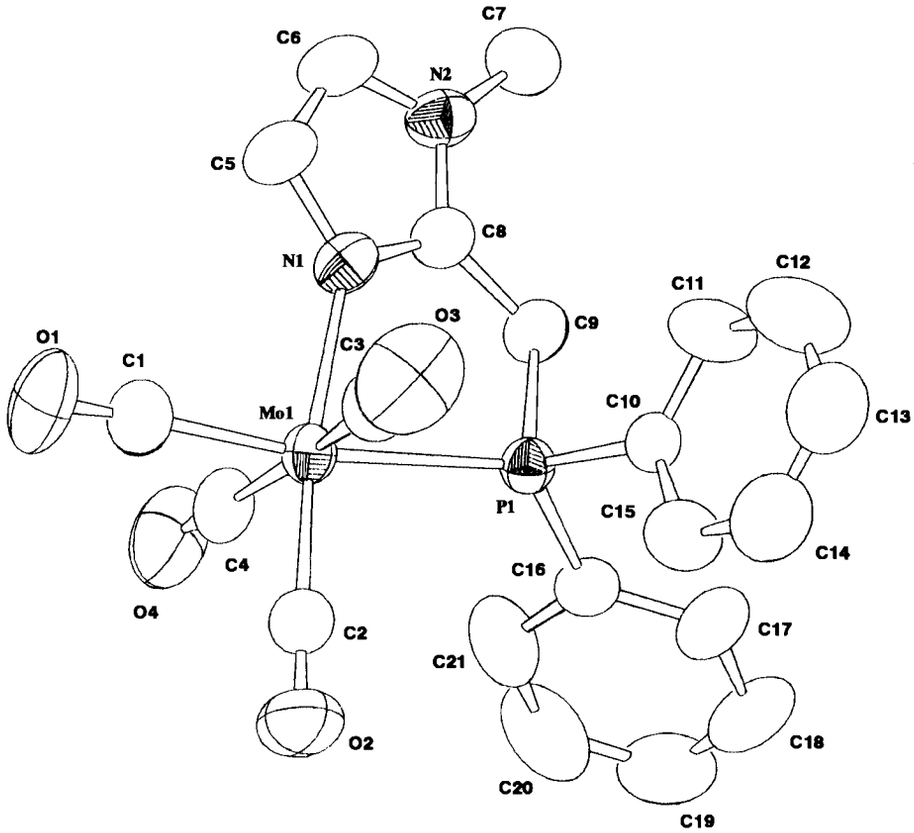


Fig. 1 An ORTEP drawing of the structure of complex **1**. Hydrogen atoms have been omitted for clarity.

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

Mo1–P1	2.5053(6)	P1–C10	1.814(2)
Mo1–N1	2.264(2)	P1–C16	1.831(3)
Mo1–C1	1.997(3)	O1–C1	1.140(4)
Mo1–C2	1.945(3)	O2–C2	1.173(4)
Mo1–C3	2.043(3)	O3–C3	1.130(4)
Mo1–C4	2.027(3)	O4–C4	1.135(4)
P1–C9	1.850(2)	N1–C8	1.353(3)
P1–Mo1–N1	75.34(5)	P1–Mo1–C1	171.73(9)
P1–Mo1–C2	97.25(8)	P1–Mo1–C3	92.03(9)
P1–Mo1–C4	93.72(8)	N1–Mo1–C1	96.7(1)
N1–Mo1–C2	172.47(9)	N1–Mo1–C3	91.4(1)
N1–Mo1–C4	90.8(1)	C1–Mo1–C2	90.7(1)
C1–Mo1–C3	86.0(1)	C1–Mo1–C4	88.4(1)
C2–Mo1–C3	87.5(1)	C2–Mo1–C4	91.1(1)
C3–Mo1–C4	174.2(1)		

