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Ligand-Induced and Reductively Induced Alkyne−Isocyanide Coupling Reactions of $[\mathrm{Mo(CNBu^t)_3(PhC{\equiv}CPh)(\eta^5\text{-}C_5Me_5)][BF_4]}$

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The complex $[\mathrm{Mo(CO)(PhC{\equiv}CPh)_2(\eta^5\text{-}C_5Me_5)][BF_4]}$ reacts with 3 equiv of $\mathrm{CNBu^t}$ to yield the mixed alkyne−isocyanide complex $[\mathrm{Mo(CNBu^t)_3(PhC{\equiv}CPh)(\eta^5\text{-}C_5Me_5)][BF_4]}$, **1**. Reaction of **1** with a fourth equivalent of $\mathrm{CNBu^t}$ generates $[\mathrm{Mo\{{=}C(NHBu^t)C(Ph){=}C(Ph)CN\}(CNBu^t)_2(\eta^5\text{-}C_5Me_5)][BF_4]}$, **2**, containing an η^3-vinylcarbene ligand formed from the coupling of two of the coordinated isocyanide ligands with the diphenylacetylene, with concomitant protonation of one of these isocyanide fragments and dealkylation of the other. Complex **2** may be deprotonated to give $[\mathrm{Mo\{C({=}NBu^t)C(Ph){=}C(Ph)CN\}(CNBu^t)_2(\eta^5\text{-}C_5Me_5)]}$, **3**. Protonation of **1** with $\mathrm{HBF_4{\cdot}Et_2O}$ generates $[\mathrm{Mo\{{=}C(Ph)C(Ph)C{=}NHBu^t\}(CNBu^t)_2(\eta^5\text{-}C_5Me_5)][BF_4]_2}$, **4**, by inducing the coupling of a protonated isocyanide ligand with diphenylacetylene, and **4** reacts with $\mathrm{CNBu^t}$ to give **2**. A similar reaction of **4** with $\mathrm{P(OMe)_3}$ generates $[\mathrm{Mo\{{=}C(NHBu^t)C(Ph){=}C(Ph)CN\}(CNBu^t)\{P(OMe)_3\}(\eta^5\text{-}C_5Me_5)][BF_4]}$, **5**, involving the same coupling and elimination pattern. The diphenylacetylene and $\mathrm{CNBu^t}$ ligands of **1** may also be reductively coupled. Thus, treatment of **1** with sodium−mercury amalgam and subsequent protonation with $\mathrm{HBF_4{\cdot}Et_2O}$ gives the metallacyclopentatriene-like $[\mathrm{Mo\{{=}C(NHBu^t)C(Ph){=}C(Ph)C(NHBu^t)\}(CNBu^t)(\eta^5\text{-}C_5Me_5)][BF_4]}$, **6**, or $[\mathrm{Mo\{{=}C(NHBu^t)C(Ph)C(Ph)CH{-}NHBu^t\}(CNBu^t)(\eta^5\text{-}C_5Me_5)][BF_4]}$, **7**, depending upon the solvent. Complex **7** contains an *N*-protonated η^4-monoazadiene ligand with a pendant carbene functionality that is also coordinated to the metal. The crystal structures of **1**, **2**, **3**, **6**, and **7** have been determined.

Introduction

We have recently reported the results of our investigations of the reactivity of mixed CNxyl−diphenylacetylene (CNxyl = 2,6-dimethylphenylisocyanide) compounds of molybdenum.[1] Our initial intention was to examine redox-induced reactions between these two coordinated ligands, but instead we found that they are readily thermally coupled. This paper describes a parallel investigation of similar systems with *tert*-butylisocyanide, $\mathrm{CNBu^t}$, and reports substantially different results. Thus, $[\mathrm{Mo(CNBu^t)_3(PhC{\equiv}CPh)(\eta^5\text{-}C_5Me_5)][BF_4]}$, **1**, formed from the reaction between $\mathrm{CNBu^t}$ and $[\mathrm{Mo(CO)(PhC{\equiv}CPh)_2(\eta^5\text{-}C_5Me_5)][BF_4]}$, does undergo reaction with further $\mathrm{CNBu^t}$ to give products containing thermally coupled ligands, but these are of different structural types from those previously reported. Compound **1** can also be reduced, yielding metallacyclic systems formed by coupling isocyanide and alkyne ligands.

Results

Synthesis of $[\mathrm{Mo(CNBu^t)_3(PhC{\equiv}CPh)(\eta^5\text{-}C_5Me_5)][BF_4]}$. A $\mathrm{CH_2Cl_2}$ solution of $[\mathrm{Mo(CO)(PhC{\equiv}CPh)_2(\eta^5\text{-}C_5Me_5)][BF_4]}$[2] reacts readily with 3 equiv of $\mathrm{CNBu^t}$ to produce the mixed alkyne−isocyanide complex $[\mathrm{Mo(CNBu^t)_3(PhC{\equiv}CPh)(\eta^5\text{-}C_5Me_5)][BF_4]}$, **1**, which may be isolated in good yield as an orange crystalline solid. (Microanalytical and IR data for all compounds are given in Table 1.) By contrast, the CNxyl analogue could not be prepared as a solid,[1] but the cyclopentadienyl analogue is known.[3] Compound **1** shows the expected three ν(CN) bands in the IR spectrum (2163m sh, 2139s, and 2120m sh $\mathrm{cm^{-1}}$) and has two peaks in the ^{13}C NMR spectrum, at 62.5 and 72.8 ppm, typical of a coordinated alkyne acting as a two-electron donor.[4] The room-temperature ^{1}H NMR spectrum (Table 2) shows broad peaks for the *tert*-butyl groups of the isocyanide ligands, probably because of a fluxional process involving rotation of the $\mathrm{Mo(CNBu^t)_3}$ tripod, similar to that observed in $[\mathrm{Mo(CO)(CNR)_3(\eta^5\text{-}C_5Me_5)}]^+$.[5] At −40 °C these signals are resolved into two sharp signals in a 2:1 ratio.

