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Carbene complexes

XXII *. Preparation, properties and structures of the *N*,*N*-functionalized bis(amino)carbenemolybdenum(0) carbonyls $[Mo(CO)_4\{CN(CH_2CH:CH_2)(CH_2)_2N(CH_2CH:CH_2)\}]$ and $+Mo(CO)_3\{CN[(CH_2)_3PPh_2](CH_2)_2N\{(CH_2)_3PPh_2\}]_n$ **

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Abstract

Treatment of 1,2-bis(γ-diphenylphosphinopropylamino)ethane [obtained from 1,2-bis(allylamino)ethane and $2PPh_2H$ and $CH(NMe_2)(OMe)_2$] yielded the electron-rich enetetramine $\ddagger CN(R)(CH_2)_2NR]_2$ [R = $(CH_2)_3PPh_2$] [abbreviated as $L_2^{(CH_2)_3PPh_2}$]. Although L_2^{All}, the analogue in which R = $CH_2CH:CH_2$, is unknown, the carbenemolybdenum title compounds $[Mo(CO)_4(L^{All})]$ (**3**) and $+Mo(CO)_3\{L^{(CH_2)_3PPh_2}\}]_n$ (**4**) have been prepared from $[Mo(CO)_6]$: for **3** from $CH(NMe_2)(OMe)_2 + [All(H)N(CH_2)]_2$ and for **4** from $L_2^{(CH_2)_3PPh_2}$. In **3** only one of the R groups behaves in a ligating mode. L^{All} being a chelating ligand, **3** is thus a rare example of a metal complex having both carbene- and η^2-alkene-ligation and the first for molybdenum. The presumed polymeric structure of **4** is believed to arise from one of the P^{III} sites behaving in a chelating fashion with the other in a bridging mode. Treatment of **3** with ^{13}CO stereoselectively gave the isotopomer in which a CO *trans* to a CO was displaced, the *trans* effect thus being parallel to the *trans* influence (X-ray data); a coproduct was *cis*-$[Mo(CO)_4(^{13}CO)(L^{All})]$. Similarly, *cis*-$[Mo(CO)_4(L^{All})(PEt_3)]$ was the sole product of reaction between **3** and PEt_3, which upon irradiation yielded *fac*- together with *mer*-$[Mo(CO)_3(L^{All})(PEt_3)]$. Thermolysis of **3** afforded $AllC:N(CH_2)_2NAll$ as the only organic product. The X-ray structure of **3** showed that the mutually *trans* Mo–CO bonds are significantly longer [av. 2.037(5) Å] than Mo–CO *trans* to carbene [1.984(4) Å] or alkene [1.975(5) Å], with $Mo-C_{carb}$ at 2.229(4) Å.

1. Introduction

This series of papers deals with the chemistry of electron-rich carbenemetal complexes $[M(CXY)L_n]$, L_n representing the sum of all other ligands, apart from one carbene CXY, within the inner coordination sphere of the transition metal M. In general, at least one of the groups X or Y attached to the carbene–carbon atom, C_{carb}, has been nitrogen-centred; only in Part 21 was reference made to complexes of the Fischer-type, in that case having o-$C_{carb}(OEt)CH_2C_6H_4CH_2C_{carb}$-(OEt) as bridging ligand [1]. With that exception, our synthetic strategy was to use a metal centre as a carbene-trapping template. The organic precursor, the carbenoid, was sometimes a Vilsmeier reagent such as $CH(NMe_2)Cl_2$, but more often an electron-rich enetetramine (olefin) such as I, abbreviated as L_2^R, in which R is a primary alkyl or an unhindered aryl group. Variants of I included those having (i) six-membered rings,

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* For Part XXI, see ref. 1. No reprints available.

** Dedicated to Professor G.P. Chiusoli, a respected colleague, in recognition of his many significant contributions to organometallic chemistry, on the occasion of his 70th birthday.

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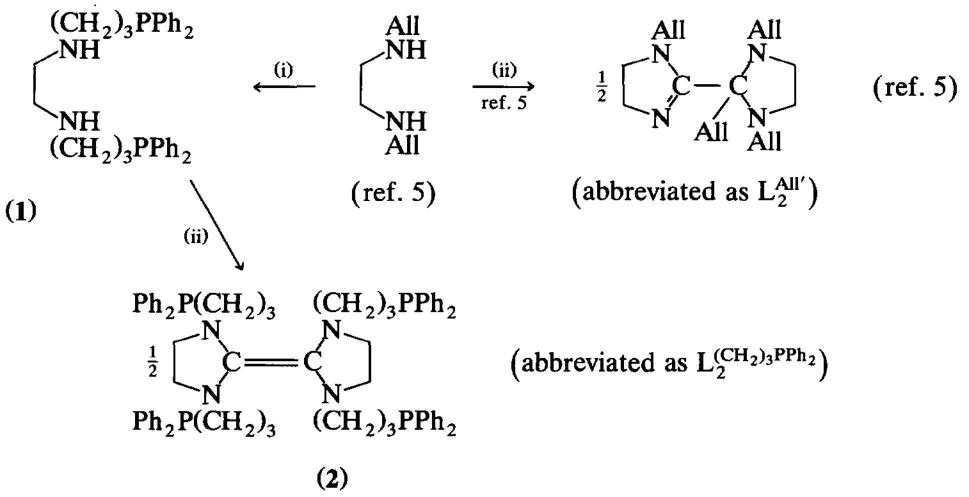
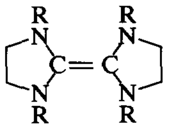


Scheme 1. Synthesis of the *N*-functionalized electron-rich enetetramine **2** [$\mathrm{L}_2^{(\mathrm{CH}_2)_3\mathrm{PPh}_2}$] and an attempt to make the tetra-allyl analogue $\mathrm{L}_2^{\mathrm{All}}$ [5] from All(H)N$(\mathrm{CH}_2)_2$N(H)All (**1**) (All = $\mathrm{CH}_2\mathrm{CH{:}CH}_2$). Reagents and conditions: (i) $2\mathrm{PPh}_2\mathrm{H}$, AIBN (cat.), *hν* (350 nm), 17 h, *ca.* 25°C; (ii) $\mathrm{CH(NMe_2)(OMe)_2}$, c-$\mathrm{MeC_6H_{11}}$, 3 h, 130°C and distilled ($-2\mathrm{MeOH}$, $-\mathrm{Me_2NH}$).

