# N,N',N'',N'''-FUNCTIONALISED ELECTRON-RICH ALKENES AND THEIR ROLE IN TRANSITION-METAL CHEMISTRY

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ABSTRACT. Treatment of $CH(OMe)_2NMe_2$ with $RNH(CH_2)_2NHR$ afforded either the electron-rich alkene $\{CNR(CH_2)_2NR\}_2$ ($[L^R]_2$) or, alternatively, the isomer $RN(CH_2)_2N:C-C(R')N(R)(CH_2)_2NR$ ($[L^R]'_2$), depending on the nature of the substituent R at nitrogen. In the case of $R = CH_2CH:CH_2$, the product was $[L^R]'_2$ ($R = R'$); whereas when $R = (CH_2)_3PPh_2$, $(CH_2)_2CH:CH_2$, or $CH_2CH:CHMe$, the product was $[L^R]_2$. An amino-Claisen-type rearrangement was observed for $[L^R]_2$ ($R = CH_2CH:CHMe$) $\xrightarrow{\Delta}$ $[L^R]'_2$ [$R' = R$ or $CH(Me)CH:CH_2$]. MNDO SCF calculations on model compounds $[L^{Me}]_2$ and $[L^{Me}]'_2$ showed that the latter is appreciably the more stable. The following transition metal compounds have been made: $[RhCl(CO)(L^{(CH_2)_3PPh_2})]$, *trans*-$[PdCl_2(L^{CH_2CH:CH_2})_2]$, and *cis*-$[Mo(CO)_4(L^{CH_2CH:CH_2})]$; the X-ray structures of the latter two were determined. Several reactions of the molybdenum complex have been investigated.

1. Introduction

The objectives of this work were to synthesise functionalised electron-rich alkenes of type (1) (abbreviated as $[L^R]_2$) in which the group R has ω-donor functionality, so that a derived transition metal complex would have the potential of being a chelate of type

(1)   (2a)   (2b)
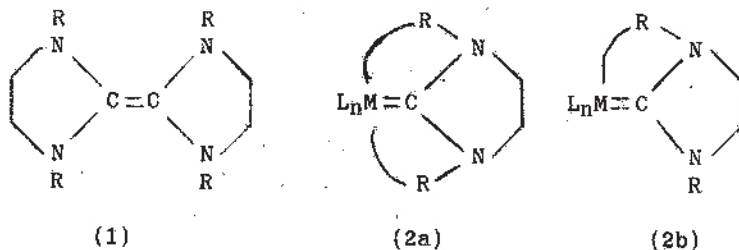
(2a) or (2b). Accordingly, the group R was chosen so as to contain either an ω-tertiary phosphine or ω-alkene group.

Previously, we had studied the chemistry of compounds (1) (R = a primary alkyl or an unhindered aryl group) and related enetetramines in which (i) the two 5-membered rings were replaced by 6-membered rings; (ii) an NR group in each ring was replaced by S; (iii) there was optical activity, e.g., (3); or (iv) the groups R were part of a macrocycle, e.g., (4).

(3)

(4)
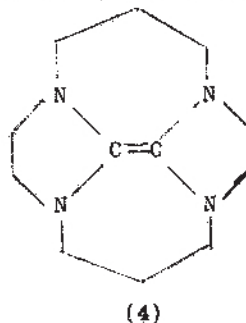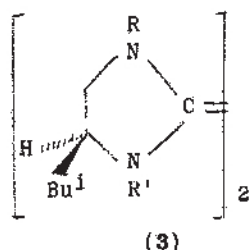
The general synthetic route to electron-rich alkenes $[L^R]_2$ (1) involves distilling the appropriate diamine $RNH(CH_2)_2NHR$ (R = a primary alkyl or an unhindered aryl group) with the dimethylacetal of N,N-dimethylformamide, equation (1); the equilibrium is driven to the right by continuous removal by distillation of MeOH and Me_2NH.

$$2\ RNH(CH_2)_2NHR + 2\ CH(OMe)_2NMe_2 \rightleftharpoons [L^R]_2 + 2\ Me_2NH + 4\ MeOH \qquad (1)$$
$$(1)$$
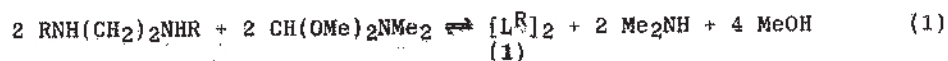
Our earlier work on the electron-rich alkenes (1) showed that their chemistry is dominated by their high degree of nucleophilicity. Thus, (i) they are powerful reducing agents, e.g., abstracting a chlorine atom from a chloro-alkane or an organometallic chloride; (ii) they have an extensive carbene-transition metal chemistry, in some ways analogous to that of a tertiary phosphine, e.g., see Scheme 1; (iii) other electrophiles often also induce scission of the formal C=C bond [e.g., + HA → $L^R(H)A$]; and (iv) they may behave as bases (N- or C-centred).
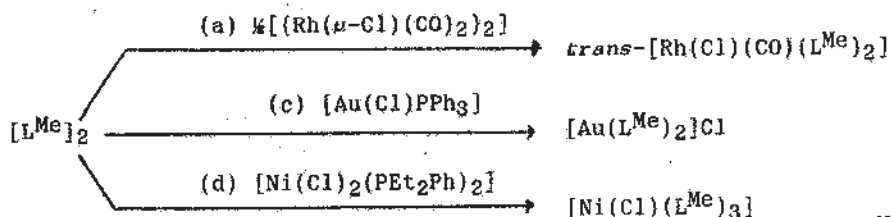
SCHEME 1. Some typical reactions of the electron-rich alkene $[L^{Me}]_2$