Allowing a thf−*n*-hexane solution of the compound to evaporate gave crystals of **1** suitable for X-ray diffraction; the crystal structure of the cation of **1** is shown in Figure 1, and selected bond lengths and angles are given in Table 3. The compound is based upon a square

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Table 1. Microanalytical and IR Data for Compounds 1−7

compound	IR	microanalysis (%)[a]		
	$\nu(\mathrm{CNBu^t})/\mathrm{cm^{-1}}$ [b]	C	H	N
$[\mathrm{Mo(CNBu^t)_3(PhC{\equiv}CPh)}(\eta^5\text{-}\mathrm{C_5Me_5})][\mathrm{BF_4}]$, **1**	2165w, 2140, 2123m	62.7 (62.8)	7.2 (7.0)	5.5 (5.6)
$[\mathrm{Mo\{{=}C(NHBu^t)C(Ph){=}C(Ph)CN\}(CNBu^t)_2}(\eta^5\text{-}\mathrm{C_5Me_5})][\mathrm{BF_4}]$, **2**	2192w[c] 2147, 2123	61.9 (62.2)	7.0 (6.9)	7.2 (7.2)
$[\mathrm{Mo\{C({=}NBu^t)C(Ph){=}C(Ph)CN\}(CNBu^t)_2}(\eta^5\text{-}\mathrm{C_5Me_5})]$, **3**	2180w[c] 2107, 2056m	69.9 (70.2)	7.6 (7.7)	8.1 (8.2)
$[\mathrm{Mo\{{=}C(Ph)C(Ph){=}C{=}NHBu^t\}(CNBu^t)_2}(\eta^5\text{-}\mathrm{C_5Me_5})][\mathrm{BF_4}]_2$, **4**	2185, 2171 sh	56.4 (56.2)	6.6 (6.4)	4.9 (5.0)
$[\mathrm{Mo\{{=}C(NHBu^t)C(Ph){=}C(Ph)CN\}(CNBu^t)\{P(OMe)_3\}}(\eta^5\text{-}\mathrm{C_5Me_5})][\mathrm{BF_4}]$, **5**	2192w[c] 2135	55.7 (56.1)	6.4 (6.6)	5.0 (5.2)
$[\mathrm{Mo\{{=}C(NHBu^t)C(Ph){=}C(Ph)C(NHBu^t)\}(CNBu^t)}(\eta^5\text{-}\mathrm{C_5Me_5})][\mathrm{BF_4}]$, **6**	2122	62.7 (62.7)	7.6 (7.3)	5.4 (5.6)
$[\mathrm{Mo\{{=}C(NHBu^t)C(Ph)C(Ph)CHNHBu^t\}(CNBu^t)}(\eta^5\text{-}\mathrm{C_5Me_5})][\mathrm{BF_4}]_2$, **7**	2176	56.1 (56.2)	6.6 (6.4)	5.0 (5.0)

[a] Calculated values in parentheses. [b] In $\mathrm{CH_2Cl_2}$. [c] Terminal CN.

Table 2. NMR Spectroscopic Data (δ, J/Hz) for Compounds 1−7 (all spectra recorded at room temperature in $\mathrm{CD_2Cl_2}$ unless otherwise stated)

