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FULL PAPER

Molybdenum-based alkyne–isocyanide coupling reactions: synthesis of a reactive diiminometallacyclopentene complex

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The complex [Mo(CO)(PhC≡CPh)$_2$(η-C$_5$Me$_5$)][BF$_4$] reacted with three equivalents of 2,6-dimethylphenyl isocyanide, CNxyl, to give the tris(isocyanide) complex [Mo(PhC≡CPh)(CNxyl)$_3$(η-C$_5$Me$_5$)][BF$_4$] **1**. With four equivalents of CNxyl, alkyne–isocyanide coupling leads to the formation of the diiminometallacyclopentene [Mo{C(=Nxyl)C(Ph)=C(Ph)C=Nxyl}(CNxyl)$_2$(η-C$_5$Me$_5$)][BF$_4$] **2** which decomposes in thf at room temperature to give the tetrakis(isocyanide) complex [Mo(CNxyl)$_4$(η-C$_5$Me$_5$)][BF$_4$] **3**. In dichloromethane, **2** gives the diiminocyclobutene xylN=CC(Ph)=C(Ph)C=Nxyl **4**, the η^2-iminoacyl complex [MoCl(CNxyl)$_2$(η^2-xylN=CCH$_2$Cl)(η-C$_5$Me$_5$)][BF$_4$] **5**, formed by an addition reaction with dichloromethane, and the metallacyclobutene complex [Mo{C(Ph)=C(Ph)C=N(H)xyl}(CNxyl)$_3$(η-C$_5$Me$_5$)][BF$_4$]$_2$ **6**. Complex **5** is more efficiently synthesized by photolysis of **3** in dichloromethane, but the same reaction in chloroform produces the dichloromethyl complex [MoCl(CHCl$_2$)(CNxyl)$_3$(η-C$_5$Me$_5$)][BF$_4$] **7** which thermally decomposes to [MoCl$_2$(CNxyl)$_3$(η-C$_5$Me$_5$)][BF$_4$] **8**. Reaction of **2** with HCl in diethyl ether results in protonation of the metallacyclic ring and formation of the iminium metallacyclopentene [MoCl{C(=Nxyl)C(Ph)=C(Ph)C=N(H)xyl}(CNxyl)$_2$(η-C$_5$Me$_5$)][BF$_4$] **9**. Compound **3** is oxidised by AgBF$_4$ to give the molybdenum(IV) complex [MoF(CNxyl)$_4$(η-C$_5$Me$_5$)][BF$_4$]$_2$ **10**. The molecular structures of **3**–**6**, **7**/**8** and **10** have been determined by X-ray crystallography.

Introduction

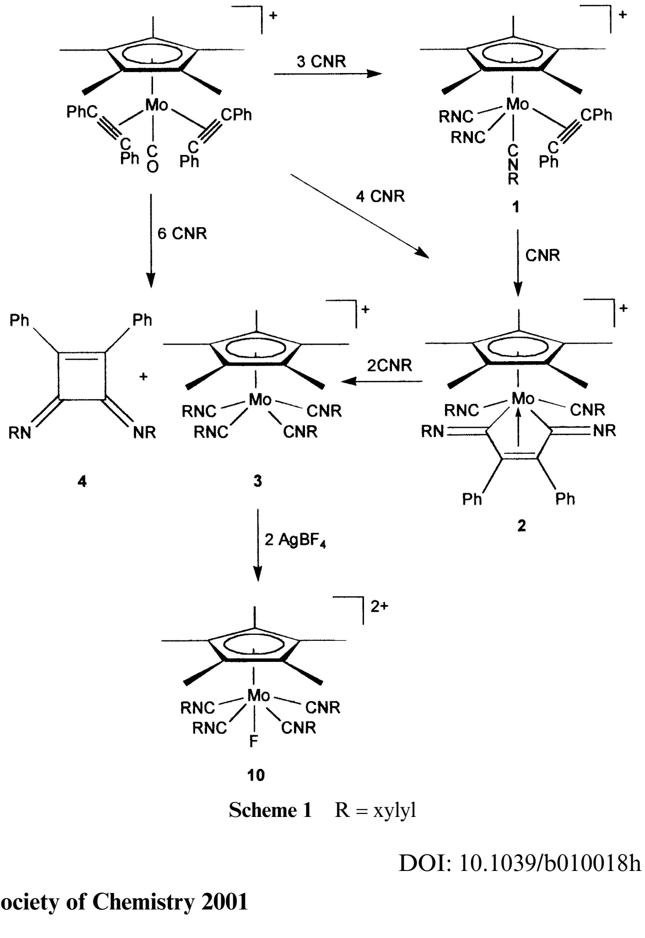
We have recently reported a series of investigations of the redox-induced reactions of co-ordinated C$_2$ ligands, including an alkyne–vinylidene interconversion[1] and the reductive coupling of co-ordinated alkynes.[2] In order to extend our methods to the linking of other unsaturated fragments, we have attempted to synthesize redox-active precursors containing alkynes and isocyanides as co-ligands. However, we now show that 2,6-dimethylphenyl isocyanide (xylNC) and [Mo(CO)(PhC≡CPh)$_2$(η-C$_5$Me$_5$)][BF$_4$] are readily *thermally* coupled, the resulting diiminometallacyclopentene complex undergoing a series of novel reactions including oxidative addition (at least formally) with CH$_2$Cl$_2$ to give an iminoacyl, ring contraction on protonation with HBF$_4$, giving an iminium metallacyclobutane complex, and formation of an iminometallacyclopentene complex with HCl.

Results and discussion

Reactions of [Mo(CO)(PhC≡CPh)$_2$(η-C$_5$Me$_5$)][BF$_4$] with 2,6-dimethylphenyl isocyanide

A dichloromethane solution of [Mo(CO)(PhC≡CPh)$_2$(η-C$_5$Me$_5$)][BF$_4$][3] readily reacts with three equivalents of CNxyl, evolving carbon monoxide and yielding a product formulated as the tris(isocyanide) [Mo(PhC≡CPh)(CNxyl)$_3$(η-C$_5$Me$_5$)][BF$_4$] **1**. An analytically pure sample has not been obtained, but the mass spectrum is consistent with this formulation and the observed IR spectrum [ν(CN) 2136w sh, 2108s and 2091m cm^{-1}] is similar to that of the crystallographically characterised compound [Mo(PhC≡CPh)(CNBu^t)$_3$(η-C$_5$Me$_5$)][BF$_4$].[4]

Reaction of complex **1** at 0 °C with a further equivalent of CNxyl, or of [Mo(CO)(PhC≡CPh)$_2$(η-C$_5$Me$_5$)][BF$_4$] with four equivalents of isocyanide at 0 °C in the presence of NEt$_3$, produced a red solution from which red crystals of [Mo{C(=Nxyl)C(Ph)=C(Ph)C=Nxyl}(CNxyl)$_2$(η-C$_5$Me$_5$)][BF$_4$] **2** were isolated. The complex was characterised by elemental analysis and IR (Table 1) and NMR spectroscopy (Table 2); it contains a diiminometallacyclopentene ring formed by isocyanide insertion into the two Mo–C$_{\text{alkyne}}$ bonds (Scheme 1).



Scheme 1 R = xylyl

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Table 1 Analytical and IR spectroscopic data for compounds **2**–**10**

Compound	Colour	Yield (%)	Analysis (%)[a] C	Analysis (%)[a] H	Analysis (%)[a] N	IR[b,c]/cm^{-1} ν(CN)
$[Mo\{C(=Nxyl)C(Ph)=C(Ph)C=Nxyl\}(CNxyl)_2(\eta\text{-}C_5Me_5)][BF_4]$ **2**	Red	76	70.4 (70.4)	5.8 (6.0)	5.6 (5.5)	2127, 2096, 1701w br
$[Mo(CNxyl)_4(\eta\text{-}C_5Me_5)][BF_4]$ **3**	Red-orange	92	65.4 (65.6)	6.3 (6.1)	6.3 (6.7)	2128w, 2056, 1999w
xylN=CC(Ph)=C(Ph)C=Nxyl **4**	Yellow	46	86.9 (87.2)	6.3 (6.4)	5.9 (6.4)	1726m, 1684m
$[MoCl(CNxyl)_2(xylN=CCH_2Cl)(\eta\text{-}C_5Me_5)][BF_4]$ **5**	Red-brown	51	56.6 (57.3)	5.2 (5.6)	4.9 (5.3)	2160w sh, 2142s
$[Mo\{C(Ph)=C(Ph)C=N(H)xyl\}(CNxyl)_3(\eta\text{-}C_5Me_5)][BF_4]_2\cdot CH_2Cl_2$ **6**·CH_2Cl_2	Yellow	85	62.1 (61.9)	5.7 (5.5)	4.7 (4.7)	2153m, 2127, 2104m; 2147m sh, 2131s, sh, 2118[d,e]
$[MoCl(CHCl_2)(CNxyl)_3(\eta\text{-}C_5Me_5)][BF_4]$ **7**	Red-brown	58	54.3 (54.4)	5.4 (5.2)	5.0 (5.1)	2174w sh, 2156, 2135m
$[MoCl\{C(=Nxyl)C(Ph)=C(Ph)C=N(H)xyl\}(CNxyl)_2(\eta\text{-}C_5Me_5)][BF_4]\cdot thf$ **9**·thf	Red	42	67.9 (68.0)	6.3 (6.2)	4.6 (5.0)	2154, 2094, 2136m, 2085m[d,f]
$[MoF(CNxyl)_4(\eta\text{-}C_5Me_5)][BF_4]_2$ **10**	Yellow	79	58.3 (58.2)	5.6 (5.4)	6.0 (5.9)	2193w sh, 2173

[a] Calculated values in parentheses. [b] In CH_2Cl_2 unless stated otherwise. [c] Strong absorptions unless stated otherwise; m = medium, w = weak, br = broad, sh = shoulder. [d] In Nujol. [e] ν(NH) 3323w cm^{-1}. [f] ν(NH) 3311w cm^{-1}.