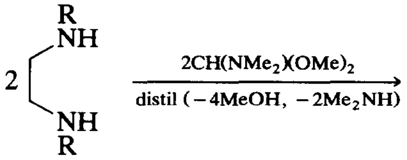


(I)

(ii) one S in place of one NR group in each ring, (iii) $\mathrm{L}_2^{\mathrm{RR}'}$ rather than $\mathrm{L}_2^{\mathrm{R}}$ [2], (iv) the groups R as part of a tetra- or tri-cyclic system [3], and (v) centres of optical activity. This chemistry has been reviewed [3].

The objectives of the work described in this and a forthcoming paper were to seek carbenemetal complexes $[\mathrm{M(L^R)L}_n]$ in which the group R has *ω*-donor functionality, so that $\mathrm{L^R}$ has the potential of being a chelating or a bridging bidentate ligand. In this paper, we report on carbonylmolybdenum(0) complexes containing an $\mathrm{L}^{\mathrm{CH_2CH{:}CH_2}}$ ($\mathrm{L^{All}}$) or $\mathrm{L}^{(\mathrm{CH}_2)_3\mathrm{PPh}_2}$ ligand.

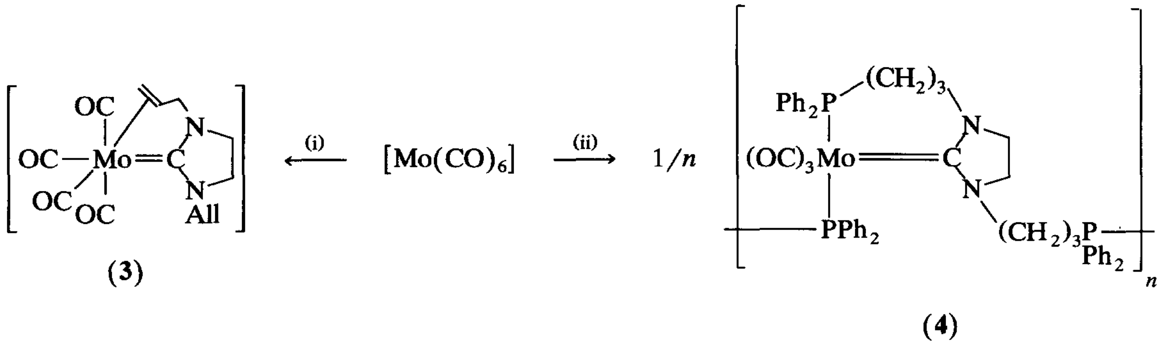
Our general approach to carbenemetal complexes $[\mathrm{M(L^R)L}_n]$ in which R is for example Me, $\mathrm{CH_2Ph}$, or Ph, was to use an enetetramine such as **I** as a precursor. For instance $[\mathrm{Mo(CO)_5(L^{Me})}]$ was made by heating $[\mathrm{Mo(CO)_6}]$ and $\mathrm{L}_2^{\mathrm{Me}}$ in methylcyclohexane at 100°C [4]. Compounds **I** are usually obtained according to eqn. (1).



(1)

For the case of R = All, however, we have previously shown that this reaction does not yield $\mathrm{L}_2^{\mathrm{All}}$ but rather an isomer $\mathrm{L}_2^{\mathrm{All}'}$ (see Scheme 1), presumably as a consequence of a rapid [3,3]- and/or [1,3]-sigmatropic amino-Claisen rearrangement of a transient $\mathrm{L}_2^{\mathrm{All}}$ [5]. Hence an alternative approach is reported here; in reaction (i) of Scheme 2, it is likely that the molybdenum centre may have trapped the labile $\mathrm{L}_2^{\mathrm{All}}$.

In a preliminary communication [6], brief reference was made to some of the results presented here.



Scheme 2. Synthesis of *N*-functionalized-carbenemolybdenum(0) carbonyls **3** and **4** (All = $\mathrm{CH}_2\mathrm{CH{:}CH}_2$). Reagents and conditions: (i) All(H)N$(\mathrm{CH}_2)_2$N(H)All + $\mathrm{CH(NMe_2)(OMe)_2}$, c-$\mathrm{MeC_6H_{11}}$, 100°C, 2 h; (ii) $\frac{1}{2}\mathrm{L}_2^{\mathrm{R}}$ [R = $(\mathrm{CH}_2)_3\mathrm{PPh}_2$], PhMe, 110°C, 2 h.