compound	^{1}H (δ/ppm)	^{13}C (δ/ppm)
$[\mathrm{Mo(CNBu^t)_3(PhC{\equiv}CPh)}\ (\eta^5\text{-}\mathrm{C_5Me_5})]\text{-}[\mathrm{BF_4}]$, **1**[a]	1.34 (s, 18H, $\mathrm{Bu^t}$), 1.55 (s, 9H, $\mathrm{Bu^t}$), 1.84 (s, 15H, $\mathrm{C_5Me_5}$), 6.97−7.40 (m, 10H, Ph)	11.7 ($\mathrm{C_5}\mathit{Me}_5$), 30.7, 31.1 ($\mathrm{C}\mathit{Me}_3$), 57.7, 58.5 ($\mathit{C}\mathrm{Me_3}$), 62.5, 72.8 ($\mathit{C}\mathrm{Ph}$), 103.6 ($\mathit{C}_5\mathrm{Me_5}$), 125.7, 126.1, 126.7, 128.5, 128.8, 128.9, 129.4, 131.8, 136.6, 139.6 (*Ph*), 156.1, 169.1 (*C*N)
$[\mathrm{Mo\{{=}C(N(H)Bu^t)C(Ph){=}C(Ph)CN\}\text{-}(CNBu^t)_2}(\eta^5\text{-}\mathrm{C_5Me_5})][\mathrm{BF_4}]$, **2**	1.17 (s, 9H, $\mathrm{Bu^t}$), 1.24 (s, 9H, $\mathrm{Bu^t}$), 1.71 (s, 9H, $\mathrm{Bu^t}$), 1.88 (s, 15H, $\mathrm{C_5Me_5}$), 6.92−7.35 (m, 10H, Ph)	9.7 ($\mathrm{C_5}\mathit{Me}_5$), 29.3, 30.4, 31.1 ($\mathrm{C}\mathit{Me}_3$), 58.8, 59.9, 62.9 ($\mathit{C}\mathrm{Me_3}$), 68.1, 73.6 ($\mathit{C}\mathrm{Ph}$), 103.6 ($\mathit{C}_5\mathrm{Me_5}$), 125.2 (*Ph*), 126.5 ($\mathit{C}{\equiv}\mathrm{N}$), 127.2, 127.4, 128.6, 128.8, 131.9, 137.9, 139.4 (*Ph*), 162.6, 167.7 (*C*N), 244.5 ($\mathrm{Mo}{=}\mathit{C}$)
$[\mathrm{Mo\{C({=}NBu^t)C(Ph){=}C(Ph)CN\}(CNBu^t)_2}\text{-}(\eta^5\text{-}\mathrm{C_5Me_5})]$, **3**	0.98 (s, 9H, $\mathrm{Bu^t}$), 1.20 (s, 9H, $\mathrm{Bu^t}$), 1.56 (s, 9H, $\mathrm{Bu^t}$), 1.77 (s, 15H, $\mathrm{C_5Me_5}$), 6.81−7.37 (m, 10H, Ph)	8.9 ($\mathrm{C_5}\mathit{Me}_5$), 30.9, 31.0, 31.6 ($\mathrm{C}\mathit{Me}_3$), 34.26 ($\mathit{C}\mathrm{Ph}$), 56.9, 57.6, 60.9 ($\mathit{C}\mathrm{Me_3}$), 63.9 ($\mathit{C}\mathrm{Ph}$), 99.8 ($\mathit{C}_5\mathrm{Me_5}$), 122.8, 125.1, 126.5, 127.3, 127.3 (*Ph*), 128.9 ($\mathit{C}{\equiv}\mathrm{N}$), 131.6, 143.0, 144.5 (*Ph*), 180.9, 187.9 (*C*N), 205.7 ($\mathrm{Mo}{=}\mathit{C}$)
$[\mathrm{Mo\{{=}C(Ph)C(Ph){=}C{=}NHBu^t\}(CNBu^t)_2}\text{-}(\eta^5\text{-}\mathrm{C_5Me_5})][\mathrm{BF_4}]_2$, **4**	1.20, 1.62, 1.65 (each s, 9H, $\mathrm{Bu^t}$), 2.04 (s, 15 H, $\mathrm{C_5Me_5}$), 7.03−7.08 (m, 2H, Ph), 7.30−7.35 (m, 3H, Ph), 7.75−7.97 (m, 5H, Ph), 10.41 (br s, 1H, NH)	11.0 ($\mathrm{C_5}\mathit{Me}_5$), 28.1, 29.7, 29.8 ($\mathrm{C}\mathit{Me}_3$), 60.7, 61.3, 61.4, 66.7 (3 × $\mathit{C}\mathrm{Me_3}$ and 1 × $\mathit{C}\mathrm{(Ph){=}C{=}N}$), 109.8 ($\mathit{C}_5\mathrm{Me_5}$), 127.1, 129.5, 130.3, 130.7, 132.5, 137.7, 138.1 (*Ph*), 205.5 ($\mathit{C}{=}\mathrm{N}$), 288.4 ($\mathrm{M}{=}\mathit{C}$)
$[\mathrm{Mo\{{=}C(NHBu^t)C(Ph)C(Ph)CN\}(CNBu^t)\text{-}\{P(OMe)_3\}}(\eta^5\text{-}\mathrm{C_5Me_5})][\mathrm{BF_4}]$, **5**[b]	1.15, 1.18 (each s, 9 H, $\mathrm{Bu^t}$), 1.86 (s, 15 H, $\mathrm{C_5Me_5}$), 3.82 (d, 9H, $^3J(\mathrm{HP}) = 10.6$ Hz, OMe), 7.05−7.45 (m, 10H, Ph)	10.4 ($\mathrm{C_5}\mathit{Me}_5$), 29.6, 29.9 ($\mathrm{C}\mathit{Me}_3$), 55.2 (d, $^2J_{\mathrm{CP}} = 9.8$ Hz, $\mathrm{O}\mathit{C}\mathrm{H_3}$), 58.9, 64.2 ($\mathit{C}\mathrm{Me_3}$), 73.7 (d, $^2J_{\mathrm{CP}} = 4.9$ Hz, $\mathit{C}\mathrm{Ph}$), 104.4 ($\mathit{C}_5\mathrm{Me_5}$), 125.6, 127.4, 127.6, 128.0, 128.3, 128.4, 132.1, 136.3, 140.7 (*Ph* and $\mathit{C}{\equiv}\mathrm{N}$), 249.2 (d, $^2J_{\mathrm{CP}} = 15.7$ Hz, $\mathrm{M}{=}\mathit{C}$)
$[\mathrm{Mo\{{=}C(NHBu^t)C(Ph){=}C(Ph)C(NHBu^t)\}\text{-}(CNBu^t)}(\eta^5\text{-}\mathrm{C_5Me_5})][\mathrm{BF_4}]$, **6**	1.27, 1.30, 1.43 (each s, 9 H, $\mathrm{Bu^t}$), 1.69 (s, 15 H, $\mathrm{C_5Me_5}$), 7.02−7.48 (m, 10H, Ph) 7.53 (s, 1H, NH) 9.04 (br s, 1H, NH)	8.9 ($\mathrm{C_5}\mathit{Me}_5$), 30.2, 30.3, 30.7 ($\mathrm{C}\mathit{Me}_3$), 48.6, 49.3 ($\mathit{C}\mathrm{Ph}$), 57.4, 58.6, 63.1 ($\mathit{C}\mathrm{Me_3}$), 104.6 ($\mathit{C}_5\mathrm{Me_5}$), 125.0, 125.0, 125.5, 126.9, 128.0, 128.2, 129.3, 140.7, 143.2 (*Ph*), 165.2 ($\mathit{C}\mathrm{NBu^t}$), 234.0, 248.7 ($\mathrm{M}{=}\mathit{C}$)
$[\mathrm{Mo\{{=}C(NHBu^t)C(Ph)C(Ph)CHNHBu^t\}\text{-}(CNBu^t)}(\eta^5\text{-}\mathrm{C_5Me_5})][\mathrm{BF_4}]_2$, **7**	1.17, 1.45, 1.69 (each s, 9 H, $\mathrm{Bu^t}$), 1.85 (s, 15 H, $\mathrm{C_5Me_5}$), 3.05 (d, 1H, $^3J(\mathrm{HH})$ 8.8 Hz, CH), 7.10−7.15 (m, 2H, Ph), 7.32−7.57 (m, 9H, Ph and NH), 9.42 (br s, 1H, NH)	11.0 ($\mathrm{C_5}\mathit{Me}_5$), 28.8, 30.2, 30.3 ($\mathrm{C}\mathit{Me}_3$), 61.4, 62.6, 63.8 ($\mathit{C}\mathrm{Me_3}$), 68.6, 85.2, 95.4 ($\mathrm{M\text{-}}\mathit{C}$), 111.8 ($\mathit{C}_5\mathrm{Me_5}$), 127.6, 128.2, 129.9, 130.1, 130.6, 130.7, 130.8, 131.1, 131.7, 132.2 (*Ph*), 234.4 ($\mathrm{M}{=}\mathit{C}$)