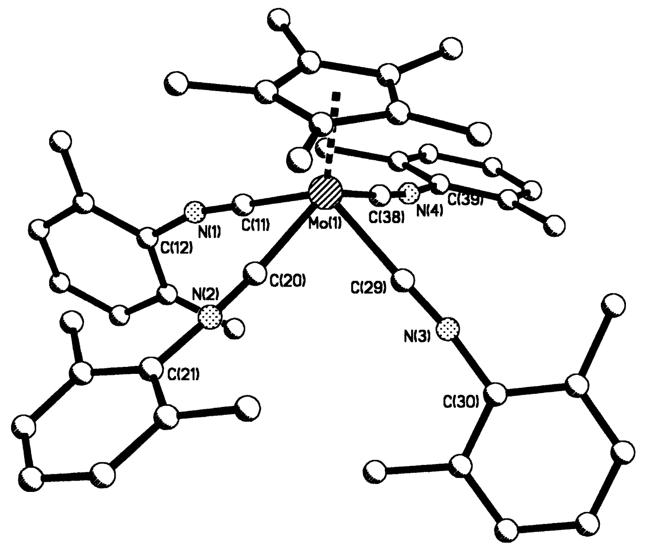


Fig. 1 The molecular structure of the cation of complex **3**. Hydrogen atoms have been omitted for clarity.

The IR spectrum of complex **2** shows two ν(CN) bands, at 2127 and 2096 cm^{-1}, due to *cis* isocyanide ligands and a broad absorption between 1650 and 1700 cm^{-1} due to ν(C=N) of the imino groups. The relatively high energy of ν(C=N) supports the description of **2** as a metallacyclopentene rather than a metallacyclopentadiene complex,[5] the lack of conjugation between the imine and alkene double bonds resulting from twisting at the imino carbon atoms to allow the C=C bond to interact with the metal. The room temperature ^{1}H and ^{13}C NMR spectra of **2** are broad but much sharper at −60 °C; eight peaks in the ^{1}H NMR spectrum, assigned to the methyl groups of the four isocyanide residues, indicate that rotation around the C–N–C$_{xyl}$ axis is slow at low temperature, and that at this temperature there is an asymmetry present in the structure that renders all of the methyl groups inequivalent. This is consistent with the ^{13}C NMR spectrum which shows four peaks in the range δ 170 to 200 due to the C atoms of the CNxyl fragments and two between δ 70 and 80 due to the alkene carbons.

The reaction between co-ordinated alkyne and free isocyanide has been observed before in low valent transition metal complexes[5–9] as has the related reaction between co-ordinated isocyanide and free alkyne.[10,11] However, previous examples have been confined to the iron, cobalt and nickel groups and this is the first diiminometallacyclopentene complex of an earlier transition metal.

The diiminobutene ligand is displaced when complex **2** reacts with two more equivalents of CNxyl, yielding the tetrakis(isocyanide)molybdenum(II) compound $[Mo(CNxyl)_4(\eta\text{-}C_5Me_5)][BF_4]$ **3**, analogous to the briefly reported species $[Mo(CNR)_4(\eta\text{-}C_5H_5)]^+$ (R = alkyl or aryl),[12,13] and the diiminocyclobutene xylN=CC(Ph)=C(Ph)C=Nxyl **4**. The two products, subsequently more readily obtained simply by refluxing a thf solution of $[Mo(CO)(PhC{\equiv}CPh)_2(\eta\text{-}C_5Me_5)][BF_4]$ with six equivalents of CNxyl (Scheme 1), were characterised not only by elemental analysis and IR (Table 1) and NMR spectroscopy (Table 2) but also by X-ray crystallography.

The structure of the cation of complex **3** is shown in Fig. 1 and important bond lengths and angles are given in Table 3. The molybdenum environment is pseudo-square pyramidal with the four isocyanide carbon atoms forming the basal plane and the centroid of the C_5Me_5 ring the apex. The molybdenum atom is 0.94 Å above the basal plane which is inclined at an angle of 2.1° to the plane of the C_5Me_5 ring. The molybdenum–isocyanide distances are in the range 2.033(8) to 2.075(8) Å, and the isocyanide (C≡N) carbon–nitrogen distances are between 1.164(8) and 1.195(8) Å.