Our work in this area has recently been reviewed.[1]

2. Results and Discussion

### 2.1 SYNTHESIS OF N,N',N'',N'''-FUNCTIONALISED ELECTRON-RICH ALKENES

It was envisaged that the final step in the synthesis would be that of equation (1). Accordingly, the first requirement was to obtain the appropriate N,N'-dialkyl-1,2-diaminoethane $RNH(CH_2)_2NHR$. Four candidate molecules were chosen, namely those in which R = $CH_2CH:CH_2$, $(CH_2)_3PPh_2$, $(CH_2)_2CH:CH_2$, or $CH_2CH:CHMe$; these required synthesis.

1-Aminobut-3-ene was prepared from allyl cyanide and AlH_3. 1-Aminobut-2-ene was made by a Gabriel phthalimide synthesis, starting with 1-bromobut-2-ene.

N,N'-Diallyl-1,2-diaminoethane was prepared from 1,2-dibromoethane and allylamine.[2]

The diamine $RNH(CH_2)_2NHR$ [R = $(CH_2)_3PPh_2$] was obtained from $R'NH(CH_2)_2NHR'$ (R' = $CH_2CH:CH_2$) by treatment with Ph_2PH under photolysis in the presence of AIBN.

In three of the cases, reaction according to equation (1) led to the appropriate electron-rich alkene $[L^R]_2$. However, when the same procedure was carried out in an attempt to obtain the allyl derivative, the isomer $[L^{CH_2CH:CH_2}]'_2$ (5) was obtained, equation (2, R = R' = $CH_2CH:CH_2$). The latter was identified by its n.m.r. spectra: the ^{13}C data were particularly informative, as they showed that (5) contained three types of allyl group. Figure 1.

$$2\ RNH(CH_2)_2NHR \xrightarrow[\text{$-2\ Me_2NH,\ -4\ MeOH$}]{2\ CH(OMe)_2NMe_2} \qquad (2)$$

(5)
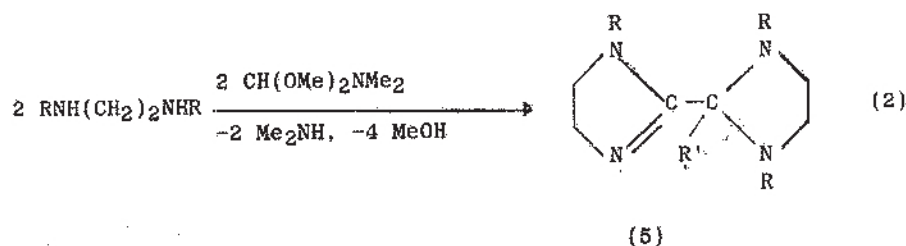
2.2. [3,3]- AND [1,3]-SIGMATROPIC AMINO-CLAISEN REARRANGEMENTS OF ELECTRON-RICH ALKENES [1,3,1',3'-TETRA-ALLYL-BIS(2,2'-IMIDAZOLIDENE)S]

When the electron-rich alkene (1) (R = $CH_2CH:CHMe$) was heated in toluene under reflux for 3 h, a regiospecific rearrangement was observed to give the compound (5) [R = $CH_2CH:CHMe$, R' = $CH(Me)CH:CH_2$], the result of a [3,3] sigmatropic amino-Claisen-type rearrangement. On the other hand, photolysis of the same substrate gave not only this compound but also the [1,3] rearranged isomer [R = R' = $CH_2CH:CHMe$].