[a] Recorded at −40 °C. [b] Also shows δ (^{31}P) = 162.0 ppm.

pyramid with the centroid of the $\mathrm{C_5Me_5}$ ligand forming the apex, and the three terminal carbon atoms of the isocyanides basal vertices; the angle C(21)−C(11)−C(16) between these three atoms is 93°. The molybdenum atom lies 0.53 Å above the plane formed by these three atoms, which is at an angle of 7.2° to the cyclopentadienyl ring. The carbon atom C(27) of the diphenylacetylene ligand lies approximately 1 Å below the fourth corner of the square base. The $\mathrm{Mo{-}C_{isocyanide}}$ distances are in the range previously reported for $\mathrm{Mo{-}CNBu^t}$ compounds,[5] although at 2.06 Å the bond Mo(1)−C(11) *trans* to the alkyne is shorter than the other two (2.12, 2.14 Å). The C≡C distance of 1.27 Å is virtually the same as that seen in $[\mathrm{Mo(PhC{\equiv}CPh)}(\eta^5\text{-}\mathrm{C_5H_5})_2]$, the only previously crystallographically characterized molybdenum compound containing diphenylacetylene acting as a two-electron donor.[6]

Formation of Metallacycles. Reaction of **1** with a further equivalent of $\mathrm{CNBu^t}$, or of $[\mathrm{Mo(CO)(PhC{\equiv}CPh)_2}(\eta^5\text{-}\mathrm{C_5Me_5})][\mathrm{BF_4}]$ with 4 equiv of $\mathrm{CNBu^t}$, produces $[\mathrm{Mo\{{=}C(NHBu^t)C(Ph){=}C(Ph)CN\}(CNBu^t)_2}(\eta^5\text{-}\mathrm{C_5Me_5})][\mathrm{BF_4}]$, **2** (Scheme 1), containing an η^3(4e)-vinylcarbene; overall, the reaction involves coordination of a fourth isocyanide molecule, insertion of the diphenylacetylene into two of the metal−isocyanide bonds, the gain of one proton, and the loss of $[\mathrm{Bu^t}]^+$. Formation of **2** is slow,

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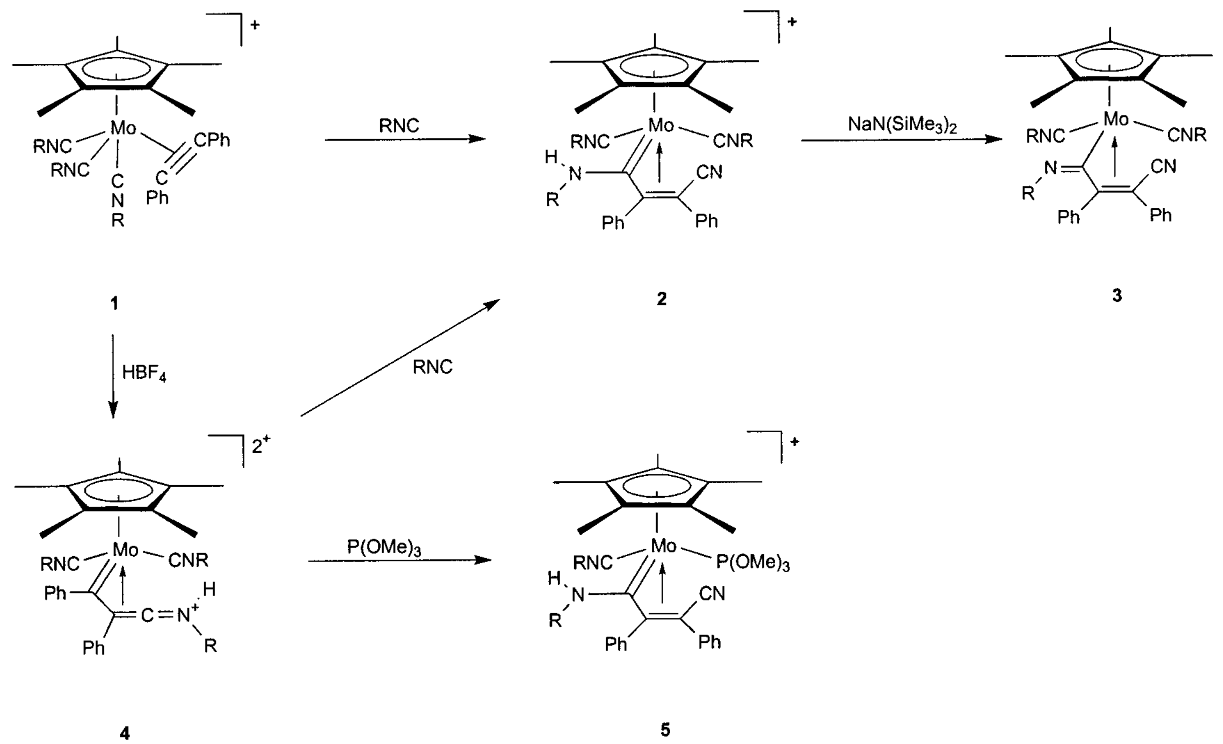
[6] (a) De Cian, A.; Colin, J.; Schappacher, M.; Ricard, L.; Weiss, R. *J. Am. Chem. Soc.* **1981**, *103*, 1850.

Scheme 1[a]



[a] R = Bu^t.