Table 2 NMR spectroscopic data[a] (δ, J/Hz) for compounds **2**–**10**

Compound	^{1}H	^{13}C
2[b]	1.43 (3H, s, $C_6H_3Me_2$), 1.65 (3H, s, $C_6H_3Me_2$), 1.72 (3H, s, $C_6H_3Me_2$), 1.74 (3H, s, $C_6H_3Me_2$), 1.85 (15H, s, $C_6H_3Me_2$), 2.08 (3H, s, $C_6H_3Me_2$), 2.19 (3H, s, $C_6H_3Me_2$), 2.70 (3H, s, $C_6H_3Me_2$), 2.83 (3H, s, $C_6H_3Me_2$), 6.00 (1H, t, J 4, $C_6H_3Me_2$ or C_6H_5), 6.70–7.70 (20H, m, $C_6H_3Me_2$ and C_6H_5), 8.39 (1H, br s, ($C_6H_3Me_2$ or C_6H_5)	11.4 (C_5Me_5), 18.1, 18.9, 19.2, 19.6, 19.8, 20.0, 20.1, 20.7 ($C_6H_3Me_2$), 72.0, 87.3 (CPh), 107.8 (C_5Me_5), 123.0, 124.0, 125.1, 125.1, 126.9, 127.6, 127.7, 127.8, 128.0, 128.1, 128.4, 128.6, 128.7, 128.7, 129.8, 130.1, 120.4, 130.5, 131.1, 131.9, 132.2, 132.6, 134.8, 136.3, 136.8, 136.9, 146.3, 146.4 (C_6H_5 and $C_6H_3Me_2$), 170.6, 170.7 (C=N), 184.2, 195.9 (CC=N)
3	2.14 (15H, s, C_5Me_5), 2.28 (24H, s, $C_6H_3Me_2$), 7.09–7.18 (12H, m, $C_6H_3Me_2$)	11.2 (C_5Me_5), 18.5 ($C_6H_3Me_2$), 104.9 (C_5Me_5), 128.7, 128.9 and 133.9 ($C_6H_3Me_2$), 189.4 (C=N)
4[b]	1.83 (6H, s, $C_6H_3Me_2$), 2.27 (6H, s, $C_6H_3Me_2$), 6.52–8.19 (16H, m, $C_6H_3Me_2$ and C_6H_5)	18.3, 18.7 ($C_6H_3Me_2$), 123.2, 123.6, 126.6, 126.6, 127.5, 127.6, 127.7, 128.1, 129.0, 129.1, 129.7, 130.0, 132.0, 146.2, 147.9 (C_6H_4 and $C_6H_3Me_2$), 163.2, 165.5, 165.7, 167.0 (cyclobutene ring)
5	2.06 (6H, s, $C_6H_3Me_2$), 2.26 (15H, s, C_5Me_5), 2.28 (12H, s, $C_6H_3Me_2$), 5.17 (2H, s, CH_2Cl), 6.91–7.32 (9H, m, $C_6H_3Me_2$)	13.2 (C_5Me_5), 19.1 and 19.7 ($C_6H_3Me_2$), 44.2 (CH_2Cl), 110.3 (C_5Me_5), 125.4, 128.1, 129.0, 129.2, 131.2, 133.1, 137.0 and 138.1 ($C_6H_3Me_2$), 166.4 (C≡N), 210.0 (C=N)
6	[c] First isomer: 1.87 (3H, s, $C_6H_3Me_2$), 2.13 (6H, s, $C_6H_3Me_2$), 2.38 (3H, s, $C_6H_3Me_2$), 2.45 (15H, s, C_5Me_5), 2.55 (12H, s, $C_6H_3Me_2$), 9.90 (1H, s, NH) Second isomer: 1.56 (3H, s, $C_6H_3Me_2$), 1.82 (3H, s, $C_6H_3Me_2$), 2.01 (12H, s, $C_6H_3Me_2$), 2.39 (15H, s, C_5Me_5), 2.51 (6H, s, $C_6H_3Me_2$), 10.77 (1H, s, NH)	[d] 11.8, 12.7 (C_5Me_5); 18.1, 18.7, 18.9, 19.2, 19.7, 19.9, 20.5, 20.5 ($C_6H_3Me_2$); 108.9, 111.6 (C_5Me_5); 124.9, 126.0, 126.5, 126.8, 127.8, 128.0, 128.3, 128.5, 128.6, 128.7, 128.9, 129.1, 129.2, 129.4, 129.5, 129.7, 129.8, 130.2, 130.7, 131.2, 131.7, 131.8, 131.9, 132.0, 132.2, 132.9, 133.1, 133.6, 134.9, 135.2, 135.8, 136.1, 137.1, 138.7, 138.8, 139.72, 141.8 ($C_6H_3Me_2$ and C_6H_5); 161.9 (MoCPh); 166.08, 168.04 (C≡N), 188.1 {MoC(Ph)-C(Ph)}, 214.9 (NH=C–Mo)
7	2.15 (15H, s, C_5Me_5), 2.56 (12H, mm, $C_6H_3Me_2$), 2.61 (6H, s, $C_6H_3Me_2$), 7.08 (1H, s, $CHCl_2$), 7.22–7.28 (6H, m, $C_6H_3Me_2$), 7.32–7.39 (3H, m, $C_6H_3Me_2$)	12.9 (C_5Me_5), 19.4 and 19.7 ($C_6H_3Me_2$), 86.6 ($CHCl_2$), 110.7 (C_5Me_5), 129.1, 131.1, 131.3, 136.5 and 136.8 ($C_6H_3Me_2$)
9[b]	1.07 (3H, s, $C_6H_3Me_2$), 1.73 (3H, s, $C_6H_3Me_2$), 1.86 (3H, s, $C_6H_3Me_2$), 2.16 (15H, s, C_5Me_5), 2.33 (3H, br s, $C_6H_3Me_2$), 2.46 (6H, s, $C_6H_3Me_2$), 2.57 (3H, s, $C_6H_3Me_2$), 2.66 (3H, s, $C_6H_3Me_2$), 5.58 (1H d, J 8, $C_6H_3Me_2$), 5.89 (1H, d, J 7, $C_6H_3Me_2$), 6.20–7.31 (20H, m, $C_6H_3Me_2$ and C_6H_5), 9.28 (1H, s, NH)	12.5 (C_5Me_5); 17.5, 18.2, 19.6, 19.8, 20.4, 20.8, 22.0 ($C_6H_3Me_2$); 108.6 (C_5Me_5); 121.7, 122.3, 124.2, 126.0, 126.1, 126.3, 126.6, 126.8, 126.8, 126.9, 126.9, 127.0, 127.4, 128.6, 128.7, 129.0, 129.2, 130.1, 130.3, 133.0, 133.1, 134.5, 134.7, 135.0, 138.1, 140.0 ($C_6H_3Me_2$ and C_6H_5); 152.7, 160.6 (C=C); 165.4, 171.5 (C≡N); 180.6 (C=N); 204.5 (NH=C)
10[e]	2.47 (24H, s, $C_6H_3Me_2$), 2.61 (15H, s, C_5Me_5), 7.24–7.45 (12H, m, $C_6H_3Me_2$)	14.5 (C_5Me_5), 19.2 ($C_6H_3Me_2$), 116.3 (C_5Me_5), 129.4, 132.3 and 136.4 ($C_6H_3Me_2$)

[a] At room temperature in CD_2Cl_2 unless otherwise stated. [b] Recorded at −60 °C at 400 MHz. [c] See text for nature of isomers; relative ratio approximately 2 : 1. Signals due to the aromatic protons of the two isomers are superimposed, in the range δ 6.32–7.52. [d] Peaks for the two isomers are superimposed. [e] ^{19}F NMR (relative to CCl_3F): δ 152.69, 152.74 [BF_4]; 158.13 [MoF].

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

Mo(1)–C(11)	2.033(8)	N(2)–C(20)	1.178(8)
Mo(1)–C(38)	2.054(8)	N(2)–C(21)	1.390(9)
Mo(1)–C(20)	2.058(8)	N(3)–C(29)	1.164(8)
Mo(1)–C(29)	2.075(8)	N(3)–C(30)	1.394(9)
N(1)–C(11)	1.195(8)	N(4)–C(38)	1.173(8)
N(1)–C(12)	1.412(9)	N(4)–C(39)	1.407(8)
C(11)–Mo(1)–C(38)	77.7(3)	C(20)–N(2)–C(21)	175.6(8)
C(11)–Mo(1)–C(20)	76.5(3)	C(29)–N(3)–C(30)	172.7(7)
C(38)–Mo(1)–C(20)	130.2(3)	C(38)–N(4)–C(39)	174.1(7)
C(11)–Mo(1)–C(29)	120.2(3)	N(1)–C(11)–Mo(1)	176.9(6)
C(38)–Mo(1)–C(29)	78.5(3)	N(2)–C(20)–Mo(1)	174.6(6)
C(20)–Mo(1)–C(29)	78.8(3)	N(3)–C(29)–Mo(1)	177.8(7)
C(11)–N(1)–C(12)	165.2(8)	N(4)–C(38)–Mo(1)	176.2(6)

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

N(1)–C(21)	1.266(2)	C(18)–C(21)	1.508(2)
N(1)–C(2)	1.425(2)	C(19)–C(20)	1.383(2)
N(2)–C(18)	1.267(2)	C(19)–C(28)	1.459(2)
N(2)–C(10)	1.439(2)	C(20)–C(22)	1.467(2)
C(18)–C(19)	1.491(2)	C(20)–C(21)	1.500(2)
C(21)–N(1)–C(2)	120.5(1)	C(28)–C(19)–C(18)	131.0(1)
C(18)–N(2)–C(10)	115.7(1)	C(19)–C(20)–C(22)	135.0(1)
N(2)–C(18)–C(19)	135.5(1)	C(19)–C(20)–C(21)	92.1(1)
N(2)–C(18)–C(21)	136.7(1)	C(22)–C(20)–C(21)	132.8(1)
C(19)–C(18)–C(21)	87.7(1)	N(1)–C(21)–C(20)	141.6(1)
C(20)–C(19)–C(28)	136.4(1)	N(1)–C(21)–C(18)	131.0(1)
C(20)–C(19)–C(18)	92.6(1)	C(20)–C(21)–C(18)	87.4(1)

The structure of compound **4** (Fig. 2, Table 4) is similar to that of the trifluoromethyl analogue $F_3CN{=}\overline{CC(Ph){=}C(Ph)C}{=}NCF_3$[14] in showing two inequivalent imino-nitrogen substituents; one is *cis* to the C=C bond and the other *trans*. The ^{1}H NMR spectrum of **4** at −20 °C shows two different environments for the two xylyl rings, *i.e.* that the solid state structure is maintained in solution at low temperature. However, at room temperature the spectrum is broadened, suggesting that hindered rotation around the carbon–nitrogen double bonds renders the two imino-nitrogen substituents equivalent. The formation of **4** by cyclisation of the C(=Nxyl)C(Ph)=C(Ph)-C=Nxyl ligand on liberation from **2** is not unexpected; there are two previous reports of the formation of **4** by the metal-mediated 2+1 coupling of CNxyl with PhC≡CPh.[10]

Reactions of complex 2

Complex **2** is the precursor to a series of novel metallacycles (Scheme 2). Although stable in the solid state and in solution at low temperatures, it decomposes in solution at room temperature. In thf the major product is the tetrakis(isocyanide) complex **3**, formed by elimination of diphenylacetylene. In dichloromethane, however, a black solution results which shows IR peaks for **1**, **3** and **4** as well as strong absorptions at 2141 and 2127 cm^{-1}. Allowing a dichloromethane–diethyl ether solution of **2** to stand for one week produced both red and yellow crystals suitable for X-ray diffraction. The former (giving the band at 2141 cm^{-1}) were identified by a single crystal X-ray analysis as the η^2-iminoacyl compound $[MoCl(CNxyl)_2(\eta^2\text{-xylN=CCH}_2Cl)(\eta\text{-}C_5Me_5)][BF_4]$ **5**, and the latter (giving rise to the band at 2127 cm^{-1}) as the iminium metallacyclobutene