Table 3 Selected bond lengths (Å) and angles (°) for compound **4**

Mo1–P1	2.5266(7)	P1–C18	1.840(3)
Mo1–N1	2.273(2)	O1–C1	1.153(4)
Mo1–C1	1.976(3)	O2–C2	1.158(4)
Mo1–C2	1.949(3)	O3–C3	1.140(4)
Mo1–C3	2.024(3)	O4–C4	1.137(4)
Mo1–C4	2.039(3)	C9–C10	1.551(4)
P1–C9	1.876(3)	C10–C11	1.485(6)
P1–C12	1.819(3)	N1–C8	1.331(4)
P1–Mo1–N1	74.03(6)	P1–Mo1–C1	169.5(1)
P1–Mo1–C2	100.85(10)	P1–Mo1–C3	92.84(9)
P1–Mo1–C4	93.00(10)	N1–Mo1–C1	95.5(1)
N1–Mo1–C2	174.9(1)	N1–Mo1–C3	92.1(1)
N1–Mo1–C4	94.1(1)	C1–Mo1–C2	89.6(1)
C1–Mo1–C3	86.2(1)	C1–Mo1–C4	88.91(1)
C2–Mo1–C3	88.2(1)	C2–Mo1–C4	86.0(2)
C3–Mo1–C4	172.5(1)		

Crystallographic studies of complexes 1 and 4

Slow evaporation of an ethanolic solution of complex **1** yielded light yellow crystals suitable for X-ray analysis. The molecular structure of **1** is presented in Fig. 1 as an ORTEP diagram;[13] selected bond distances and bond angles are listed in Table 2. The distorted octahedral geometry around molybdenum comprises of one imidazolyl nitrogen and one phosphorus donor from the PN ligand and four carbonyl ligands. The coordination of the PN ligand results in the formation of a five membered chelate ring. The Mo–P distance of 2.5053(6) Å is in the range reported previously for other phosphine complexes of molybdenum carbonyls. The Mo–N distance is 2.264(2) Å which is significantly shorter than those reported for a closely related compound $[Mo(CO)_4(Ph_2PC_6H_4NH_2)]$, 2.326(2) Å, and other molybdenum tetracarbonyl complexes of P–N ligands.[14,15] The Mo–C distances for the carbonyls *trans* to the phosphorus and nitrogen are 1.997(3) and 1.945(3) Å respectively. The significant shortening of the Mo–C (CO) bond *trans* to the imidazolyl nitrogen donor reflects the higher donor: acceptor ratio of the nitrogen donor relative to a phosphine ligand. Both of these Mo–C bond distances are shorter than those for the mutually *trans* axial carbonyls, as is expected for the poorer π acceptor ability of phosphorus and imidazole compared with carbonyl. The Mo–C bond distances of the mutually *trans* carbonyls are 2.043(3) Å for C3 and 2.027(3) Å for C4.

The geometry around molybdenum reveals a distortion of the carbonyls away from the PN ligand, presumably due to steric hindrance. The bite angle P1–Mo1–N1 is 75.34(5)°, which is significantly smaller than the ideal angle (90°). All P–Mo–C and N–Mo–C angles slightly exceed 90°, with the largest deviations being 97.25(8) and 96.7(1)° for P1–Mo1–C2 and N1–Mo1–C1, respectively. The distortion from an idealized octahedral geometry is also apparent by noting that *trans* C3–Mo1–C4 and P1–Mo1–C1 angles vary from 174.2(1) to 171.73(9)°.

Crystals of complex **4** suitable for X-ray analysis were also obtained from an ethanolic solution. The ORTEP diagram of **4**