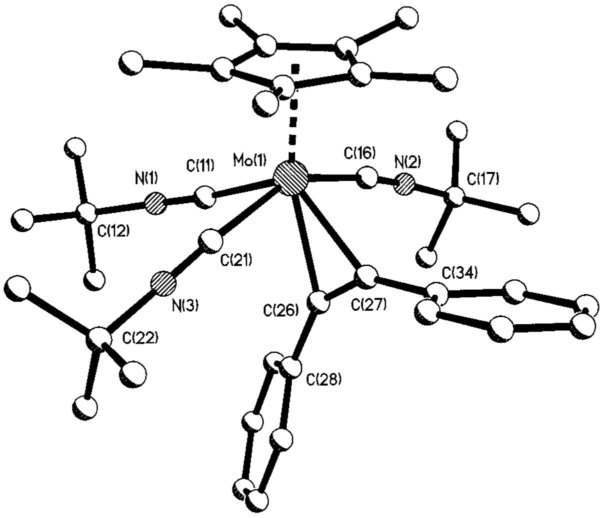


Figure 1. Structure of the cation of **1**. Hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Compound 1

Mo(1)–C(11)	2.061(4)	C(11)–N(1)	1.152(4)
Mo(1)–C(21)	2.115(4)	C(16)–N(2)	1.154(5)
Mo(1)–C(16)	2.139(4)	C(21)–N(3)	1.155(4)
Mo(1)–C(27)	2.174(4)	C(26)–C(27)	1.267(5)
Mo(1)–C(26)	2.206(3)		
C(11)–Mo(1)–C(21)	81.60(14)	C(27)–Mo(1)–C(26)	33.62(13)
C(11)–Mo(1)–C(16)	88.89(14)	N(1)–C(11)–Mo(1)	174.5(3)
C(21)–Mo(1)–C(16)	150.57(14)	C(11)–N(1)–C(12)	168.1(4)
C(11)–Mo(1)–C(27)	119.31(13)	N(2)–C(16)–Mo(1)	173.9(3)
C(21)–Mo(1)–C(27)	80.00(13)	C(16)–N(2)–C(17)	173.6(4)
C(16)–Mo(1)–C(27)	80.60(13)	N(3)–C(21)–Mo(1)	172.7(3)
C(11)–Mo(1)–C(26)	85.73(13)	C(21)–N(3)–C(22)	178.1(4)
C(21)–Mo(1)–C(26)	74.81(13)	C(27)–C(26)–C(28)	146.3(4)
C(16)–Mo(1)–C(26)	76.77(13)	C(26)–C(27)–C(34)	147.5(4)

taking 3–4 days at room temperature, and protons are presumably either adventitious or come from the rearrangement of the eliminated [Bu^t]$^+$ moiety to $(CH_3)_2C{=}CH_2$ and H$^+$.[7] However, upon adding HBF_4 to a mixture of **1** and CNBu^t, complete conversion to **2** is achieved in about 30 s.

Complex **2** shows three bands in the ν(CN) region of the IR spectrum. In CH_2Cl_2, the terminal cyanide stretch gives a weak band at 2192 cm^{-1}, and the two isocyanides give strong absorptions at 2147 and 2123 cm^{-1}. The N–H stretch gives a broad band at 3280 cm^{-1} in Nujol. The amino proton is apparent as a broad peak at 7.98 ppm in the ^{1}H NMR spectrum, and the strongly deshielded carbenoid atom is at 244 ppm in the ^{13}C spectrum. There are nine ^{13}C peaks observed between 125 and 140 ppm in this spectrum; eight are due to the two phenyl rings and one to the cyanide group, but the latter has not been specifically assigned.

Crystals suitable for X-ray analysis were grown by allowing *n*-hexane to diffuse into a concentrated CH_2Cl_2 solution of **2**; the cation of **2** is shown in Figure 2, and Table 4 contains selected bond lengths and angles. The carbon atoms C(17) and C(18) originating from the diphenylacetylene are bonded to the metal by single bonds (Mo–C distances of 2.27 and 2.32 Å, respectively); the double bond between Mo(1) and C(29) is much shorter (2.02 Å). The angles around this carbenoid atom C(29) sum to 356.4°, showing that it is sp^2 hybridized with an appropriately planar coordination geometry. The amine proton H(2A) was located in the refinement and is situated such that N(2) and its two connected atoms are coplanar with C(29) and the atoms bonded to it. This allows some delocalization of the amine lone pair into the metal–carbon antibonding orbital, creating

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[7] Smith, M. B.; March, J. *Advanced Organic Chemistry*, 5th ed.; Wiley-Interscience: New York, 2001.

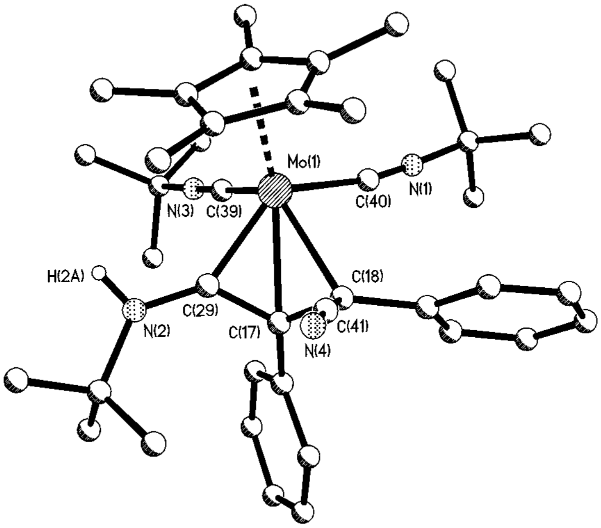


Figure 2. Structure of the cation of **2**. Hydrogen atoms [except H(2A)] have been omitted for clarity.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Compound 2