TABLE 1. Compounds **1**, **3** and **4**: yields, b.p. or m.p. and analytical data

Compound	M.p. (°C)	Yield (%)	Analysis (Found (calcd.) (%))		
			C	H	N
$[\text{Ph}_2\text{P}(\text{CH}_2)_3\text{N(H)CH}_2]_2$ (**1**)	36–38	66	74.9 (75.0)	7.7 (7.4)	5.7 (5.7)
cis-$[\overline{\text{Mo(CO)}_4(\text{L}^{\text{All}}})]$ (**3**)	67–68	30	43.0 (43.5)	4.1 (3.9)	8.1 (7.9)
$\left[cis\text{-Mo(CO)}_3(\text{L}^{(\text{CH}_2)_3\text{PPh}_2})\right]_n$ (**4**)	–	25	61.4 (61.5)	5.2 (5.1)	4.0 (4.0)

2. Experimental details

2.1. General procedure

These have been described previously [5]. Yields, melting and microanalytical data for **1**, *cis*-$[\overline{\text{Mo(CO)}_4(\text{L}^{\text{All}}})]$ (**3**) and $\left[\text{Mo(CO)}_3\{\text{L}^{(\text{CH}_2)_3\text{PPh}_2}\}\right]_n$ (**4**) are shown in Table 1 and IR data are in Table 2. Nuclear magnetic resonance spectral data are in Table 3: ^{1}H and ^{31}P for compounds **1**, **3** and *cis*-$[\text{Mo(CO)}_4(\text{L}^{\text{All}})(\text{PEt}_3)]$ (**6**), and in Table 4: ^{13}C for compounds **1**, $\text{L}_2^{(\text{CH}_2)_3\text{PPh}_2}$ (**2**), and **6**.

2.2. Preparation of $[Ph_2P(CH_2)_3N(H)CH_2]_2$ (1)

A mixture of diphenylphosphine (8.7 g, 0.047 mol), 1,2-bis(*N*-allylamino)ethane [5] (3.2 g, 0.023 mol), and 2,2′-azobis(2-methylpropionitrile) (0.13 g) was irradiated (350 nm) for 17 h, with stirring under argon. The unchanged starting materials were removed from the viscous residue by heating *in vacuo*. The remaining oil was dissolved in tetrahydrofuran (THF) and the solution filtered through Celite. Volatile material was removed from the filtrate *in vacuo* to leave **1** as a viscous oil, which separated as a white microcrystalline solid (7.74 g, 66%). m.p. 36–38°C, from hot ethanol.

2.3. Preparation of $L_2^{(CH_2)_3PPh_2}$ (2)

A mixture of the diamine (**1**) (30 mmol) and an excess of *N*,*N*-dimethylformamide dimethyl acetal (40 mmol) was heated under reflux for *ca*. 3 h in methylcyclohexane (100 cm^3). The mixture was then heated to 130°C under distillation conditions and the methanol and dimethylamine produced were removed together with solvent and excess of $\text{CH(NMe}_2)(\text{OMe})_2$. The residual oil was dissolved in benzene and the solution filtered through Celite. The solvent was removed from the filtrate *in vacuo*, affording compound **2** as a very viscous, yellow, non-volatile oil; efforts to induce it to crystallize were unsuccessful. It was characterized by (a) its ^{13}C NMR spectrum (Table 4), showing *inter alia* the presence of quaternary olefinic carbon atoms; (b) its reaction with water to give the urea $[\text{L}^{(\text{CH}_2)\text{PPh}_2}]\text{O}$; and (c) its reversible oxidation to $[\text{L}_2^{(\text{CH}_2)_3\text{PPh}_2}]^{2+}$. This oxidation was established by cyclic voltammetry in MeCN, with $E = -0.64$ V, $\Delta E_{\text{pp}} = 0.14$ V at a sweep rate of 0.1 V s^{-1} or 0.16 V at a sweep rate of 0.2 V s^{-1} and $i_{\text{p}}^{\text{r}}/i_{\text{p}}^{\text{f}} = 1$, using a platinum electrode with $[\text{N}^n\text{Bu}_4][\text{ClO}_4]$ as supporting electrolyte (0.2 mol dm^{-3} in MeCN) and $[\text{Fe(Cp)}_2]/[\text{Fe(Cp)}_2]^+$ ($E = +0.34$ V) as internal reference (E is the potential measured halfway between the potentials of peak cathodic and anodic currents; ΔE_{pp} is the potential difference between the potentials of peak cathodic and anodic currents; and $i_{\text{p}}^{\text{r}}/i_{\text{p}}^{\text{f}}$ is the ratio of peak-reverse to peak-forward currents).

TABLE 2. Compounds **1**, **3** and **4**: infrared spectroscopic data (ν_{max}) [a]

Compound	ν_{max} (cm^{-1}) (assignment)	Medium
1	3300b [ν(NH)], 1000msh [ν(PC)]	Nujol
3	2020shs, 1920bvs, 1862bvs [ν(CO)]; 1640m [ν(C=C)(free)], 1500sh [$\nu(\text{CN}_2)$]	CH_2Cl_2
4	1910shs, 1820shs, 1790shvs [ν(CO)], 1480sh [$\nu(\text{CN}_2)$]	Nujol

[a] Abbreviations: sh, sharp; b, broad, vs, very strong; s, strong; m, medium.

2.4. Preparation of $\left[Mo(CO)_3(L^{(CH_2)_3PPh_2})\right]_n$ (4)

A toluene solution of $\text{L}_2^{(\text{CH}_2)_3\text{PPh}_2}$ (0.9 g, 0.86 mmol) was added to a stirred suspension of $[\text{Mo(CO)}_6]$ (0.45 g, 1.7 mmol) in toluene. When the mixture was heated the $[\text{Mo(CO)}_6]$ dissolved. Refluxing for 2 h gave a pale yellow powder and a brown solution. The powder was filtered off, washed with benzene, and identified as compound **4** (0.3 g, 25%); it was a microcrystalline solid, insoluble in hot or cold CH_2Cl_2, THF, MeCN, DMSO, or PMe_3.