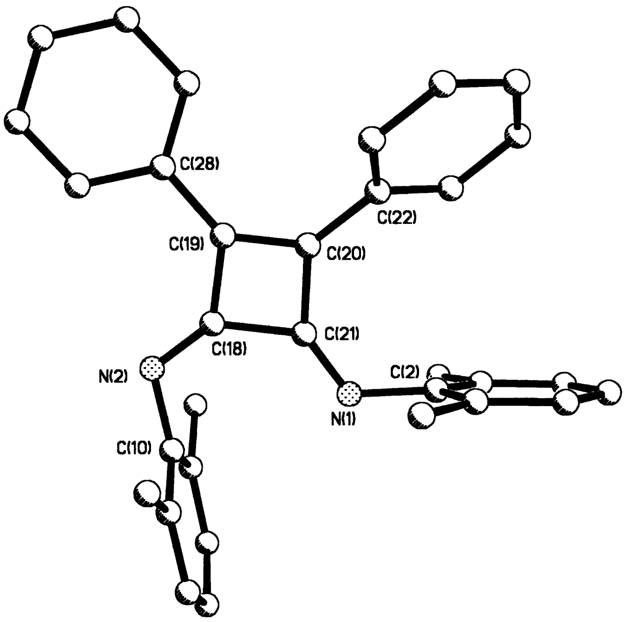
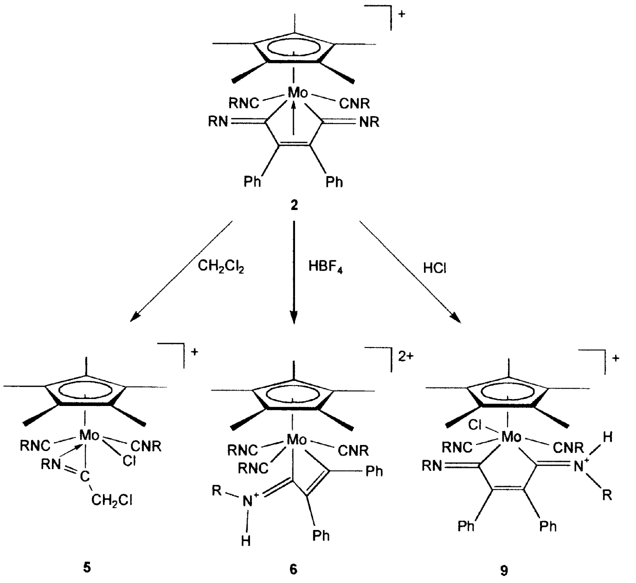


Fig. 2 The molecular structure of compound **4**. Hydrogen atoms have been omitted for clarity.



Scheme 2 R = xylyl

complex $[\overline{\text{Mo}\{\text{C(Ph)=C(Ph)C}}\text{=N(H)xyl}\}(\text{CNxyl})_3(\eta\text{-C}_5\text{Me}_5)][\text{BF}_4]_2$ **6** (see below).

The structure of the cation of complex **5** is shown in Fig. 3, and important bond lengths and angles are given in Table 5. The molybdenum–isocyanide distances are relatively long and the isocyanide carbon–nitrogen distances relatively short compared with those of the molybdenum(II) complex **3** reflecting weak π-back donation from the formally molybdenum(IV) centre of **5**. The Mo–C and Mo–N distances to the iminoacyl ligand [2.074(6) and 2.193(5) Å respectively], and the carbon–nitrogen double bond of this ligand [1.267(7) Å] are very similar to those of the only molybdenum–iminoacyl compound previously crystallographically characterised, namely $[\text{Mo(CO)}_2(\eta^2\text{-PhN=CMe})(\eta\text{-C}_5\text{H}_5)]$.[15]

At room temperature, the ^{13}C and ^{1}H NMR spectra show two environments (in a 2 : 1 ratio), rather than three, for the 2,6-dimethylphenyl groups, indicating that rapid η^2–η^1–η^2 interconversion of the iminoacyl ligand (*i.e.* involving rotation around the Mo–C bond) renders the two isocyanide ligands equivalent.

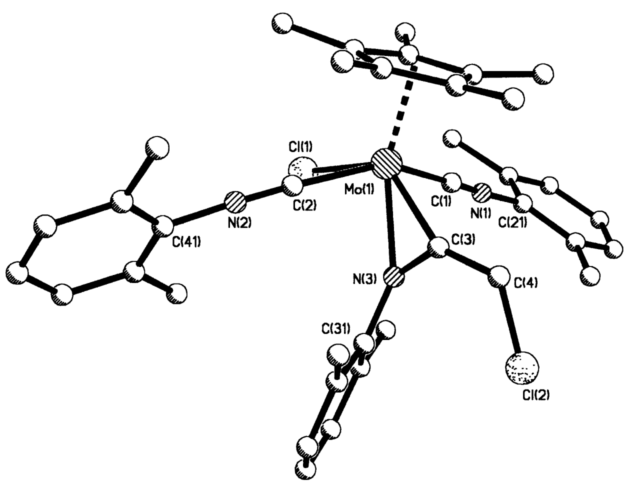


Fig. 3 The molecular structure of the cation of complex **5**. Hydrogen atoms have been omitted for clarity.

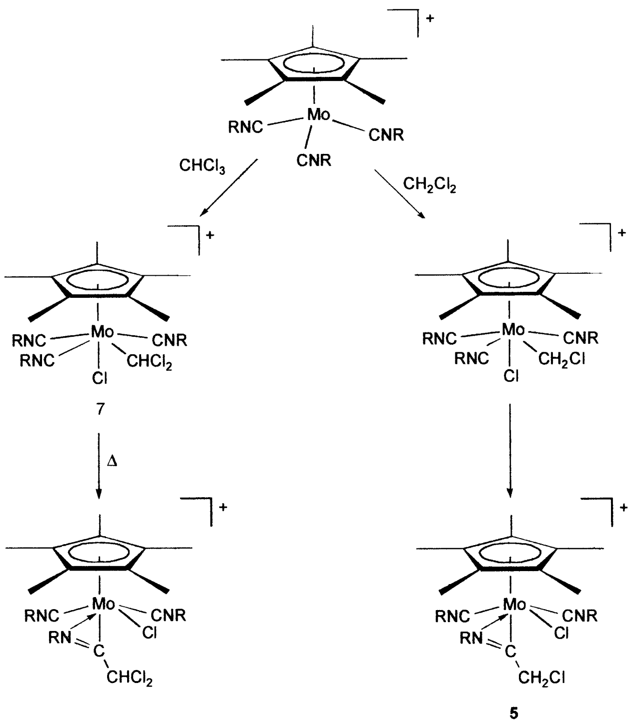
Table 5 Selected bond lengths (Å) and angles (°) for complex **5**

Mo(1)–C(3)	2.074(6)	N(2)–C(2)	1.153(6)
Mo(1)–C(1)	2.097(6)	N(2)–C(41)	1.415(7)
Mo(1)–C(2)	2.146(6)	N(3)–C(3)	1.267(7)
Mo(1)–N(3)	2.193(6)	N(3)–C(31)	1.430(7)
Mo(1)–Cl(1)	2.463(2)	C(3)–C(4)	1.485(8)
N(1)–C(1)	1.158(6)	C(4)–Cl(2)	1.785(6)
N(1)–C(21)	1.405(7)		
C(3)–Mo(1)–C(1)	84.8(2)	C(2)–N(2)–C(41)	172.6(5)
C(3)–Mo(1)–C(2)	89.7(2)	N(1)–C(1)–Mo(1)	175.8(5)
C(1)–Mo(1)–C(2)	152.6(2)	N(2)–C(2)–Mo(1)	168.9(5)
C(3)–Mo(1)–N(3)	34.4(2)	C(3)–N(3)–C(31)	136.6(5)
C(1)–Mo(1)–N(3)	81.0(2)	C(3)–N(3)–Mo(1)	67.6(3)
C(2)–Mo(1)–N(3)	79.4(2)	C(31)–N(3)–Mo(1)	151.5(4)
C(3)–Mo(1)–Cl(1)	126.7(2)	N(3)–C(3)–C(4)	132.1(5)
C(1)–Mo(1)–Cl(1)	82.5(2)	N(3)–C(3)–Mo(1)	77.9(3)
C(2)–Mo(1)–Cl(1)	79.3(2)	C(4)–C(3)–Mo(1)	149.8(4)
N(3)–Mo(1)–Cl(1)	92.4(1)	C(3)–C(4)–Cl(2)	114.7(4)
C(1)–N(1)–C(21)	173.1(6)		

The metal-bound chloride and the chloromethyl substituent of the iminoacyl ligand of complex **5** apparently originate from dichloromethane. It is probable that the iminoacyl ligand is formed by insertion of an isocyanide into a metal–alkyl bond,[16] and likely that the alkyl is in turn formed by oxidative addition of CH_2Cl_2 to a reactive 16-electron metal centre (Scheme 3). There are precedents for the formation of η^2-iminoacyls by alkylation of an isocyanide complex, but these have all involved recognised alkylating agents such as methyl iodide or $[\text{OMe}_3][\text{BF}_4]$.[11,15,17,18] Previous syntheses[5,7,9–11,19] of chelating diiminometallacyclopentene complexes related to **5** have all been carried out in hydrocarbon solvents such as toluene or pentane. Presumably this is why there have been no reports of the type of reactivity now described.