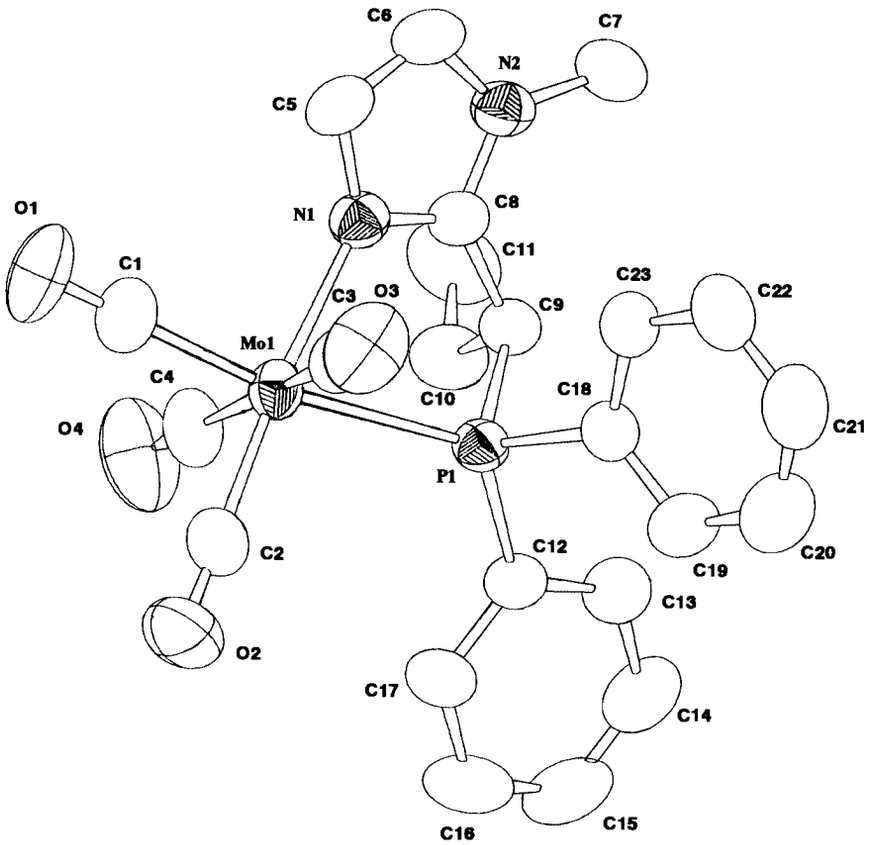


Fig. 2 An ORTEP drawing of the structure of complex **4**. Hydrogen atoms have been omitted for clarity.

is presented in Fig. 2; selected bond distances and bond angles are in Table 3. The structural differences of **4** from **1** can be ascribed to the larger steric bulk of the ethyl substituted PN ligand. To minimize the steric interactions between the substituted ethyl group and the other parts of the ligand, the Mo–P and P–C bond distances slightly increased relative to those found for **1**. The Mo1–P1 bond distance is 2.5266(7) Å which is 0.02 Å longer than that of **1**. The P–C bond distance of 1.876(3) Å for C9 of **4** is considerably elongated compared with the corresponding 1.850(2) Å for C9 of **1**. The increased steric interaction has also affected the dimensions of the $Mo(CO)_4$ portion of the molecule. The angles P1–Mo1–C2 [100.85(10)°] and N1–Mo1–C4 [94.1(1)°] are significantly larger compared with the corresponding angles of **1** [97.25(8) and 90.8(1)° respectively]. The Mo–C bond distances for the carbonyls *trans* to the phosphorus and nitrogen are 1.976(3) and 1.949(3) Å respectively, those for carbonyls *trans* to each other are 2.024(3) for C3 and 2.039(3) for C4.

Conclusion

An air stable molybdenum(0) tetracarbonyl complex of the PN ligand has been synthesized in good yield which is selectively deprotonated by the action of strong bases to give the carbanion **1a**. Several alkylated derivatives have been prepared by treating this carbanion with alkyl halides. Mono deuteriated and silylated derivatives have also been prepared similarly by using deuterium oxide and trimethylsilyl chloride respectively. The functional groups PPh_2, COPh have also been successfully attached to the backbone of the PN ligand. This attachment afforded a pendant free donor site which can act as a bridging ligand and/or be co-ordinated to the same metal center. Therefore, those may provide a wide choice of metals for preparing either homo- or hetero-bimetallic complexes. It is also possible to condense various amines with the substituted keto derivatives, resulting in the formation of potential tripodal ligands. Therefore, we can synthesize a variety of modified PN ligands conveniently from this co-ordinated carbanion.

Experimental

Methods

All reactions were run in oven-dried glassware under an atmosphere of N_2 gas. Anhydrous THF used in reactions was distilled prior to use from sodium–benzophenone. All chemicals were reagent grade used as received. The ligand 2-(diphenylphosphinomethyl)-1-methylimidazole (PN) was prepared according to our previously reported method.[7]

Instruments

All NMR spectra were recorded with a JEOL JMTC 400/54 or 300/54 spectrometer. Tetramethylsilane was used as an internal reference for ^1H and ^{31}P NMR spectra were referenced to 85% H_3PO_4 sealed in a melting point capillary tube. The IR spectra were recorded with the KBr disk method on a Horiba FT-300 spectrometer. Elemental analyses were performed by Faculty of Pharmaceutical Science, Kanazawa University.