2.5. Preparation of cis-$[\overline{Mo(CO)_4(L^{All}})]$ (3)

A mixture of $[\text{Mo(CO)}_6]$ (6.33 g, 24 mmol), 1,2-bis(allylamino)ethane (3.37 g, 24 mmol), and $\text{CH(NMe}_2)(\text{OMe})_2$ (3.14 g, 26 mmol) in methylcyclohexane was kept at 100°C for 2 h. Unchanged solid $[\text{Mo(CO)}_6]$ was removed by filtration. Volatiles with traces of

TABLE 3. Compounds **1**, **3** and **6**: ^{1}H and ^{31}P NMR spectroscopic chemical shift (δ) data at 305 K

Compound	Solvent	$N(CH_2)N$	$CH_2:CH$ (free)	$CH_2:CH$ (free)	Other	δ (^{31}P)
1	$CDCl_3$	2.6m			1.1s [b]	−156.9s
3	C_6D_6	2.1–2.5m	5.0m	5.5–5.6m		
$[Mo(CO)_4(L^{All})(PEt_3)]$ (**6**)	C_6D_6	2.8s	4.9–5.1m	5.5–5.9m		−123.2s

[a] Abbreviations: s, singlet; m, multiplet. [b] $\delta(NH)$.

$[Mo(CO)_6]$ were evaporated *in vacuo* from the filtrate. The residual yellow oil was dissolved in Et_2O/hexane. Yellow crystals of compound **3** (1.55 g, 30%) separated when the solution was kept at −30°C.

2.6. *Preparation of cis-[Mo(CO)$_4$(L^{All})(PEt$_3$)] (6)*

cis-$[Mo(CO)_4(L^{All})]$ (**3**) (0.2 g, 0.56 mmol) was dissolved in a mixture of C_6H_6/C_6D_6. Triethylphosphine (0.065 g, 0.55 mmol) was added with stirring at room temperature. After 1 h, the solution was transferred to a 10 mm NMR tube; the ^{31}P, ^{13}C, and ^{1}H NMR spectra indicated that the title compound, **6**, had been formed quantitatively.

2.7. *Reaction of cis-[Mo(CO)$_4$(L^{All})] (3) with ^{13}CO*

A benzene solution of compound **3** in a 10 mm NMR tube was cooled to liquid nitrogen temperature. The tube was charged with ^{13}CO on a vacuum line, then sealed, wrapped in aluminium foil, and allowed to warm to room temperature. The ^{13}C NMR spectrum was recorded, and revealed that $^{13}CO/^{12}CO$ exchange had occurred by displacement of a CO ligand *trans* to another.

2.8. *UV irradiation of cis-[Mo(CO)$_4$(L^{All})(PEt$_3$)] (6)*

A sealed 10 mm NMR tube containing complex **6** (0.26 g, 0.56 mmol) in a mixture of C_6H_6/C_6D_6 was irradiated (300–350 nm) at room temperature. The progress of the reaction was monitored by the disappearance in the ^{31}P NMR spectrum of the signal assigned to complex **6** and the appearance of two new peaks at δ 122.8 and 120.8. After 40 h, the conversion was almost complete. The ^{13}C NMR spectrum of the mixture showed two different coordinated alkenes (δ 83.2, 69.8, 65.3, and 61.7).

TABLE 4. Compounds **1**, **2**, **3** and **4**: ^{13}C NMR spectroscopic chemical shift (δ) data at 305 K [a]

Compound	Solvent	$N(CH_2)_2N$	$CH_2:CH$ (free)	$CH_2:CH$ (free)	C_{carb}	Others
1	$CDCl_3$	49.4				50.9 [b]
2	C_6D_6	49.3			125.9	153.1 [b]
3	C_6D_6	48.2, 48.9	117.7	133.4	224.2	65.8 [c] 83.5 [d]
4	C_6D_6	47.7	117.7	133.8	223.7	54.9 [e]
6	C_6D_6					CO [f]

[a] Unless otherwise stated, singlet. [b] Ph_2PCH_2 (doublet), $^{1}J(^{31}P-^{13}C) = 13.4$ Hz. [c] $CH_2:CH$ (coordinated). [d] $CH_2:CH$ (coordinated). [e] NCH_2CH. [f] For **6**, δ(CO): (i) *trans*- to PEt_3 216, $^{2}J(^{13}C-^{31}P) = 26.6$ Hz; (ii) *trans*- to C_{carb}, 217.7, $^{2}J(^{13}C-^{31}P) = 8.3$ Hz; and (iii) *trans*- to CO, 211, $^{2}J(^{13}C-^{31}P) = 9.5$ Hz.

2.9. *Thermolysis of cis-[Mo(CO)$_4$(L^{All})] (3)*

A sealed 10 mm NMR tube containing a C_6D_6 solution of complex **3** was heated at 65°C. The ^{1}H NMR spectrum of the solution was recorded periodically after 1, 3, 5, 24, and 72 h. The initially yellow solution became heterogeneous and a brown oil separated. The heterocycle $AllC:N(CH_2)_2NAll$ (**5**) was the only detectable product after 72 h; it was identified as follows: ^{1}H NMR: a doublet of triplets at δ 3.8 ($J = 5.8$ Hz) assigned to $CH_2C=$; ^{13}C NMR: a quaternary C at δ 162 and a methylene signal at δ 42.

2.10. *X-Ray structure determination of cis-[Mo(CO)$_4$(L^{All})] (3)*

Single crystals (0.5 × 0.25 × 0.30 mm^3) were mounted inside a Lindemann capillary and sealed under argon.

Crystal data

$C_{13}H_{14}MoN_2O_4$, $M = 358.2$, monoclinic, space group $P2_1/n$, $a = 7.866(2)$, $b = 16.450(9)$, $c = 11.680(4)$ Å, $\beta = 101.63(2)°$, $U = 1480.3$ Å, $Z = 4$, $D_c = 1.60$ g cm^{-3}, $F(000) = 720$, $\mu(MoK\alpha) = 8.7$ cm^{-1}.