Mo(1)–C(29)	2.018(3)	N(2)–C(29)	1.311(4)
Mo(1)–C(39)	2.058(4)	N(3)–C(39)	1.150(4)
Mo(1)–C(40)	2.129(3)	N(4)–C(41)	1.147(4)
Mo(1)–C(17)	2.267(3)	C(17)–C(29)	1.436(4)
Mo(1)–C(18)	2.318(3)	C(17)–C(18)	1.469(4)
N(1)–C(40)	1.146(4)	C(18)–C(41)	1.445(5)

C(29)–Mo(1)–C(39)	84.20(12)	C(18)–C(17)–Mo(1)	73.19(17)
C(29)–Mo(1)–C(40)	129.99(12)	C(41)–C(18)–C(17)	113.8(3)
C(39)–Mo(1)–C(40)	81.24(12)	C(41)–C(18)–Mo(1)	110.5(2)
C(29)–Mo(1)–C(17)	38.61(11)	C(17)–C(18)–Mo(1)	69.46(17)
C(29)–Mo(1)–C(18)	65.76(11)	N(2)–C(29)–C(17)	134.0(3)
C(39)–Mo(1)–C(18)	126.11(12)	N(2)–C(29)–Mo(1)	144.3(2)
C(40)–Mo(1)–C(18)	85.47(11)	C(17)–C(29)–Mo(1)	80.14(18)
C(17)–Mo(1)–C(18)	37.35(10)	N(3)–C(39)–Mo(1)	178.2(3)
C(29)–C(17)–C(18)	109.2(3)	N(1)–C(40)–Mo(1)	170.7(3)
C(29)–C(17)–Mo(1)	61.26(16)	N(4)–C(41)–C(18)	176.7(4)

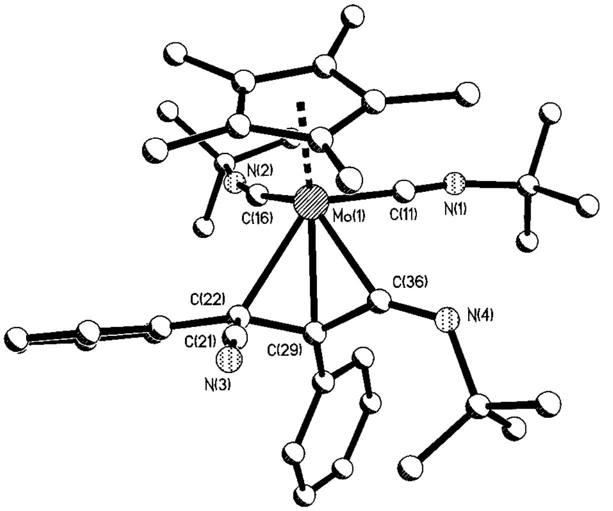


Figure 3. Structure of **3**. Hydrogen atoms have been omitted for clarity.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for Compound 3

Mo(1)–C(11)	2.032(7)	N(2)–C(16)	1.164(7)
Mo(1)–C(16)	2.078(7)	N(3)–C(21)	1.137(8)
Mo(1)–C(36)	2.104(6)	N(4)–C(36)	1.270(8)
Mo(1)–C(29)	2.238(6)	C(21)–C(22)	1.460(9)
Mo(1)–C(22)	2.326(6)	C(22)–C(29)	1.464(9)
N(1)–C(11)	1.161(8)	C(29)–C(36)	1.473(9)

C(11)–Mo(1)–C(16)	81.8(2)	N(3)–C(21)–C(22)	175.4(7)
C(11)–Mo(1)–C(36)	79.0(2)	C(21)–C(22)–C(29)	113.1(5)
C(16)–Mo(1)–C(36)	124.6(2)	C(21)–C(22)–Mo(1)	108.8(4)
C(36)–Mo(1)–C(29)	39.5(2)	C(29)–C(22)–Mo(1)	68.0(3)
C(11)–Mo(1)–C(22)	127.9(2)	C(22)–C(29)–C(36)	109.1(5)
C(16)–Mo(1)–C(22)	88.7(2)	C(22)–C(29)–Mo(1)	74.6(3)
C(36)–Mo(1)–C(22)	65.2(2)	C(36)–C(29)–Mo(1)	65.3(3)
C(29)–Mo(1)–C(22)	37.4(2)	N(4)–C(36)–C(29)	143.5(6)
N(1)–C(11)-Mo(1)	178.1(5)	N(4)–C(36)–Mo(1)	140.8(5)
N(2)–C(16)–Mo(1)	170.6(5)	C(29)–C(36)–Mo(1)	75.2(3)

a substantial degree of carbon–nitrogen double-bond character. Thus, the distance C(29)–N(2) is only 1.31 Å.

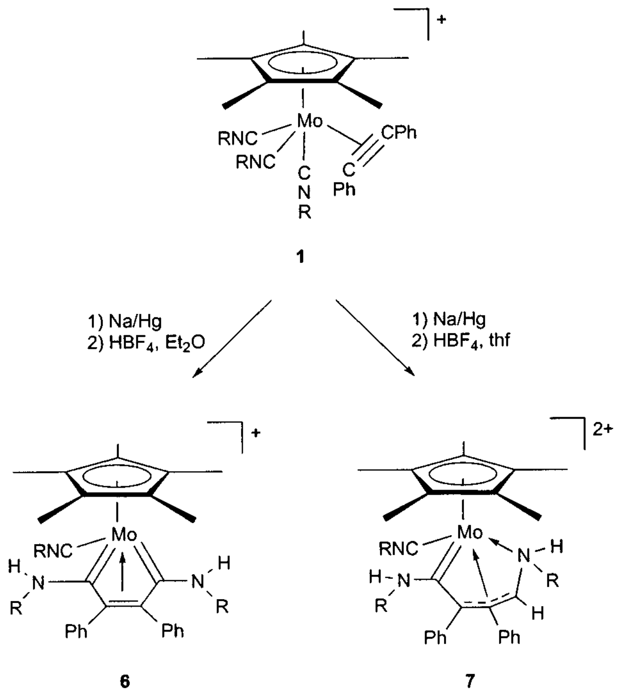
Complex **2** may be deprotonated with $NaN(SiMe_3)_2$ to generate the neutral compound $[Mo\{C(=NBu^t)C(Ph)=C(Ph)CN\}(CNBu^t)_2(\eta^5\text{-}C_5Me_5)]$, **3**, containing an η^3(3e)-monoazadienyl ligand (Scheme 1). This reaction is reversible; treatment of **3** with HBF_4 regenerates **2**. The IR spectrum of **3** has ν(CN) for the isocyanide ligands at 2107 and 2056 cm^{-1}, at lower wavenumbers than in **2** because of the lack of a charge on the complex and the concomitant increase in metal-to-isocyanide back-donation. The terminal cyanide vibration is also moved to lower energy (2180 cm^{-1}). The NMR spectra of **3** are very similar to those of **2**, the only significant difference in the ^1H spectrum being the disappearance of the N*H* peak and in the ^{13}C spectrum the upfield shift of the α-carbon atom of the ring from 245 ppm (as a carbene) to 206 ppm (as an imine). The crystal structure of **3** (Figure 3 and Table 5) is also very similar to that of the cation of **2**, especially in the metallacyclic unit. For example, Mo(1) and the atoms C(36), C(29), N(4), and C(37) of the monoazadienyl ligand are again almost coplanar. At 2.10 Å the Mo(1)–C(36) distance is slightly longer and the C(36)–N(4) distance slightly shorter (1.27 Å) than their counterparts in **2**, in accord with the formal change in bonding, but both are still within double-bond range.