Preparations

$[Mo(CO)_4(PN)]$ 1. The PN·HBr (2 mmol, 0.72 g) was dissolved in 50 ml of 95% ethanol followed by addition of 280 μl triethylamine (2 mmol). After 10 min, 0.53 g of molybdenum hexacarbonyl (2 mmol) was added, followed by 0.08 g of $NaBH_4$ (2.1 mmol), and the mixture refluxed under nitrogen for 3 h. The solution was cooled to room temperature under a N_2 atmosphere, then 20 ml of water were added. The mixture was stored at −20 °C for 1 h and filtered. The solid was redissolved into acetone and filtered. Evaporation of acetone from the filtrate gave pale yellow microcrystals which were dried *in vacuo* (yield 0.83 g, 85%) (Found: C, 51.53; H, 3.40; N, 5.75. $C_{21}H_{17}MoN_2O_4P$ requires C, 51.63; H, 3.51; N, 5.73%).

[Mo(CO)$_4$(MeImCHDPPh$_2$)] 2. A solution of compound **1** (1 mmol, 0.49 g) in tetrahydrofuran (5 ml) was treated with a solution of 1.4 M methyllithium (1 mmol, 714 μl) in diethyl ether. The mixture was stirred for 1 h, D_2O (1.2 mmol, 22 μl) then added and stirred for 30 min. All solvents were removed and the residue was extracted into chloroform. The product was isolated as yellow microcrystals (yield 0.40 g, 83%) by evaporation of the solvent.

[Mo(CO)$_4$(MeImCHMePPh$_2$)] 3. A solution of compound **1** (1 mmol, 0.49 g) in tetrahydrofuran (5 ml) was treated as above, and the resultant carbanion was then treated with methyl iodide (1.2 mmol, 75 μl). After 30 min all the solvents were removed and the product was extracted into chloroform. Evaporation of the solvent and addition of ethanol (1 ml) gave the desired product as yellow microcrystals (yield 0.41 g, 82%) (Found: C, 52.19; H, 3.69; N, 5.42. $C_{22}H_{19}MoN_2O_4P$ requires C, 52.60; H, 3.81; N, 5.57%).

[Mo(CO)$_4$(MeImCHEtPPh$_2$)] 4. The ethyl substituted derivative **4** was prepared similarly to **3** using ethyl iodide as alkylating agent and isolated as yellow microcrystals (yield 77%) (Found: C, 53.36; H, 3.95; N, 5.24. $C_{23}H_{21}MoN_2O_4P$ requires C, 53.50; H, 4.01; N, 5.42%).

[Mo(CO)$_4${MeImCH(CH$_2$CH=CH$_2$)PPh$_2$}] 5. A solution of compound **1** (1 mmol, 0.49 g) in diethyl ether (120 ml) was treated with 1.6 M nBuLi (1 mmol, 625 μl) in hexane. The mixture was stirred for 1 h, allyl bromide (1 mmol, 86 μl) then added and stirred for 40 min. All the solvents were removed *in vacuo* and the product was extracted into chloroform. Removal of chloroform gave the product as a yellow powder (yield 0.38 g, 73%) (Found: C, 54.00; H, 3.91; N, 5.44. $C_{24}H_{21}MoN_2O_4P$ requires C, 54.55; H, 4.00; N, 5.30%).

[Mo(CO)$_4$(MeImCHSiMe$_3$PPh$_2$)]·0.5H$_2$O 6. A solution of complex **1** (1 mmol, 0.49 g) in diethyl ether (120 ml) was treated with 1.6 M nBuLi (1 mmol, 625 μl) in hexane. The mixture was stirred for 1 h, trimethylsilyl chloride (1 mmol, 127 μl) then added rapidly and stirred for 30 min. All the solvents were removed by an evaporator and addition of ethanol (3 ml) and water (2 ml) gave the silyl derivative as a pale yellow powder (yield 0.43 g, 75%) (Found: C, 50.47; H, 4.29; N, 4.98. $C_{24}H_{25}MoN_2O_4PSi\cdot0.5H_2O$ requires C, 50.62; H, 4.60; N, 4.92%).