Data collection

Unique data were recorded at room temperature on an Enraf-Nonius CAD 4 diffractometer using MoKα X-radiation by an $\omega-2\theta$ scan with a maximum scan time of 1 min. Two standard reflections monitored every hour, showed no significant variation. Reflections were corrected for Lorentz and polarization (L_p) effects and also for absorption [7]. 2161 Reflections with $|F^2| > \sigma(F^2)$ were used in the structure refinement, where $\sigma(F^2) = [\sigma^2(I) + (0.04I)^2]^{1/2}/L_p$. The structure was solved by heavy atom methods, and refined with anisotropic thermal parameters for non-hydrogen atoms. The hydrogen atoms were located by a difference Fourier synthesis and refined with isotropic temperature factors. Full-matrix least-squares refinement led to $R = 0.038$ and $R' = 0.043$, the maximum shift error being 0.08 and the weighting $w = 1/\sigma^2(F)$. The Enraf-Nonius SDP package was used, employing a PDP 11/34A computer. Tables of torsion angles, anisotropic thermal parameters, hydrogen atom coordinates, and structure factors are available from one of the authors (PBH).

3. Results and discussion

3.1. Synthesis of $L_2^{(CH_2)_3PPh_2}$ (2)

1,2-Bis(γ-diphenylphosphinopropylamino)ethane (**1**) was prepared from commercially available 1,2-bis(allylamino)ethane and diphenylphosphine by the standard photochemical hydrophosphination of the olefinic double bonds, as shown in reaction (i) of Scheme 1. The course of the reaction was readily monitored spectroscopically by the gradual disappearance of ν(PH) in the IR spectrum or allylic signals in the ^{1}H NMR spectrum.

Compound **1**, a low melting solid, was identified by microanalysis (Table 1), IR (Table 2), and ^{1}H and ^{31}P (Table 3) and ^{13}C (Table 4) NMR spectral data.

Heating compound **1** with the dimethylacetal of dimethylformamide in cyclohexane and then distilling afforded $L_2^{(CH_2)_3PPh_2}$ (**2**) [reaction (ii) *in* Scheme 1] as a viscous, non-volatile residual oil, which was exceedingly air-sensitive. Consequently its identity was established merely by its ^{13}C NMR spectrum (Table 4) which showed the presence of the quaternary olefinic carbon atoms, its aerial oxidation to the urea $[L^{(CH_2)_3PPh_2}]O$ [ν(CO)], its reversible 2-electron-oxidation to $[L_2^{(CH_2)_3PPh_3}]^{2+}$, and its conversion to the carbenemolybdenum complex, **4**, or to $[Rh(CO)Cl\{L^{(CH_2)_3PPh_2}\}]$, having a trigonal bipyramidal Rh^{I} environment with the phosphorus atoms of the tripodal $L^{(CH_2)_3PPh_2}$ ligand occupying axial sites [8].

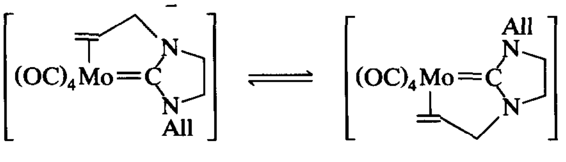
3.2. Synthesis and characterization of the N,N′-functionalized bis(amino)carbenemolybdenum(0) carbonyls 3 and 4

Using the standard reaction of eqn. (1), the pale yellow amorphous carbenemolybdenum complex of empirical formula $Mo(CO)_3\{L^{(CH_2)_3PPh_2}\}$ was obtained (for analyses, see Table 1) from $L_2^{(CH_2)_3PPh_2}$ (**2**) and $CH(NMe_2)(OMe)_2$, as shown in reaction (ii) of Scheme 2. The low yield (Table 1) is attributed to problems of separation. It is formulated as **4** (Scheme 2).

A similar method using L_2^{All} in place of $L_2^{(CH_2)_3PPh_2}$ was not available, as attempts to make L_2^{All} led to the isomer $L_2^{All'}$ (reaction (ii) of Scheme 1) [5]. However, from $[Mo(CO)_6]$, All(H)NCH$_2$CH$_2$N(H)All, and $CH(NMe_2)(OMe)_2$, a modest yield of the yellow crystalline *N*,*N*′-bis(allylamino)carbenemolybdenum complex *cis*-$[Mo(CO)_4(L^{All})]$ (**3**) (yield and analyses in Table 1) was obtained (see (i) in Scheme 2). Also present among the products, but not separated, were $L_2^{All'}$ and various molybdenum-containing products, as deduced from IR and NMR spectra; unreacted $[Mo(CO)_6]$ was removed by sublimation.

Complex **4** is believed to be a polymer having repeating tricarbonylmolybdenum(0) units in which the remaining three octahedral ligating sites at Mo are occupied by C$_{carb}$ and two P atoms (one from the chelating carbene ligand and the other from a bridging carbene ligand of a neighbouring unit). This would be consistent with the insolubility of **4**, even in hot Me$_2$SO, HCONMe$_2$, or PMe$_3$. A significant co-product in its formation is believed to be *cis*- and *trans*-$[Mo(CO)_4\{L_2^{(CH_2)_3PPh_2}\text{–}P,P'\}]$ on the basis of IR [ν(C:C) 1680 cm^{-1}] and ^{13}P NMR spectral data: $\delta(^{31}P)$ 42 and 52 (*cf*. *cis*- and *trans*-$[Mo(CO)_4(PBuPh_2)_2]$ [9]). A related (enetetramine)chromium complex *cis*-$[Cr(CO)_4(L_2^{Me}\text{–}N,N')]$ has been crystallographically characterized [10].