Similar sigmatropic rearrangements have previously been observed for the case of $[L^R]_2$ (R = CH_2Ph)[3] and for some endotricyclic electron-rich alkenes (6) (R = CH_2Ph).[4] Two of these rearranged
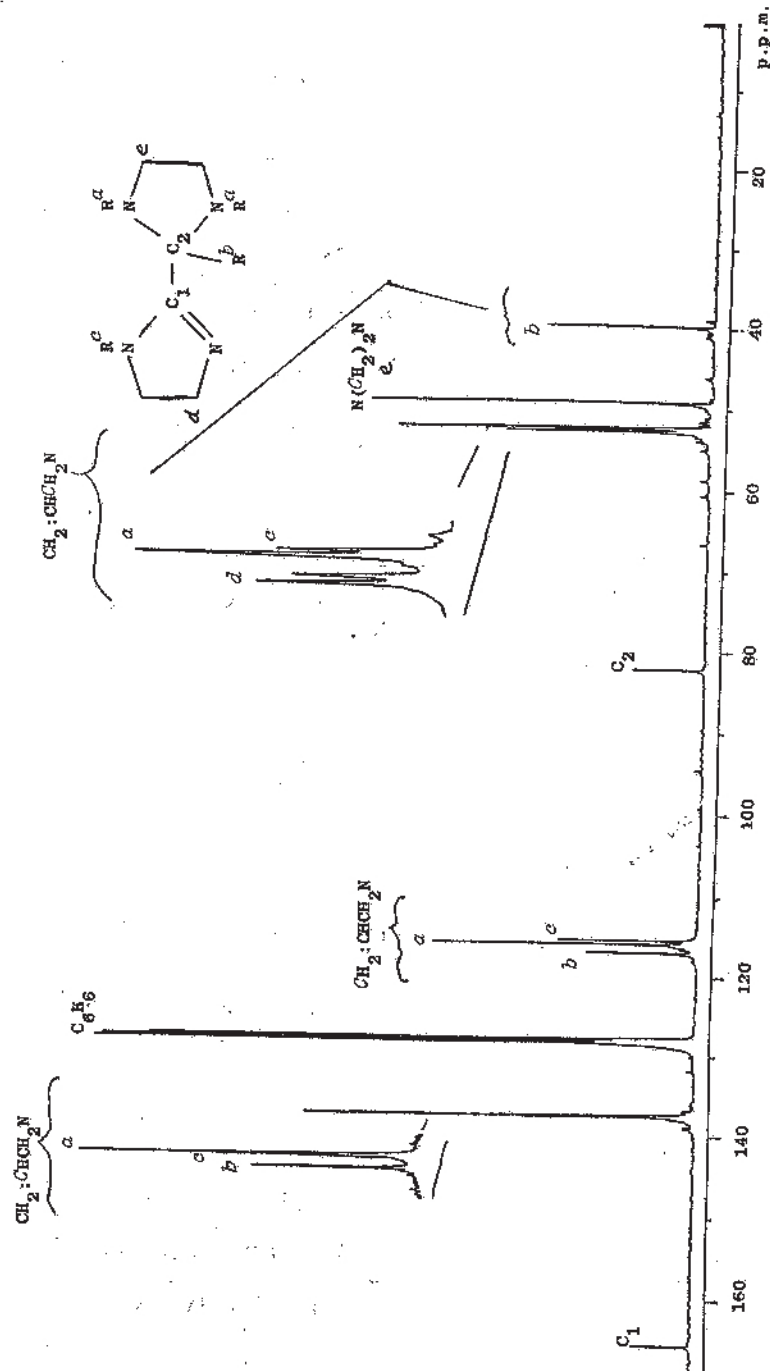
Fig. 1. The ^{13}C n.m.r. spectrum of $[L\overset{CH_2CH:CH_2}{\underset{2}{}}]'_2$ (5, $R = CH_2CH:CH_2 = R'$) in $C_6H_6\sim C_6D_6$ at 90.6 MHz and 305 K.

products $[L^{CH_2Ph}]'_2$[5] and (7)[6] have been crystallographically characterised.[5]

(CH$_2$)$_m$ ... structure (6) and (7)
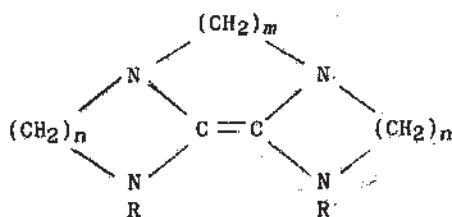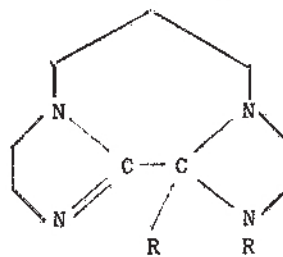
(6)   (7)

We propose that the thermal allylic isomerisations $[L^R]_2 \xleftrightarrow{c}$ $[L^R]'_2$ are intramolecular [3,3] sigmatropic rearrangements involving a cyclic transition state of type (8); and corresponding photochemical transformations are either wholly or in part intermolecular, [1,3], possibly involving free radical intermediates. Such rearrangements are, we suggest, thermodynamically favoured and are kinetically accessible if R is allylic or R or R is otherwise resonance stabilised, e.g., R = CH$_2$Ph, and not sterically hindered, as in R = (CH$_2$)$_2$CH:CH$_2$; see also ref. 7.
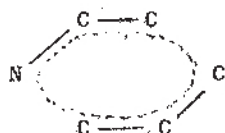
(8)