To investigate the formation of **2** further, a solution of **1** was reacted with HBF_4 in the absence of additional isocyanide. In thf, this results in the rapid precipitation of a dark green compound **4**, which is stable in the solid state but decomposes (mainly to **2**) if left in solution for extended periods. For this reason crystals suitable for X-ray diffraction have not been obtained, but on the basis of the analytical data discussed below **4** is formulated as $[Mo\{=C(Ph)C(Ph)=C=NHBu^t\}(CNBu^t)_2(\eta^5\text{-}C_5Me_5)][BF_4]_2$, an η^3(4e)-iminiumvinylcarbene complex (Scheme 1). The reaction is fully reversible; deprotonation of **4** with NEt_3 results in the rapid conversion of **4** back to **1**.

The solution IR spectrum of **4** shows two strong ν(CN) absorptions bands (2185s and 2170s sh cm^{-1}), consistent with a bis(isocyanide) structure, and a band at 1668 cm^{-1} attributable to ν(C=N). In Nujol, an additional band at 3243 cm^{-1} is present due to the N–H stretch. ^1H NMR spectroscopy indicates three different Bu^t groups, as well as a single broad N*H* peak at 10.41 ppm. The ^{13}C NMR spectrum contains a resonance at 288 ppm, due to the M=*C* unit, and another at 205 ppm due to the *C*=N moiety. Elemental analysis also agrees with the above formulation.

Addition of $CNBu^t$ to a CH_2Cl_2 solution of **4** results in instant formation of **2**. Furthermore, addition of

Scheme 2[a]



[a] R = Bu^t.

P(OMe)$_3$ to a solution of **4** generates [Mo{=C(NHBu^t)C(Ph)=C(Ph)CN}(CNBu^t){P(OMe)$_3$}(η^5-C$_5$Me$_5$)][BF$_4$], **5**, a vinylcarbene analogous to **2** but with a trimethyl phosphite ligand instead of one of the isocyanides (Scheme 1). The IR and NMR spectral parameters of **5** are similar to those of **2**, except that $^2J_{\rm CP}$ coupling is observed in the ^{13}C NMR spectrum in the signals due to the metal-bound carbon atoms.

Reduction of 1. The cyclic voltammogram of **1** shows a fully reversible diffusion-controlled oxidation wave at 0.60 V, followed by an irreversible process at 1.05 V, but attempts to isolate products from the chemical oxidation of **1** have been unsuccessful. There is also an ill-defined reduction wave at approximately −1.2 V.

To investigate the reductive coupling of the isocyanide and alkyne ligands, a thf solution of **1** was treated with sodium−mercury amalgam. Isolation of the product gave red-orange crystals, which were identified by X-ray diffraction as the metallacyclopentatriene-like complex [Mo{=C(NHBu^t)C(Ph)=C(Ph)C(NHBu^t)}(CNBu^t)(η^5-C$_5$Me$_5$)][BF$_4$], **6** (Scheme 2). As the formula of **6** differs from that of the starting material **1** only by the addition of two hydrogen atoms, it appears that two-electron reduction of **1** is followed by the addition of two protons to give the observed product.

The IR spectrum of **6** has a single ν(CN) band at 2126 cm^{-1}, with ν(NH) apparent at 3346 and 3260 cm^{-1} in Nujol. The ^{1}H NMR spectrum shows three different Bu^t resonances and N*H* signals at 7.53 and 9.04 ppm. The ^{13}C spectrum shows the two α-carbon atoms of the metallacyclic ring at 234 and 249 ppm, consistent with their carbenoid character, with the two β-carbon atoms of this ring at around 49 ppm. The contact carbon atom of the remaining isocyanide is at 165 ppm, typical of a coordinated isocyanide.