As complex **5** contains three isocyanide residues, an alternative synthesis was attempted by treating the tris(isocyanide) complex **1** directly with dichloromethane. However, **1** is stable in this solvent for longer than the time involved in iminoacyl formation. Equally, it could be envisaged that in the presence of CH_2Cl_2 the loss of one isocyanide from the tetrakis(isocyanide) complex **3** could lead to **5**; once again, however, $[\text{Mo(CNxyl)}_4(\eta\text{-C}_5\text{Me}_5)][\text{BF}_4]$ is stable in dichloromethane. While the amounts of the other species (**3**, **5** and **6**) present in the reaction mixture vary according to the conditions, the cyclised ligand **4** is always present. It may be, therefore, that release of strain and an increase in conjugation within the organic π framework upon elimination of **4** from **2** drives the formation of **5**.

Given the postulated mechanism, it was envisaged that if the 16-electron intermediate $[\text{Mo(CNxyl)}_3(\eta\text{-C}_5\text{Me}_5)]^+$ could be generated in CH_2Cl_2 iminoacyl formation might occur. To this



Scheme 3 R = xylyl

end, a solution of the tetrakis(isocyanide) species **3** in CH_2Cl_2 was irradiated using UV light from a 500 W mercury discharge lamp. After 60 minutes, IR spectroscopy indicated that all the starting material had been consumed, to be replaced largely by **5**. The yield of 51% obtained using this method is notably higher than the 20–30% obtained when starting from **2**.

It is known that more electron-withdrawing alkyls are less prone to insertion into metal–isocyanide bonds.[20] Thus, in order to isolate a stable mixed alkyl–isocyanide intermediate analogous to $[MoCl(CH_2Cl)(CNxyl)_3(\eta\text{-}C_5Me_5)][BF_4]$ (Scheme 3) a $CHCl_3$ solution of **3** was irradiated with UV light. This was successful in producing $[MoCl(CHCl_2)(CNxyl)_3(\eta\text{-}C_5Me_5)][BF_4]$ **7** which was isolated as circular orange-brown crystallites from the reaction mixture. The IR spectrum of **7** shows the three expected isocyanide bands, and the dichloromethyl group is clearly apparent as a singlet at δ 7.08 in the ^1H NMR spectrum and at δ 86.6 in the ^{13}C NMR spectrum. Complex **7** can be converted into an iminoacyl analogous to **5** by heating under reflux in thf (Scheme 3).

Metal dichloroalkyls are prone to decompose to the corresponding metal chloro compound *via* a bimolecular pathway that also liberates an alkene. For example, $[IrCl(CHCl_2)(PMe_3)(\eta\text{-}C_5Me_5)]$, which appears to be the only other reported example of an 18-electron half-sandwich dichloromethyl complex, decomposes to give $[IrCl_2(PMe_3)(\eta\text{-}C_5Me_5)]$.[21] Such behaviour has also been observed in the mass spectrum of **7**; as well as showing a molecular ion at $m/z = 744$, a peak of similar intensity at $m/z = 757$ corresponds to the ion $[MoCl(C_2H_2Cl_2)(CNxyl)_3(\eta\text{-}C_5Me_5)]^+$ which is derived from the transfer of a CH group from one metal centre to another and which may be regarded as an intermediate in the bimolecular elimination of dichloroethene from **7**.

Alkene elimination also occurred during attempts to grow crystals of complex **7** suitable for X-ray diffraction (by allowing diethyl ether to diffuse into a solution of the complex in $CHCl_3$). Thus, the crystal chosen for the structural study was found to be composed of approximately 10% of **7** and 90% of the elimination product $[MoCl_2(CNxyl)_3(\eta\text{-}C_5Me_5)][BF_4]$ **8**, with the dichloromethyl group of **7** and the second chlorine atom of **8** disordered over the same site. The geometry around the molybdenum atom is a distorted octahedron, with the centroid of the cyclopentadienyl ring and the disordered group at the axial positions, and the three isocyanides and one chloride ligand equatorial (Fig. 4; selected bond lengths and angles are given in Table 6). This is the same arrangement as in the isoelectronic complex $[NbCl_2(CNxyl)_3(\eta\text{-}C_5Me_5)]$.[22]

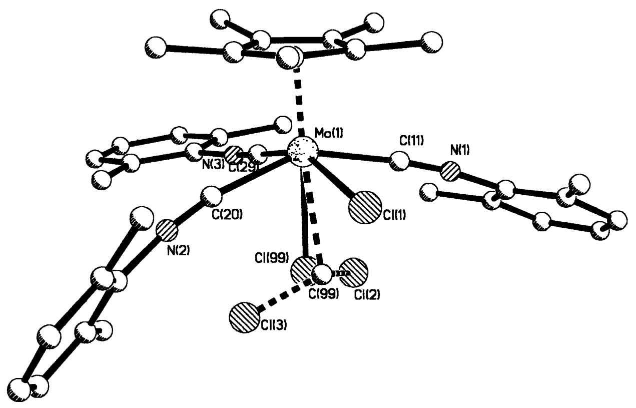


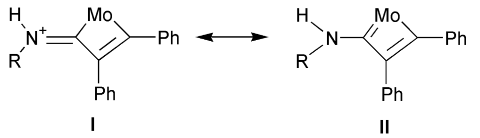
Fig. 4 The molecular structure of the cation of complex **7/8** showing the disordering of the $CHCl_2$ and Cl ligands. Hydrogen atoms have been omitted for clarity.

Table 6 Selected bond lengths (Å) and angles (°) for complex **7/8**

Mo(1)–C(29)	2.086(3)	N(1)–C(11)	1.154(4)
Mo(1)–C(11)	2.114(3)	N(2)–C(20)	1.148(4)
Mo(1)–C(20)	2.138(3)	N(3)–C(29)	1.155(3)
Mo(1)–Cl(1)	2.476(1)	C(99)–Cl(3)	1.75(5)
Mo(1)–C(99)	2.48(6)	C(99)–Cl(2)	1.88(6)
Mo(1)–Cl(99)	2.487(1)		
C(29)–Mo(1)–C(11)	91.5(1)	C(20)–Mo(1)–Cl(99)	76.5(1)
C(29)–Mo(1)–C(20)	91.8(1)	Cl(1)–Mo(1)–Cl(99)	79.8(1)
C(11)–Mo(1)–C(20)	151.2(1)	C(99)–Mo(1)–Cl(99)	10.1(11)
C(29)–Mo(1)–Cl(1)	153.7(1)	C(11)–N(1)–C(12)	171.5(3)
C(11)–Mo(1)–Cl(1)	82.8(1)	C(20)–N(2)–C(21)	173.0(3)
C(20)–Mo(1)–Cl(1)	81.6(1)	C(29)–N(3)–C(30)	166.7(3)
C(29)–Mo(1)–C(99)	83.5(11)	N(1)–C(11)–Mo(1)	174.4(2)
C(11)–Mo(1)–C(99)	73.0(13)	N(2)–C(20)–Mo(1)	169.4(2)
C(20)–Mo(1)–C(99)	79.0(13)	N(3)–C(29)–Mo(1)	178.7(2)
Cl(1)–Mo(1)–C(99)	70.2(11)	Cl(3)–C(99)–Cl(2)	102(2)
C(29)–Mo(1)–Cl(99)	73.9(1)	Cl(3)–C(99)–Mo(1)	111(3)
C(11)–Mo(1)–Cl(99)	76.9(1)	Cl(2)–C(99)–Mo(1)	105(2)

X-Ray structural studies show complex **6** (Fig. 5, Table 7) to be $[\overline{\text{Mo}\{\text{C(Ph)=C(Ph)C}}\text{=N(H)xyl}\}(\text{CNxyl})_3(\eta\text{-C}_5\text{Me}_5)][\text{BF}_4]_2$. The iminium metallacyclobutene unit formally arises from protonation of one of the isocyanide residues within the diiminometallocyclopentene moiety of **2** and deinsertion of the other. Imine nitrogen atoms such as those present in **2** are susceptible to protonation[19] and, indeed, higher yields of **6** result from the direct reaction between **2** and $HBF_4\cdot Et_2O$ in CH_2Cl_2.