In order to test the thermodynamic assumption with regard to the rearrangement, we carried out molecular orbital calculations on model compounds $[L^R]_2$ and $[L^R]'_2$. It was impracticable to do these for cases more complicated than R = Me, and MNDO was the MO method of choice.[8] This gave the following heats of formation: $[L^{Me}]_2$, 204.6 kJ mol^{-1} and $[L^{Me}]'_2$, 168.1 kJ mol^{-1}, whence ΔH for the isomerisation in the gaseous phase is predicted to be -36.5 kJ mol^{-1}.

To test further the validity of the MNDO method, we show (Table I) that there is a good correlation between MNDO calculated and experimental geometrical parameters for $[L^{Me}]_2$ (electron diffraction)[9] and $[L^{CH_2Ph}]'_2$ (x-ray;[5] experimental data for $[L^{Me}]'_2$ are not to hand).

2.3 SYNTHESIS AND CHARACTERISATION OF AN N,N'-BIS[(γ-DIPHENYLPHOSPHINOALKYL)AMINO]CARBENERHODIUM(I) COMPLEX

Treatment of [{Rh(CO)$_2$(μ-Cl)}$_2$] with $[L^{(CH_2)_3PPh_2}]_2$ in refluxing xylene afforded the appropriate yellow carbenerhodium(I) complex (9) in 60% yield, m.p. 217-218 $^{\circ}$C; we believe it to have 5-co-ordinate rhodium, with geometry approximating to trigonal bipyramidal about the metal and the two phosphorus atoms in trans-axial positions.

The evidence for this formulation (9) is based on (i) satisfactory microanalyses; (ii) an electron impact mass spectrum, which showed the highest peak to correspond to the parent molecular ion -CO; and (iii) n.m.r. data. From the ^{13}C n.m.r. spectrum we

Table I. Some experimental (e.s.d.s in parentheses) and MNDO-calculated structural parameters for $[L^R]_2$ (1) and $[L^R]'_2$ (5)


(1)   (5)
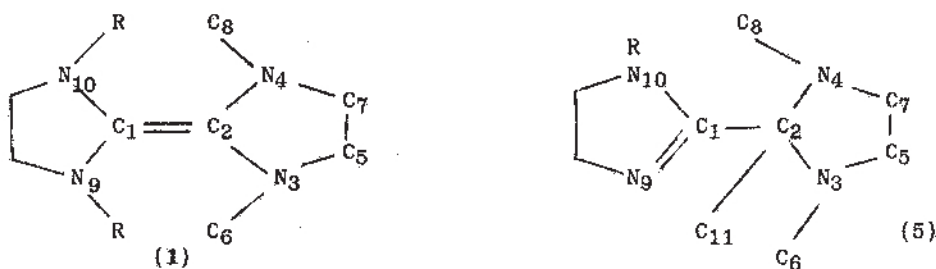
	Electron diffraction[9] (1, R = Me)	MNDO (1, R = Me)	MNDO (5, R = Me)[a]	X-Ray (5, R = CH$_2$Ph)[5]
Bond lengths (Å)				
C_1-C_2	1.387(11)	1.376	1.536(4)	1.554
C_2-N_3	1.401(4)	1.440	1.466(4)/1.475(4)	1.478[b]
N_3-C_5	1.491(6)	1.484	1.453(4)/1.456(4)	1.468
N_3-C_6	1.465(6)	1.484	–	–
C_5-C_7	1.529(9)	1.542	–	–
C_1-N_9	–	–	1.392(2)	1.418
C_1-N_{10}	–	–	1.276(3)	1.312
Bond angles (°)				
$C_1C_2N_3$	123.7(0.3)	125.0	115.3(2)/107.8(2)	111.6
$C_2N_3C_6$	117.7(0.5)	118.2	–	–
$C_1C_2C_{11}$	–	–	107.9(2)	110.9
$C_2C_1N_{10}$	–	–	120.6(2)	119.8
$C_2C_1N_9$	–	–	124.2(2)	128.5
Dihedral angles (°)				
$C_1C_2N_3C_6$	53.5(8)	48.4	–	–
plane A $N_{10}C_1N_9$				
plane B $N_3C_2N_4$	–		89.2	82.5

[a]Average error, 0.016 Å or 2.7°.[11]

[b]Although C_2N_3 and C_2N_4 are different in the crystal structure of (5, R = CH$_2$Ph),[5] in (5, R = Me) they were assumed to be equal.

identify C_{carb} at -204 p.p.m.; it is also clear that there are two different phenyl rings. The ^{31}P n.m.r. spectrum showed a single phosphorus resonance as a doublet centred at -128 p.p.m., with $^1J(^{103}Rh^{31}P) = 125.7$ Hz. The high value of the coupling constant supports the assignment.[10] The i.r. spectrum (nujol mull) showed $\nu(CO)$ at 1980 cm^{-1}, $\nu(CN_2)$ at 1510 cm^{-1}, and $\nu(Rh-Cl)$ at 345 cm^{-1}.