The ^{1}H NMR spectrum of *cis*-$[Mo(CO)_4(L^{All})]$ (**3**) was quite complicated. The 27-line signal from the ring methylenes centred at δ 2.3 was accurately computer-simulated on the basis of its belonging to an ABCD spin system, consistent with only one of the two allyl groups at the two nitrogen atoms binding to the metal. Thus, the ^{1}H NMR spectrum is assigned (Table 3) on the basis of the assumption that, in benzene solution, complex **3** has an identical equilibrium molecular structure to that in the crystal (Fig. 1). Nevertheless, saturation transfer data revealed that in C$_6$D$_6$ solution there is a fluxional process, eqn. (2), with a first order rate constant $k = 0.503$ s^{-1}. These observations were based on NOE experiments with irradiation at the frequency of either the complexed NCH$_2$C*H*:CH$_2$ or the uncomplexed NC*H*$_2$CH:CH$_2$.



(2)

3.3. X-Ray structure of cis-[Mo(CO)$_4$-(L^{All})] (3)

The molecular structure of crystalline *cis*-$[Mo(CO)_4(L^{All})]$ (**3**) is shown in Fig. 1. Bond lengths, angles, and atomic coordinates are presented in Tables 5 and 6, respectively.

Three of the carbonyl groups [CO(1), CO(3), and CO(4)] and C$_{carb}$ (C5) in **3** define a nearly square planar environment for the central molybdenum atom which is 0.027 Å below this plane. The carbon atom C(2) of the remaining carbonyl group is *ca.* 2.00 Å below this plane while the carbon atoms of the coordinated double bond [C(12) and C(13)] are *ca.* 2.27 Å above the plane. The overall coordination environment around Mo is octahedral.

As for the carbene ligand, there is near trigonal planarity about each of C_{carb}, N(1), and N(2), the sum of the angles at these atoms being 360.0(3)°, 357.9(4)°, and 359.8(4)°, respectively; N(1) and N(2) have coordinated and free *N*-allyl substituents, respectively. The five-membered imidazolidin-2-ylidene ring containing C_{carb}, N(1), and N(2), is almost planar, with the C_{carb}–Mo, C_{carb}–N(1), and C_{carb}–N(2) bond lengths being 2.229(4), 1.341(6), and 1.326(6) Å, respectively. All these features are broadly similar to those found in *cis*- and *trans*-[Mo(CO)$_4$(L^{Me})$_2$]; Mo–C_{carb}–2.293(3) Å (*cis*), 2.232(2) Å (*trans*) and C_{carb}–N_{av} 1.337(3) Å (*cis*), 1.341(3) Å (*trans*) [11]. The dihedral angle between the imidazolidin-2-ylidene plane and the plane containing the metal atom and the chelating alkene [containing Mo, C(12), and C(13)] is 94.9°, indicative of the fact that in their π bonds with C_{carb} and C=C molybdenum employs two different and orthogonal t_{2g} orbitals.

TABLE 5. Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for *cis*-[Mo(CO)$_4$(L^{All})] (3)

Bond lengths			
Mo–C(1)	2.040(4)	Mo–C(2)	1.975(5)
Mo–C(3)	2.035(4)	Mo–C(4)	1.984(4)
Mo–C(5)	2.229(4)	Mo–C(12)	2.431(5)
Mo–C(13)	2.422(5)	O(1)–C(1)	1.146(6)
O(2)–C(2)	1.153(7)	O(3)–C(3)	1.136(6)
O(4)–C(4)	1.153(6)	N(1)–C(5)	1.341(6)
N(1)–C(7)	1.458(6)	N(1)–C(11)	1.450(6)
N(2)–C(5)	1.326(6)	N(2)–C(6)	1.474(6)
N(2)–C(8)	1.452(6)	C(6)–C(7)	1.514(8)
C(8)–C(9)	1.478(7)	C(9)–C(10)	1.278(8)
C(12)–C(13)	1.359(6)	C(11)–C(12)	1.491(6)
Bond angles			
C(1)–Mo–C(2)	86.5(2)	C(1)–Mo–C(3)	172.2(2)
C(1)–Mo–C(4)	89.5(2)	C(1)–Mo–C(5)	94.7(2)
C(1)–Mo–C(12)	110.0(2)	C(1)–Mo–C(13)	77.8(2)
C(2)–Mo–C(3)	86.9(2)	C(2)–Mo–C(4)	91.9(2)
C(2)–Mo–C(5)	98.0(2)	C(2)–Mo–C(12)	161.6(2)
C(2)–Mo–C(13)	163.9(2)	C(3)–Mo–C(4)	86.7(2)
C(3)–Mo–C(5)	90.3(2)	C(3)–Mo–C(12)	77.2(2)
C(3)–Mo–C(13)	109.0(2)	C(4)–Mo–C(5)	169.5(2)
C(4)–Mo–C(12)	96.2(2)	C(4)–Mo–C(13)	91.5(2)
C(5)–Mo–C(12)	73.3(2)	C(5)–Mo–C(13)	79.9(1)
C(12)–Mo–C(13)	32.5(1)	C(5)–N(1)–C(7)	113.5(4)
C(5)–N(1)–C(11)	121.5(3)	C(7)–N(1)–C(11)	122.9(4)
C(5)–N(2)–C(6)	113.0(4)	C(5)–N(2)–C(8)	125.9(4)
C(6)–N(2)–C(8)	120.9(4)	Mo–C(1)–O(1)	178.1(4)
Mo–C(2)–O(2)	178.2(4)	Mo–C(3)–O(3)	175.4(4)
Mo–C(4)–O(4)	177.6(4)	Mo–C(5)–N(1)	116.5(3)
Mo–C(5)–N(2)	135.7(3)	N(1)–C(5)–N(2)	107.8(3)
N(2)–C(6)–C(7)	102.7(4)	Mo–C(12)–C(13)	73.4(3)
N(2)–C(8)–C(9)	114.6(4)	C(11)–C(12)–C(13)	123.5(4)
C(8)–C(9)–C(10)	127.0(5)	N(1)–C(7)–C(6)	102.2(4)
N(1)–C(11)–C(12)	110.8(3)		
Mo–C(12)–C(11)	106.8(3)		
Mo–C(13)–C(12)	74.1(3)		