In the dication of complex **6** the angles around N(4) sum to 359.3°, *i.e.* the nitrogen atom is planar and sp^2 hybridised rather than tetrahedral and sp^3 hybridised, and the carbon–nitrogen bond distance of 1.316(5) Å is within the range expected for a CN double bond, though 0.05 Å longer than that of **4**. This suggests that the description of **6** as an iminium derivative, with charge separation and a d^2, molybdenum(IV), centre (**I**, Scheme 4), is more realistic than as a d^0, molybdenum(VI), aminometallacyclobutadiene complex (**II**, Scheme 4). The Mo–C bond lengths within the metallacyclobutene



Scheme 4 R = xylyl

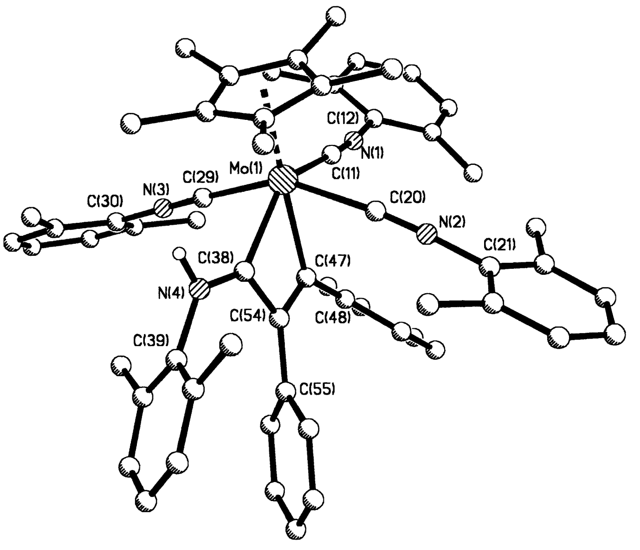


Fig. 5 The molecular structure of the dication of complex **6**. All hydrogen atoms, apart from the *N*-bound H atom of the C(Ph)=C(Ph)-C=N(H)xyl ligand, have been omitted for clarity.

Table 7 Selected bond lengths (Å) and angles (°) for complex **6**

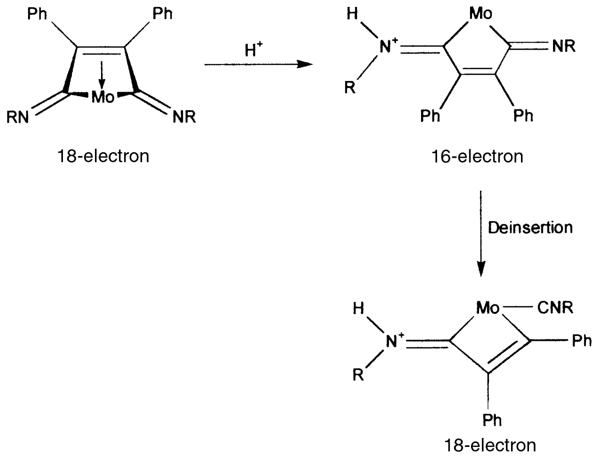
Mo(1)–C(11)	2.116(4)	N(3)–C(29)	1.157(5)
Mo(1)–C(20)	2.128(4)	N(3)–C(30)	1.425(5)
Mo(1)–C(29)	2.134(4)	N(4)–C(38)	1.316(5)
Mo(1)–C(38)	2.202(4)	N(4)–C(39)	1.457(5)
Mo(1)–C(47)	2.228(4)	C(38)–C(54)	1.457(5)
N(1)–C(11)	1.152(5)	C(47)–C(54)	1.367(5)
N(1)–C(12)	1.420(5)	C(47)–C(48)	1.479(5)
N(2)–C(20)	1.149(5)	C(54)–C(55)	1.485(6)
N(2)–C(21)	1.416(5)		
C(11)–Mo(1)–C(20)	90.2(1)	C(38)–N(4)–C(39)	127.0(4)
C(11)–Mo(1)–C(29)	85.7(2)	N(1)–C(11)–Mo(1)	176.8(4)
C(20)–Mo(1)–C(29)	150.6(2)	N(2)–C(20)–Mo(1)	174.0(4)
C(11)–Mo(1)–C(38)	139.1(2)	N(3)–C(29)–Mo(1)	177.3(4)
C(20)–Mo(1)–C(38)	82.4(1)	N(4)–C(38)–C(54)	124.4(4)
C(29)–Mo(1)–C(38)	81.8(1)	N(4)–C(38)–Mo(1)	137.6(3)
C(11)–Mo(1)–C(47)	79.9(2)	C(54)–C(38)–Mo(1)	97.9(2)
C(20)–Mo(1)–C(47)	72.5(1)	C(54)–C(47)–C(48)	124.7(4)
C(29)–Mo(1)–C(47)	78.1(1)	C(54)–C(47)–Mo(1)	99.7(3)
C(38)–Mo(1)–C(47)	59.5(1)	C(48)–C(47)–Mo(1)	134.8(3)
C(11)–N(1)–C(12)	172.6(4)	C(47)–C(54)–C(38)	102.2(4)
C(20)–N(2)–C(21)	176.6(4)	C(47)–C(54)–C(55)	125.8(4)
C(29)–N(3)–C(30)	179.1(4)	C(38)–C(54)–C(55)	132.0(3)

ring, which are similar to each other [2.202(4) and 2.228(4) Å] and much longer than molybdenum–carbon double bonds,[23] are also consistent with this description. Moreover, the Mo–C$_{\mathrm{isocyanide}}$ [2.116(4)–2.134(4) Å] and the isocyanide carbon–nitrogen [1.149(5)–1.157(5) Å] bond lengths are in the same range as those of **5**.

The geometry of the metallacycle of complex **6** is remarkably similar to those of [Co{C(Ph)=C(CO$_2$Me)C[N(Me)C$_6$H$_4$Me-*p*]}(PPh$_3$)(η-C$_5$H$_5$)][PF$_6$][6] and [Re{C(Me)C(CO$_2$Me)C(OEt)}(CO)$_4$],[24] the only other crystallographically characterised metallacyclobutenes bearing a heteroatom substituent. The former, like **6**, may be viewed as an iminium complex, and has a carbon–nitrogen double bond 0.05 Å longer than that of the related imine complex [Co{C(Ph)=C(CO$_2$Me)C(NC$_6$H$_4$Me-*p*)(PPh$_3$)(η-C$_5$H$_5$)]. The lengthening of the C–N bond implies there is some delocalisation of charge away from the nitrogen atom, creating a contribution from the aminometallacyclobutadiene resonance form and leading to bonds longer than the normal carbon–nitrogen double bond distance.

The cation [Co{C(Ph)=C(CO$_2$Me)C[N(Me)C$_6$H$_4$Me-*p*]}(PPh$_3$)(η-C$_5$H$_5$)]$^+$ occurs as two isomers in which the iminium methyl groups are *syn* or *anti* with respect to the PPh$_3$ ligand.[6] ^{1}H NMR spectroscopy shows that complex **6** also exists in solution as two isomers with the iminium proton *syn* and *anti* to the nearest dimethylphenyl ring; the (inseparable) isomers occur in a 2 : 1 ratio but it is not possible to say which is the more abundant. The spectrum shows two low field resonances for the N–*H* groups, and eight due to the methyl groups on the dimethylphenyl rings. The latter, resolved by NOE spectroscopy, appear as two sets of four signals; each set integrates in the ratio 4 : 2 : 1 : 1, indicating restricted rotation of one of the 2,6-dimethylphenyl rings in each isomer, presumably that attached to the protonated nitrogen atom. The ^{13}C NMR spectrum also contains eight resonances for the methyl groups, but only signals due to the carbon atoms of the metallacyclobutene ring of one isomer are visible.

In contrast to the deinsertion of isocyanide upon protonation with HBF$_4$, complex **2** in thf reacts with ethereal HCl to afford [MoCl{C(=Nxyl)C(Ph)=C(Ph)C=N(H)xyl}(CNxyl)$_2$(η-C$_5$Me$_5$)][BF$_4$] **9**, in which the metallacyclic ring has remained intact. A similar reaction between [Co{C(=NC$_6$H$_4$Me-*p*)C(Ph)=C(Ph)C=NC$_6$H$_4$Me-*p*}(η-C$_5$H$_5$)] and HCl gave the related cobalt compound [CoCl{C(=NC$_6$H$_4$Me-*p*)C(Ph)=C(Ph)C=N(H)C$_6$H$_4$Me-*p*}(η-C$_5$H$_5$)].[19] Clearly, the anion of the acid controls the product of protonation of **2**. Upon protonation at one of the imino nitrogen atoms the metallacyclopentene ring becomes planar, allowing delocalisation of the positive charge away from the nitrogen atom through increased conjugation. However, the alkenic bond is thus removed from a position where it can act as an electron donor to the metal centre. In compound **9** this shortfall in electron donation to the metal is overcome by co-ordination of the chloride counter ion, a two-electron donor, but with the non-coordinating [BF$_4$]$^-$ anion this is not possible. Instead, the contraction of the ring occurs to free an isocyanide as the extra donor ligand (Scheme 5), and **6** results.