We conclude that the reaction is represented by equation (3) and that the product is formulated as (9) in which both the phosphorus functionalities on the carbene ligand are implicated in bonding to rhodium.

$$[\{Rh(CO)_2(\mu-Cl)\}_2] + [L^{(CH_2)_3PPh_2}]_2 \longrightarrow$$

(3)

(9)
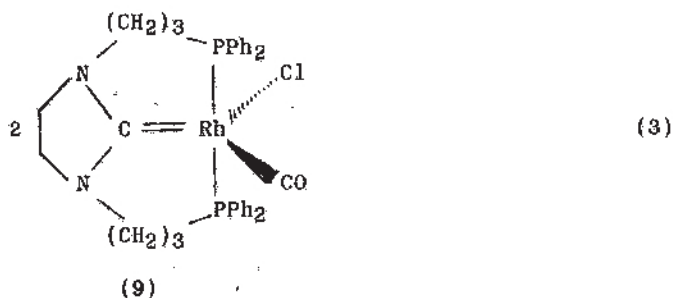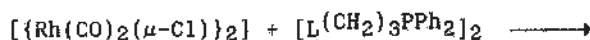
2.4 SYNTHESIS AND STRUCTURE OF A BIS[DI(N,N'-ALLYLAMINO)CARBENE]PALLADIUM(II) COMPLEX

Although the electron-rich alkene $[L^{CH_2CH:CH_2}]_2$ has proved to be inaccessible, we conceived the following strategy for its preparation. First, to convert the diamine $RNH(CH_2)_2NHR$ (R = $CH_2CH:CH_2$) into the aminal (10). Then, to protect the allylic double bond by co-ordination to Pd^{II} yielding (11), and ultimately to deaminate (11) to give the desired product. In the event, the first step to form the new aminal (10) was realised, using

(10)

(11)
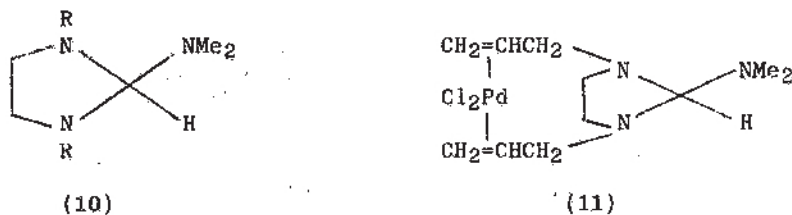
Bredereck's reagent $CH(NMe_2)_2OBu^t$. However, when (10) was treated with cis-$[PdCl_2(NCPh)_2]$ in benzene at 20° there was an instantaneous reaction yielding a mixture of a carbenepalladium(II) complex, tentatively formulated as (12) (79%), and the yellow crystalline (13) (R = $CH_2CH:CH_2$) (21%), m.p. 185-188 °C. Both were identified

(12)   **(13)**
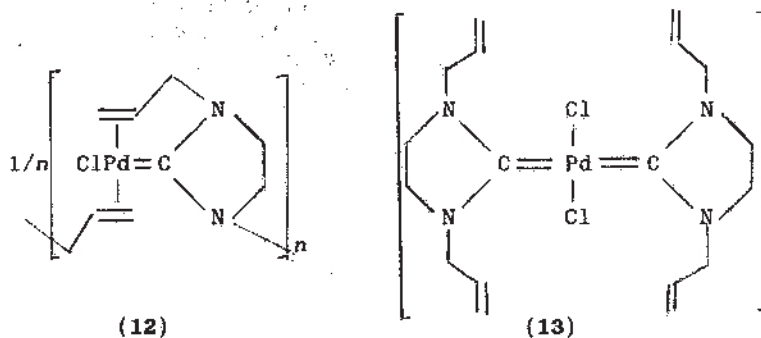
by (i) satisfactory microanalyses and (ii) i.r. data (nujol) [(12): $\nu(CN_2)$ 1510 cm^{-1}, $\nu(C=C)$ 1560-1660 cm^{-1}; (13): $\nu(CN_2)$ 1510 cm^{-1}, $\nu(C=C)$ 1640 cm^{-1}]. The X-ray structure of the crystalline complex (13) is illustrated in Figure 2.[6]

When the *trans*-complex (13) was dissolved in chloroform at *ca.* 20 °C, an isomerisation occurred yielding a mixture of *cis*- and *trans*- isomers, as revealed by ^{13}C n.m.r. spectroscopy: $\delta(^{13}C)$ (CDCl$_3$): 190, 198.7 (C_{carb}); 117.8, 118.5 (CH_2:CH); 131.8, 132.9 (CH_2:CH); 47.2 N(CH_2)$_2$; the low frequency peaks are assigned to the *cis*-isomer. The ^1H n.m.r. spectrum of (13) in CDCl$_3$ showed $\delta(^1H)$ at 3.4 N(CH_2)$_2$, 4.6 (NCH_2CH:CH$_2$), 5.1-5.4 (CH$_2$:CH), and 5.9-6.3 (CH$_2$:CH).