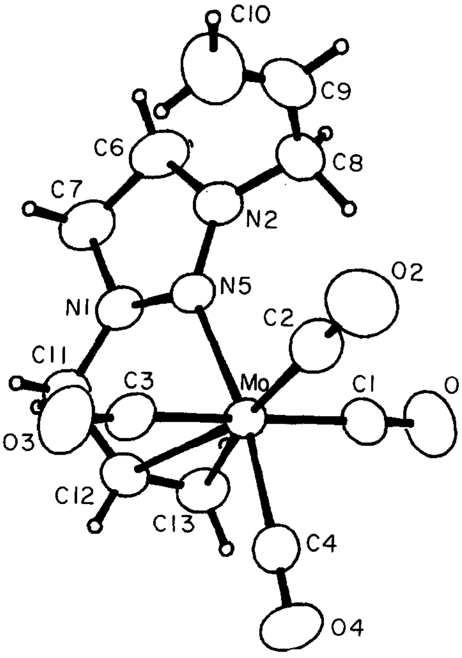


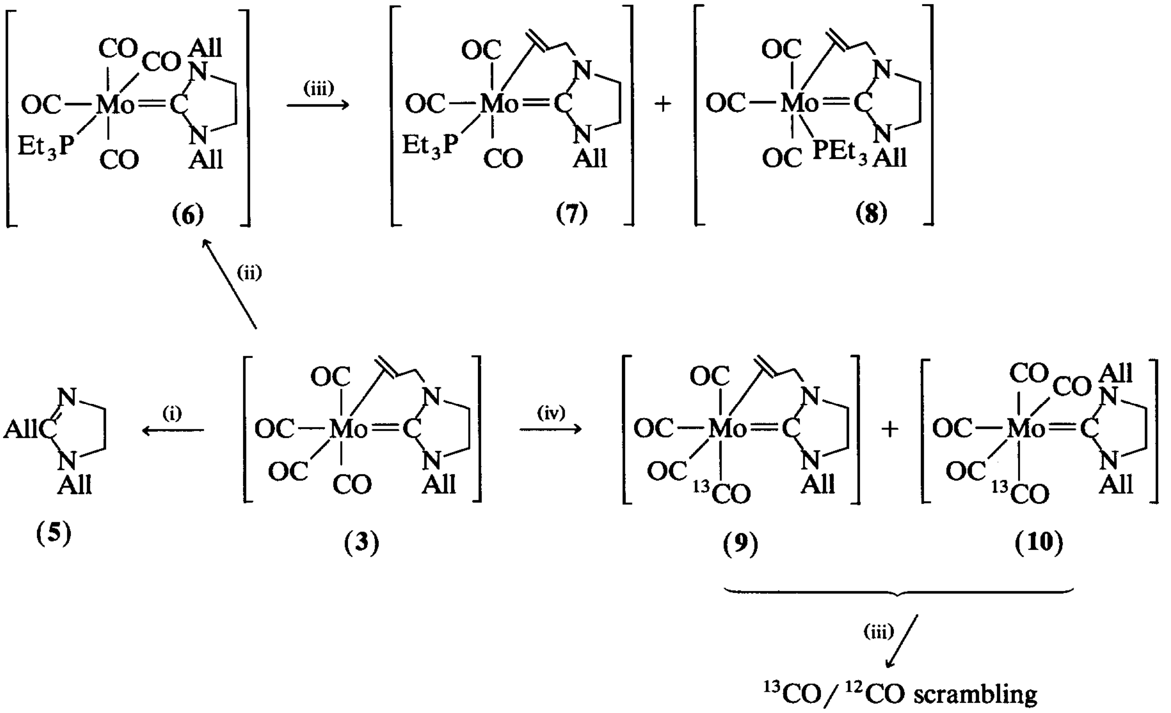
Fig. 1. X-Ray structure and atom labelling for *cis*-[Mo(CO)$_4$(L^{All})] (3).

The mutually *trans*-Mo–CO bonds, av. 2.037(5) Å, are significantly longer than Mo–CO *trans* to C_{carb}, 1.984(4) Å, consistent with previous conclusions that bis(amino)carbene ligands are poorer π-acceptors than CO [3]. The Mo–CO bond *trans* to C=C is even shorter at 1.975(2) Å. The Mo–C_{carb} bond length of 2.229(4) Å is considerably longer than each of the Mo–CO bond lengths, reflecting again the weaker π-acceptor capacity of C_{carb} compared with CO but also the slightly smaller C(sp) rather than C(sp^2) radius.

The C=C bonds of the two allyl groups reflect the fact that one is bonded to Mo [C(12)=C(13), 1.359(6) Å], whereas the other [C(9)=C(10), 1.278(8) Å] is free. The Mo–C(12) [2.431(5) Å] and Mo–C(13) [2.422(5) Å] bond lengths relating to the bonded allyl group $NCH_2C(12)H{=}C(13)H_2$ are appropriate for an η^2-bonded-alkene-Mo^0 bond; *cf.* [Mo(CO)$_3${PPh$_2$(CH$_2$)$_2$-CH=CH(CH$_2$)$_2$PPh$_2$}] with Mo–CH_{av} 2.54(4) and CH=CH 1.36(3) Å [12].