Scheme 5 R = xylyl

Despite the presence of an iminium bond like that in complex **6**, the spectroscopic data of **9** do not provide evidence for isomerism of the type observed for **6**; at −60 °C there is only one low field N–*H* peak in the ^{1}H NMR spectrum. As in the low temperature spectrum of **2**, there are eight signals for the methyl groups on the dimethylphenyl rings, and an equivalent number of peaks in the ^{13}C NMR spectrum. The lack of isomerism contrasts with that previously observed upon formation of this particular type of ligand with HCl; two isomers of [CoCl{C(=NC$_6$H$_4$Me-*p*)C(Ph)=C(Ph)C=N(H)C$_6$H$_4$Me-*p*}(η-C$_5$H$_5$)] were detected.[19]

Oxidation of complex 3

The cyclic voltammogram of complex **3** in CH$_2$Cl$_2$ showed a

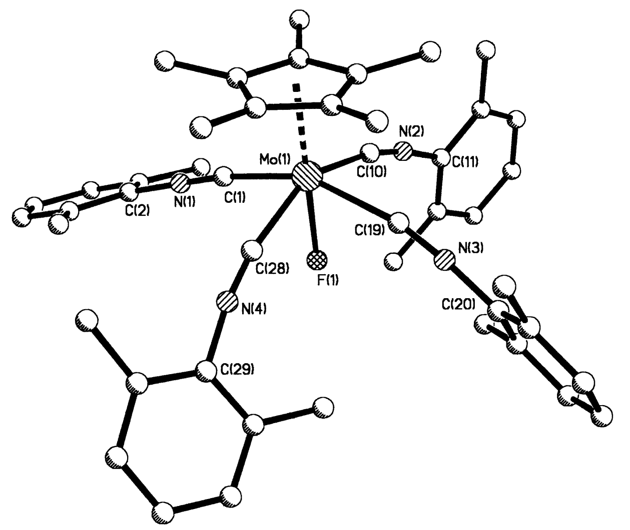


Fig. 6 The molecular structure of the dication of complex **10**. Hydrogen atoms have been omitted for clarity.

Table 8 Selected bond lengths (Å) and angles (°) for complex **10**

Mo(1)–F(1)	1.981(2)	N(2)–C(10)	1.151(4)
Mo(1)–C(1)	2.122(3)	N(2)–C(11)	1.411(4)
Mo(1)–C(28)	2.145(3)	N(3)–C(19)	1.154(4)
Mo(1)–C(19)	2.147(3)	N(3)–C(20)	1.408(4)
Mo(1)–C(10)	2.156(3)	N(4)–C(28)	1.147(4)
N(1)–C(1)	1.155(4)	N(4)–C(29)	1.407(4)
N(1)–C(2)	1.402(4)		
F(1)–Mo(1)–C(1)	77.1(1)	F(1)–Mo(1)–C(37)	148.6(1)
F(1)–Mo(1)–C(28)	76.2(1)	C(1)–N(1)–C(2)	177.9(3)
C(1)–Mo(1)–C(28)	86.9(1)	C(10)–N(2)–C(11)	172.6(3)
F(1)–Mo(1)–C(19)	76.0(1)	C(19)–N(3)–C(20)	171.6(3)
C(1)–Mo(1)–C(19)	152.9(1)	C(28)–N(4)–C(29)	170.0(3)
C(28)–Mo(1)–C(19)	84.0(1)	N(1)–C(1)–Mo(1)	173.1(3)
F(1)–Mo(1)–C(10)	75.3(1)	N(2)–C(10)–Mo(1)	169.6(3)
C(1)–Mo(1)–C(10)	90.7(1)	N(3)–C(19)–Mo(1)	167.5(3)
C(28)–Mo(1)–C(10)	151.2(1)	N(4)–C(28)–Mo(1)	166.1(3)
C(19)–Mo(1)–C(10)	85.3(1)		

reversible oxidation wave at 0.7 V implying formation of the paramagnetic dication [Mo(CNxyl)$_4$(η-C$_5$Me$_5$)]$^{2+}$. However, the yellow crystalline product formed from **3** and the chemical oxidant AgBF$_4$ in CH$_2$Cl$_2$ is the molybdenum(IV) complex [MoF(CNxyl)$_4$(η-C$_5$Me$_5$)][BF$_4$]$_2$ **10**, formed by two-electron oxidation and addition of F$^-$ from the [BF$_4$]$^-$ counter ion; the related iodo complex [MoI(CNBu^t)$_4$(η-C$_5$H$_5$)]$^{2+}$ has previously been reported,[13] and the isoelectronic niobium analogue [NbCl(CNBu^t)$_4$(η-C$_5$H$_5$)]$^+$ is also known.[25]

Its crystal structure (Fig. 6, Table 8) shows complex **10** to be related to that of the square pyramidal complex **3** with the addition of a fluoride ligand *trans* to η-C$_5$Me$_5$. However, the isocyanide ligands are displaced away from the extra ligand towards the η-C$_5$Me$_5$, and the metal atom lies 0.52 Å above the plane of the four isocyanide carbon atoms, which remains inclined at 2.5° to the plane of the C$_5$Me$_5$ ring. When compared with **3**, the longer Mo–C$_{\text{isocyanide}}$ distances [in the range 2.122(3) to 2.156(3) Å] and the shorter C–N distances [1.147(4) to 1.155(4)] indicate less Mo–C π back donation in **10**, a consequence of the higher formal oxidation state in **10** [Mo^{IV} *vs.* Mo^{II} in **3**]. The values of ν(CN) (2173s, 2193w sh cm^{-1}) are some 30 cm^{-1} higher than those for the other molybdenum(IV) compounds reported in this paper, an effect ascribed to the overall +2 charge of the cation and the presence of the highly electronegative fluorine atom.

Conclusion

The reaction of [Mo(CO)(PhC≡CPh)$_2$(η-C$_5$Me$_5$)][BF$_4$] with four equivalents of 2,6-dimethylphenyl isocyanide results in the coupling of two molecules of isocyanide with one of the coordinated alkynes to yield the diiminometallacyclopentene [Mo{C(=Nxyl)C(Ph)=C(Ph)C=Nxyl}(CNxyl)$_2$(η-C$_5$Me$_5$)][BF$_4$] **2**. This contains a five-membered ring that is twisted in order to allow the alkene double bond to bond to the metal, thus making the ligand an overall four-electron donor.

Complex **2** undergoes a series of reactions that involve the release of this twisting. This may take the form of eliminating a part of the ring, producing the tetrakis(isocyanide) compound [Mo(CNxyl)$_4$(η-C$_5$Me$_5$)][BF$_4$] **3** by loss of diphenylacetylene, or the whole of the ring as the cyclised diiminocyclobutene xylN=CC(Ph)=C(Ph)C=Nxyl **4**; the η^2-iminoacyl [MoCl(CNxyl)$_2$(η^2-xylN=CCH$_2$Cl)(η-C$_5$Me$_5$)][BF$_4$] **5** is a by-product. The twisting within the metallacycle **2** is also released upon protonation; the reaction with HBF$_4$ causes ring contraction and the formation of an iminium metallacyclobutene [Mo{C(Ph)=C(Ph)C=N(H)xyl}(CNxyl)$_3$(η-C$_5$Me$_5$)][BF$_4$]$_2$ **6**, whereas HCl allows the ring to remain intact but act as a two-electron donor in [MoCl{C(=Nxyl)C(Ph)=C(Ph)C=N(H)xyl}(CNxyl)$_2$(η-C$_5$Me$_5$)][BF$_4$] **9**; co-ordination of the chloride ion allows the metal to retain the 18-electron configuration. On UV photolysis in CH$_2$Cl$_2$, **3** loses one isocyanide to produce a reactive 16-electron centre which attacks the solvent to give the iminoacyl **5**; photolysis in CHCl$_3$ gives the chloromethyl complex [MoCl(CHCl$_2$)(CNxyl)$_3$(η-C$_5$Me$_5$)][BF$_4$] **7** which decomposes *via* a bimolecular pathway, eliminating an alkene and giving the dichloride [MoCl$_2$(CNxyl)$_3$(η-C$_5$Me$_5$)][BF$_4$] **8**. Compound **3** also reacts with two equivalents of AgBF$_4$, resulting in oxidation from Mo^{II} to Mo^{IV} followed by attack on a [BF$_4$]$^-$ counter ion to give [MoF(CNxyl)$_4$(η-C$_5$Me$_5$)][BF$_4$]$_2$ **10**.