It is evident that although [L$^{CH_2CH:CH_2}$]$_2$ has proved elusive, carbenepalladium(II) complexes in which L$^{CH_2CH:CH_2}$ is the ligand are, nevertheless, accessible by the *in situ* preparation of equation (4). The X-ray structure of (13) showed that the allyl substituents

$$[PdCl_2(NCPh)_2] \quad + \quad (10) \quad \longrightarrow \quad (13) + (14) \qquad (4)$$
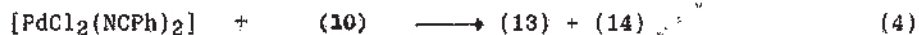
at nitrogen are not implicated in bonding to palladium, by contrast to the situation found for a related molybdenum complex (see Section 2.5).

2.5 SYNTHESIS, STRUCTURE, AND SOME REACTIONS OF A BIS[DI(*N,N'*-ALLYLAMINO)CARBENE]MOLYBDENUM(0) COMPLEX

As for the case of the bis[di(*N,N'*-allylamino)carbene]palladium(II) complex (13), an *in situ* procedure has led to the satisfactory synthesis of the yellow crystalline molybdenum(0) complex (14) (30%) m.p. 67-70 °C, in which a similar carbene ligand is featured, equation (5) (R = CH$_2$CH:CH$_2$).

$$RNH(CH_2)_2NHR + CH(OMe)_2(NMe_2) + [Mo(CO)_6] \rightarrow$$

(14)

1.462(4) Å

1.460(4) Å

Pd-Cl   2.302(1) Å

Pd-C_{carb} 2.026(3) Å

$\langle N-C_{carb} \rangle$ 1.325 Å

Angle between plane b

and $PdCl_2(C_{carb})_2$ plane: 76°
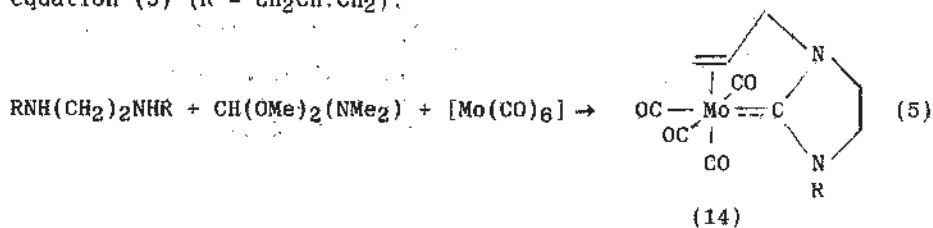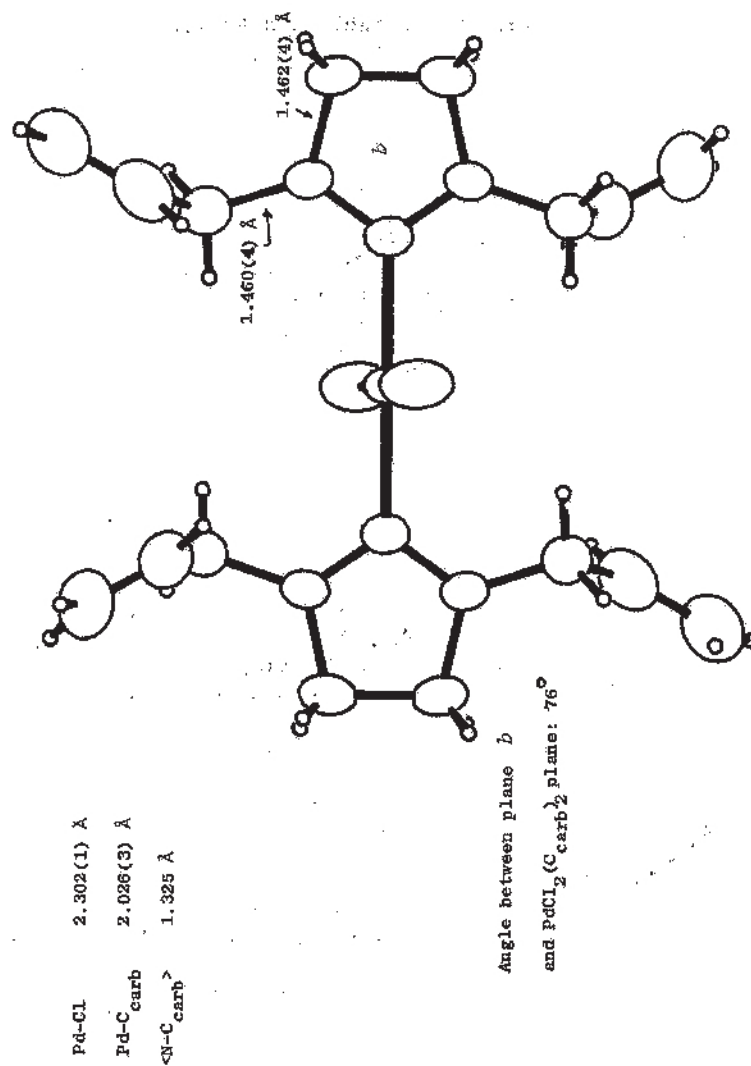
Fig. 2. X-Ray structure of $trans$-$[PdCl_2(L_2^{CH_2CH:CH_2})_2]$ (13) (ref. 6)