[Mo(CO)$_4${MeImCH(PPh$_2$)$_2$}]·0.5H$_2$O 7. This complex was prepared similarly to **3** using chlorodiphenylphosphine (yield 80%) (Found: C, 58.25; H, 3.79; N, 4.02. $C_{33}H_{26}MoN_2O_4P_2\cdot0.5H_2O$ requires: C, 58.16; H, 3.99; N, 4.11%).

[Mo(CO)$_4${MeImCH(COPh)PPh$_2$}]·H$_2$O 8. A solution of complex **1** (1 mmol, 0.49 g) in diethyl ether (120 ml) was treated with 1.6 M nBuLi (1 mmol, 625 μl) in hexane and the mixture stirred for 1 h. The yellow suspension of the carbanion was then transferred slowly *via* a cannula to a diethyl ether (5 ml) solution of benzoyl chloride (1 mmol, 116 μl) and stirred for 30 min. All the solvents were removed and the product was extracted into chloroform. The residue was then chromatographed on silica gel. Gradient elution using benzene–acetone mixture (4 : 1) gave a yellow band which was collected and solvents were removed *in vacuo*. Addition of ethanol (1 ml) gave the desired product as a yellow powder (yield 0.31 g, 51%) (Found: C, 54.98; H, 3.60; N, 4.88. $C_{28}H_{21}MoN_2O_5P\cdot H_2O$ requires C, 55.09; H, 3.79; N, 4.59%).

[Mo(CO)$_4${MeImC=CMe(OCOMe)PPh$_2$}]·0.5H$_2$O 9. A solution of compound **1** (1 mmol, 0.49 g) in tetrahydrofuran (5 ml) was treated with 1.4 M methyllithium (1 mmol, 714 μl) in diethyl ether and stirred for 1 h. Acetyl chloride (1.2 mmol, 85 μl) was then added slowly and the mixture stirred for 30 min. All the solvents were removed and the product was extracted into chloroform. The residue was then chromatographed on silica gel. Gradient elution using benzene–acetone (4 : 1) gave a yellow band which was collected and solvents were removed *in vacuo.* The residue was dissolved in ethanol (2ml) and hexane added until precipitation occurred. The precipitate was collected and dried *in vacuo* (yield 0.21 g, 37%) (Found: C, 51.88; H, 3.93; N, 4.80. $C_{25}H_{21}MoN_2O_6P\cdot0.5H_2O$ requires C, 51.65; H, 3.81; N, 4.82%).

Table 4 Crystallographic data of complexes **1** and **4**

	1	**4**
Empirical formula	$C_{21}H_{17}MoN_2O_4P$	$C_{23}H_{21}MoN_2O_4P$
M	488.29	516.34
Crystal dimensions/mm	0.40 × 0.40 × 0.60	0.25 × 0.25 × 0.40
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a/Å	17.554(1)	11.453(1)
b/Å	7.617(1)	10.396(2)
c/Å	17.100(1)	19.428(2)
β/°	108.266(7)	93.33(1)
U/Å^3	2171.2(4)	2309.3(5)
Z	4	4
μ(Mo-Kα)/cm^{-1}	7.05	6.67
Number of reflections (total)	5494	5869
(unique)	5327	5594
R_{int}	0.006	0.020
R, R'	0.026, 0.050	0.027, 0.045

X-Ray crystallographic studies

Crystallographic data are summarized in Table 4. Measurements of both complexes were performed on a Rigaku AFC7R diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71070 Å) at room temperature. Each single crystal of **1** and **4** was mounted on a glass fiber. The data were collected using an ω–2θ scan technique to a maximum 2θ value of 55° at a scan speed of 16.0° min^{-1} for **1** and at 8.0° min^{-1} (in ω) for **3**. The weak reflections ($I < 10.0\sigma(I)$) were rescanned (maximum of 5 scans) and the counts accumulated to ensure good counting statistics. Stationary background counts were recorded on each side of the reflection. The intensity data were corrected for Lorentz-polarization effects and the absorption corrections were performed on the basis of ψ scans.

The structure of complex **1** was solved by a direct method [16] and that of **4** by heavy atom Patterson methods [17] and expanded using Fourier techniques.[18] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation but not refined. All calculations were performed using the TEXSAN [19] crystallographic software package. Complex neutral atom scattering factors were taken from ref. 20.

CCDC reference number 186/1611.

See http://www.rsc.org/suppdata/dt/1999/3499/ for crystallographic files in .cif format.

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