3.4. Reactions of cis-[Mo(CO)$_4$(L^{All})] (3)

These are summarized in Scheme 3. For the most part, progress of reactions was monitored by NMR



Scheme 3. Reactions of the complex [Mo(CO)$_4$L^{All}] (3). Reagents and conditions: (i) C_6D_6, 65°C, 72 h; (ii) PEt_3, C_6H_6/C_6D_6, *ca.* 25°C, 1 h; (iii) C_6H_6/C_6D_6, *hν* (300–350 nm), *ca.* 25°C, 40 h; (iv) ^{13}CO, C_6H_6/C_6D_6, 25°C, 1 h.

spectroscopy, generally using C_6H_6/C_6D_6 as solvent; for only one complex, *cis*-[Mo(CO)$_4$(L^{All})(PEt$_3$)] (**6**) (see Tables 3 and 4), was an attempt made to separate a pure product.

Treatment of *cis*-[Mo(CO)$_4$(L^{All})] (**3**) with ^{13}CO led to the formation [reaction (iv) of Scheme 3] of (a) just a single substitution product, the isotopomer **9**, in which one of the mutually *trans*-CO ligands was displaced by ^{13}CO; and (b) the addition product [Mo(CO)$_5$(L^{All})] (**10**). When a mixture of **9** and **10** was irradiated in a sealed NMR tube at 300–350 nm, the ^{13}C label was scrambled into each of the carbonyl positions, reaction (iii) of Scheme 3. The ^{13}C NMR spectral signal at δ 208 was that due to ^{13}CO *trans* to CO in complex **10**.

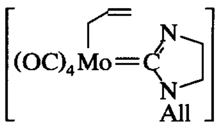
TABLE 6. Atom coordinates (×10^4) for *cis*-[Mo(CO)$_4$(L^{All})] (3)

	x	*y*	*z*
Mo	1716.4(4)	1947.1(2)	904.7(3)
O(1)	−1752(5)	1102(3)	−452(4)
O(2)	−630(5)	2730(3)	2473(3)
O(3)	4759(5)	3051(2)	2275(3)
O(4)	1049(5)	3412(2)	−847(3)
N(1)	4157(4)	544(2)	1887(3)
N(2)	2060(5)	438(2)	2813(3)
C(1)	−491(5)	1392(3)	39(4)
C(2)	254(6)	2438(3)	1911(4)
C(3)	3703(6)	2627(3)	1808(4)
C(4)	1262(6)	2865(3)	−217(4)
C(5)	2649(5)	873(2)	2019(3)
C(6)	3218(7)	−240(3)	3282(4)
C(7)	4766(6)	−107(3)	2715(4)
C(8)	397(6)	545(3)	3151(4)
C(9)	497(6)	925(4)	4310(4)
C(10)	1814(8)	1273(4)	4937(5)
C(11)	5272(5)	951(3)	1218(4)
C(12)	4223(5)	1416(3)	226(4)
C(13)	2796(6)	1110(3)	−499(4)

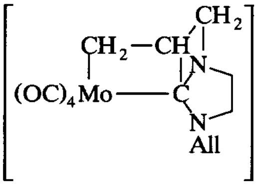
Likewise at room temperature, from an equimolar mixture of compound **3** and triethylphosphine, complex **6** was obtained quantitatively and stereoselectively [reaction (ii) of Scheme 3]. Both this and reaction (iv) serve to demonstrate that, for **3**, the *trans*-effect parallels the *trans*-influence, with CO > C_{carb}; while the transformation **3** → **6** also shows that CO > C(alkene) in *trans* effect (as it clearly also is in *trans* influence). The corresponding reaction to (ii) of **3** with the less basic PPh_3 was perceptibly slower than with PEt_3, exchange being only *ca.* 50% completed under similar reaction conditions.

In an attempt to incorporate the second alkene function of the L^{All} ligand of *cis*-[Mo(CO)$_4$(L^{All})] (**3**) into the inner coordination sphere of the metal, complex **3** was irradiated initially in a sealed NMR tube and subsequently in an open system under a flow of nitrogen gas; no displacement of CO occurred and complex **3** was recovered. However, similar irradiation of complex **6** led to CO loss and formation of a mixture of *mer*-**7** and *fac*-**8** $[\mathrm{Mo(CO)_3(L^{All})\,(PEt_3)}]$ [reaction (iii) of Scheme 3].

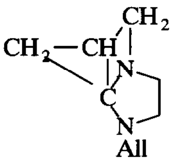
Upon heating complex **3** in $\mathrm{C_6D_6}$ at 65°C for 72 h in an NMR tube, $\mathrm{AllC{:}N(CH_2)_2NAll}$ (**5**) was the principal organic product [reaction (i) of Scheme 3]. Alternative reaction pathways might implicate as an intermediate (i) the $\mathrm{Mo^{II}}$–All complex **II** in a quasi-Claisen-type rearrangement; or (ii) successively the metallacycle **IV** and the tricycle **V**.



(II)

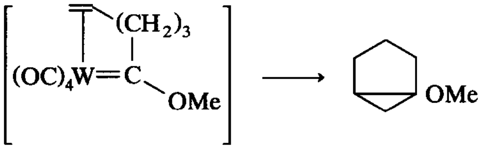


(IV)



(V)

As for (ii), a similar proposal was made to account for the thermolysis reaction of a related tetracarbonyl(carbene)alkene complex **VI** [eqn. (3)] [13]. Furthermore, ready C–N fission was observed (for which a Stevens-type rearrangement mechanism was proposed) when reacting an aminocarbene(alkene)metal(0) carbonyl (metal = Cr or W) with an alkyne [14].



(3)

(VI)

Carbene(alkene)metal complexes **VII**, exemplified by complexes **3** (the first such molybdenum derivative) and **VI** (for some other examples see ref. [15], are of interest as key intermediates in the important catalytic alkene metathesis reactions initiated by a carbenemetal complex **VIII**: complexes **VII** and **VIII** appear in the catalytic cycle (Chauvin mechanism) together with a metallacyclobutane, of which class, complex **IV** would be an example.

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