The structure of complex (**14**) was established by microanalysis, spectroscopy and, finally, by an X-ray structure (Figure 3).[5] From the latter, it is evident that, unlike in the palladium compound (**13**), the molybdenum complex (**14**) has one of the co-ordination sites around molybdenum occupied by the terminal alkene of just one of the N-allyl substituents at the carbene ligand.

Detailed ^1H and $^{13}C\{^1H\}$ n.m.r. spectra showed that the same structure cis-[$Mo(CO)_4(L^{CH_2CH=CH_2})$] (**14**) is maintained in C_6D_6 solution. The ^1H n.m.r. spectrum comprised signals at δ 2.1–2.5 [4H, computer simulated multiplet as an ABCD system, attributable to the $(CH_2)_2$ backbone of the cyclic carbene], 5.0 (2H, a multiplet due to $CH_2:CH$), and 5.5–5.6 (1H, a multiplet assigned to $CH_2:CH$). The $^{13}C\{^1H\}$ signals were found at δ 224.2 (C_{carb}), 117.7 ($CH_2:CH$ free), 133.4 ($CH_2:CH$ free), 65.8 ($CH_2:CH$ co-ordinated), 83.3 ($CH_2:CH$ co-ordinated), and 48.2, 48.9 [$N(CH_2)_2$].

The i.r. spectrum of cis-[$Mo(CO)_4(L^{CH_2CH=CH_2})$] (**14**) in CH_2Cl_2 had $\nu(CO)$ bands at 2020 (sh,s), 1920 (br,vs), and 1862 (b,vs); $\nu(C=C)$(free) at 1640 cm^{-1}; and $\nu(CN_2)$ at 1510 cm^{-1}.

As regards the solid state structure of complex (**14**) two points are noteworthy. (i) Mutually $trans$-Mo-CO bond lengths are significantly longer than the Mo-CO bond $trans$- to C_{carb}, consistent with earlier conclusions[1] that an L^R ligand is a weaker π-acceptor than CO; hence, CO $>$ L^R in $trans$-influence. (ii) The dihedral angle between the imidazolidin-2-ylidene (MoC$_{carb}$NN') plane and the plane of the chelated alkene (MoC:C) is 66.4°, suggesting that in their π-bonds with Mo the carbene and the alkene are bonded to two different mutually perpendicular t_{2g} Mo orbitals.

Some reactions of the new carbene complex (**14**) are illustrated in Scheme 2 (R = $CH_2CH:CH_2$). Reaction of (**14**) with ^{13}CO displaced a CO ligand $trans$ to another CO to yield compound (**14a**); hence, $trans$-effect trends parallel those of $trans$-influence. A second product, (**15**), resulted from an additional reaction whereby the C:C ligand of the bonded N-allyl substituent on the carbene moiety of (**14**) was displaced. When the mixture of (**14a**) and (**15**) was irradiated, the ^{13}C label was scrambled into all the carbonyl positions.

The C:C ligand of (**14**) was also displaced by a reaction with triethylphosphine to yield (**16**). Photolysis of complex (**16**) led to a mixture of fac- (**17a**) and mer- (**17b**) [$Mo(CO)_3(L^{CH_2CH:CH_2})(PEt_3)$], by elimination of one of the CO ligands and renewed ligation of C:C from the N-allyl group.