Experimental

The preparation, purification and reactions of the complexes described were carried out under an atmosphere of dry dinitrogen using deoxygenated solvents. Unless stated otherwise the new complexes are air stable in the solid state and dissolve in polar solvents such as CH$_2$Cl$_2$ and thf to give solutions which only slowly decompose in air. The compound [Mo(CO)(PhC≡CPh)$_2$(η-C$_5$Me$_5$)][BF$_4$] was prepared by a modification of the published procedure.[3] IR spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrometer, ^{1}H and ^{13}C NMR spectra on JEOL λ300 or GX400 spectrometers with SiMe$_4$ as an internal standard. Electrochemical studies were carried out as previously described.[26] Under the conditions used, $E^{\circ\prime}$ for the one-electron oxidation of [Fe(η-C$_5$H$_5$)$_2$], added as an internal calibrant, is 0.47 V. Microanalyses were carried out by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

Syntheses

[Mo{C(=Nxyl)C(Ph)=C(Ph)C=Nxyl}(CNxyl)$_2$(η-C$_5$Me$_5$)][BF$_4$] 2. [Mo(CO)(PhC≡CPh)$_2$(η-C$_5$Me$_5$)][BF$_4$] (0.456 g, 0.65 mmol) and 2,6-dimethylphenyl isocyanide (0.341 g, 2.60 mmol) were stirred for 2 h at 0 °C in dichloromethane (30 cm^3). Diethyl ether (175 cm^3) and triethylamine (4 drops) were then added, and the solution was stored at −20 °C for one week. The resulting red crystals of **2** were removed by filtration, washed briefly with diethyl ether and dried *in vacuo*, yield 0.493 g (74%).

[Mo(CNxyl)$_4$(η-C$_5$Me$_5$)][BF$_4$] 3 and xylN=CC(Ph)=C(Ph)C=Nxyl 4. [Mo(CO)(PhC≡CPh)$_2$(η-C$_5$Me$_5$)][BF$_4$] (0.133 g, 0.189 mmol) and 2,6-dimethylphenyl isocyanide (0.149 g, 1.13 mmol) were heated under reflux in thf (10 cm^3) for 2 h. The resulting solution was allowed to cool, and diethyl ether (10 cm^3) added. After storage at *ca.* 10 °C overnight the solvent was removed, and the resulting red-orange needles of **3** were washed with

Table 9 Crystal and refinement data for compounds **3**–**6**, **7** and **10**

	3·thf	**4**	**5**	**6·CH$_2$Cl$_2$**	**7/8**	**10**
Formula	$C_{50}H_{59}BF_4MoN_4O$	$C_{32}H_{28}N_2$	$C_{38}H_{44}BCl_2F_4MoN_3$	$C_{61}H_{64}B_2Cl_2F_8MoN_4$	$C_{37.09}H_{42.09}BCl_{2.10}F_4MoN_3$	$C_{46}H_{51}B_2F_9MoN_4$
M	914.76	440.56	796.41	1193.62	786.99	948.47
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$P2_1/c$
a/Å	17.409(9)	8.8714(11)	15.989(5)	16.676(2)	8.269(2)	20.315(2)
b/Å	13.762(4)	14.597(2)	15.553(5)	16.339(2)	14.598(3)	13.973(2)
c/Å	20.048(6)	19.138(3)	16.489(5)	21.027(3)	15.379(3)	16.0458(17)
α/°	—	—	—	—	103.043(18)	—
β/°	99.402(18)	91.475(16)	113.917(14)	92.014(18)	90.989(19)	100.087(8)
γ/°	—	—	—	—	92.729(19)	—
U/Å^3	4739(3)	2477.6(6)	3748.3(20)	5725.5(14)	1805.7(7)	4484.4(10)
Z	4	4	4	4	2	4
μ/mm^{-1}	0.332	0.069	0.543	0.391	0.570	0.367
Reflections collected	24924	13017	19503	30322	15784	23740
Independent reflections (R_{int})	8349 (0.1868)	4376 (0.0248)	6568 (0.0952)	10066 (0.0567)	6344 (0.0256)	7896 (0.0269)
Goodness-of-fit on F^2	0.973	1.056	1.023	0.956	0.962	1.015
Final $R1$ indices [$I > 2\sigma(I)$]	0.0719	0.0367	0.0566	0.0481	0.0326	0.0464

diethyl ether and dried under vacuum, yield 0.147 g (92%). The orange supernatant liquid was filtered through a pad of silica (*ca.* 1 cm in depth), and evaporated to dryness *in vacuo*. *n*-Hexane (5 cm^3) was added, and then ethyl acetate (*ca.* 2 cm^3) dropwise until most of the solid had dissolved. The resulting solution was filtered, and then stored at *ca.* 10 °C until yellow crystals of **4** were obtained, yield 0.038 g (46%).

[MoCl(CNxyl)$_2$(η^2-xylN=CCH$_2$Cl)(η-C$_5$Me$_5$)][BF$_4$] 5. Complex **3** (0.110 g, 0.13 mmol) was dissolved in CH$_2$Cl$_2$ (60 cm^3) in a quartz reaction vessel. Irradiation of the solution using a 500 W mercury discharge lamp for 1 h yielded an orange solution which was reduced in volume to 10 cm^3 under vacuum. Addition of diethyl ether (10 cm^3) and storage at −20 °C overnight produced red-brown crystals of **5** which were removed by filtration and dried *in vacuo*, yield 0.053 g (51%).

[Mo{C(Ph)=C(Ph)C=N(H)xyl}(CNxyl)$_3$(η-C$_5$Me$_5$)][BF$_4$]$_2$·CH$_2$Cl$_2$ 6·CH$_2$Cl$_2$. A solution of [Mo(CO)(PhC≡CPh)$_2$-(η-C$_5$Me$_5$)][BF$_4$] (0.175 g, 0.25 mmol) and 2,6-dimethylphenyl isocyanide (0.131 g, 0.99 mmol) in CH$_2$Cl$_2$ (15 cm^3) was stirred for 2 h at 0 °C. Three drops of HBF$_4$·Et$_2$O were then added, causing the solution to darken slightly. Addition of diethyl ether (15 cm^3) and storage of the mixture at *ca.* 10 °C overnight gave the product as a yellow crystalline solid, yield 0.257 g (85%).

[MoCl(CHCl$_2$)(CNxyl)$_3$(η-C$_5$Me$_5$)][BF$_4$] 7. Complex **3** (0.117 g, 0.138 mmol) was dissolved in chloroform (100 cm^3) in a quartz reaction vessel. Irradiation of the solution using a 500 W mercury discharge lamp for 30 min yielded a yellow solution which was reduced in volume to 5 cm^3 under vacuum. Addition of diethyl ether (*ca.* 7 cm^3) until the solution became turbid and storage at −10 °C overnight produced small red-brown crystals of **7** which were removed by filtration and dried *in vacuo*, yield 0.067 g (58%).

[MoCl{C(=Nxyl)C(Ph)=C(Ph)C=N(H)xyl}(CNxyl)$_2$(η-C$_5$Me$_5$)][BF$_4$]·thf 9·thf. Complex **2** (0.039 g, 0.038 mmol) was dissolved at 0 °C in thf (5 cm^3). One drop of HCl·Et$_2$O was then added and the mixture stirred for two min. Diethyl ether (2 cm^3) was then added and the solution allowed to stand overnight. Deep red crystals of **9**·thf were removed by filtration, washed with diethyl ether (2 × 10 cm^3) and dried *in vacuo*, yield 0.018 g (42%).

[MoF(CNxyl)$_4$(η-C$_5$Me$_5$)][BF$_4$]$_2$ 10. Complex **3** (0.075 g, 0.009 mmol) and AgBF$_4$ (0.035 g, 0.018 mmol) were stirred in CH$_2$Cl$_2$ (10 cm^3) in the absence of light for 5 h. The resulting green suspension was filtered through Celite to give a yellow solution to which diethyl ether (5 cm^3) was added. Storage of the mixture at *ca.* 10 °C overnight gave square yellow crystals of **10**, yield 0.067 g (79%).

Structures of compounds 3–6, 7/8 and 10

Many of the details of the crystal structure analyses of **3**–**6**, **7/8**, **9** and **10** are presented in Table 9. All structure analyses were carried out by standard low temperature area detector methods.

CCDC reference numbers 155026–155031.

See http://www.rsc.org/suppdata/dt/b0/b010018h/ for crystallographic data in CIF or other electronic format.

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