The heterocycle (**18**) was the main organic product obtained by heating [$Mo(CO)_4(L^{CH_2CH:CH_2})$] (**14**) in an n.m.r. tube at 65 °C for 72 h in C_6D_6. One possible route to (**18**) from (**14**) (a in Scheme 3) is via migration of an allyl group to molybdenum in a Claisen-type rearrangement (see Section 2.2) to yield (**19**) and final reductive coupling. Alternatively, (b in Scheme 3), a metallacycle (**20**) and then a tricycle (**21**) might be on the reaction pathway. A similar proposal was used to rationalise the thermolysis of a tungsten complex cis-[$W(CO)_4\{C(C_6H_4Me$-$p)(N(Me)CMe_2CH:CH_2)\}$] to yield p-MeC$_6$H$_4CCH_2CHCMe_2CH_2NMe$.[12] The proposed mechanisms of Scheme 3 may

Lengths (Å)

Mo-C1 2.040(4) Å
Mo-C2 1.975(5)
Mo-C3 2.035(4)
Mo-C4 1.984(4)
Mo-C5 2.229(4)
Mo-C12 2.431(5)
Mo-C13 2.422(5)

Angles (°)

C1MoC2   86.5(2)
C1MoC3   77.8(2)
C1MoC4   89.5(2)
C1MoC5   94.7(2)
C2MoC3   86.9(2)
C2MoC4   91.9(2)
C2MoC5   98.0(2)
C3MoC4   86.7(2)
C3MoC5   90.3(2)
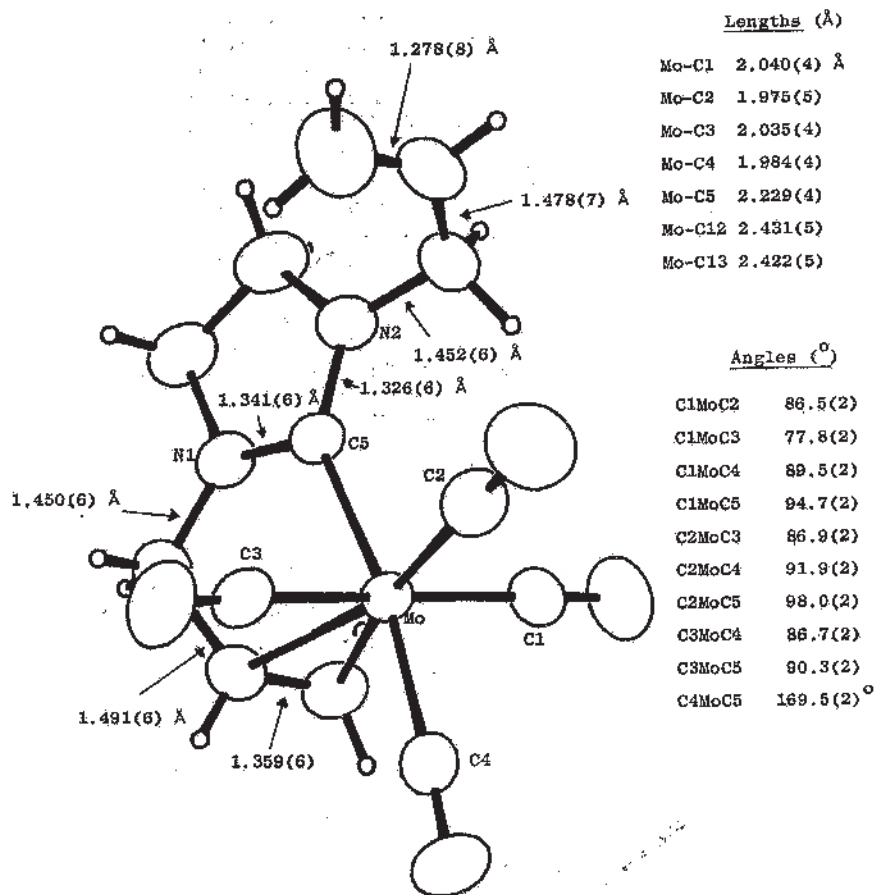C4MoC5 169.5(2)°

Fig. 3. X-Ray structure of cis-[Mo(CO)$_4$(L$^{CH_2CH:CH_2}$)] (14) (ref. 5)

be regarded as models for alkene metathesis; it is now commonly agreed that an important intermediate in such metathesis is a metal complex bearing both a carbene and an alkene ligand.

In an attempt to incorporate the second alkene function of the carbene ligand into the co-ordination sphere of molybdenum, complex (14) was irradiated: first, in a sealed n.m.r. tube and, in a second experiment, under a flow of dinitrogen. No displacement of CO occurred, and complex (14) was recovered. To test whether there was fluxionality between the N- and N'-allyl groups, variable temperature n.m.r. spectra were examined, but there was no evidence of an exchange process on the n.m.r. time scale. However, a spin saturation transfer experiment on complex (14) showed that there is indeed a fluxional process which at 75 ^{o}C has a first order rate constant of $ca.$ 0.4 s^{-1}. The experiments were carried out by examining NOE difference spectra after irradiation at the frequency of either $Mo(L^{CH_2CH:CH_2})$ or $Mo(L^{CH_2CH:CH_2})$.

3. Acknowledgements

4. References

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