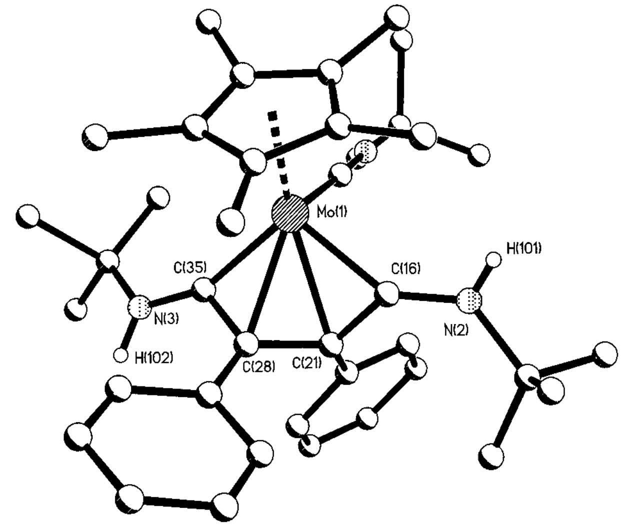


Figure 4. Structure of the cation of **6**. Most hydrogen atoms have been omitted for clarity.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for Compound 6

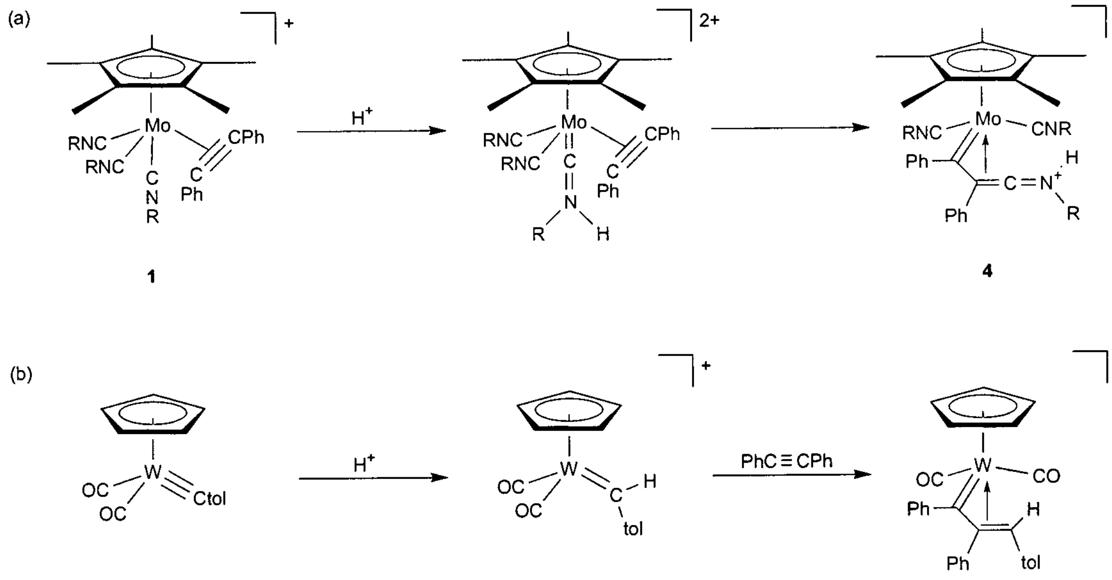
Mo(1)−C(16)	2.033(5)	C(16)−C(21)	1.426(6)
Mo(1)−C(35)	2.076(5)	C(21)−C(28)	1.461(7)
Mo(1)−C(28)	2.186(5)	C(28)−C(35)	1.449(7)
Mo(1)−C(21)	2.246(5)	C(28)−C(29)	1.479(8)
C(16)−N(2)	1.322(6)	C(35)−N(3)	1.313(6)
C(16)−Mo(1)−C(35)	103.2(2)	C(35)−C(28)−C(21)	106.1(5)
C(35)−Mo(1)−C(28)	39.7(2)	C(35)−C(28)−C(29)	126.9(5)
C(16)−Mo(1)−C(21)	38.52(18)	C(21)−C(28)−C(29)	127.0(5)
C(28)−Mo(1)−C(21)	38.46(18)	C(35)−C(28)−Mo(1)	66.1(3)
N(2)−C(16)−C(21)	133.7(5)	C(21)−C(28)−Mo(1)	73.0(3)
N(2)−C(16)−Mo(1)	145.4(4)	C(29)−C(28)−Mo(1)	126.4(4)
C(21)−C(16)−Mo(1)	78.8(3)	N(3)−C(35)−C(28)	126.8(5)
C(16)−C(21)−C(28)	113.3(4)	N(3)−C(35)−Mo(1)	157.4(5)
C(16)−C(21)−Mo(1)	62.6(3)	C(28)−C(35)−Mo(1)	74.3(3)
C(28)−C(21)−Mo(1)	68.5(3)		

The relatively low chemical shift of the β-carbon atoms suggests that they are best viewed as sp^3 hybridized and joined to each other by a single bond, and this is borne out by examination of the crystal structure (Figure 4 and Table 6). At 1.46 Å, this bond, C(21)−C(28), is in the same range as the two C$_\alpha$−C$_\beta$ single bonds, C(35)−C(28) and C(16)−C(21), while the metal−C$_\alpha$ bonds, Mo(1)−C(35) and Mo(1)−C(16), are undoubtedly double. The distances between the molybdenum atom and C(28) and C(21) are, at approximately 2.2 Å, in the range expected for Mo−C single bonds. Furthermore, the metallacyclic ring is puckered in order to bring these two β-carbon atoms to a position where they are able to bond to the metal. There is no doubt, therefore, that all four carbon atoms of this ring are bonded to the metal, to donate the six electrons that enable the metal to achieve an 18-electron configuration.

A planned synthesis of **6** was attempted by reduction of **1** with sodium−mercury amalgam and subsequent addition of HBF$_4$, and if the protonation is carried out in diethyl ether this is successful. However, in thf this procedure does not yield **6** but instead gives [Mo{=C(NHBu^t)C(Ph)C(Ph)CHNHBu^t}(CNBu^t)(η^5-C$_5$Me$_5$)][BF$_4$], **7**, formed (at least formally) by the two-electron reduction of **1** followed by *tri*protonation (Scheme 2).

The structure of the cation of **7** (Figure 5) is complicated, but it contains a planar fragment comprising N(1)−C(11)−C(16)−C(23). The carbon−carbon and carbon−nitrogen bond lengths are between those expected for single and double bonds (Table 7) and are consistent

Scheme 3. (a) Formation of 4 via an Iminocarbene and (b) Its Similarity with the Reaction Reported by Geoffroy in Ref 9 (tol = *p*-C_6H_4Me)



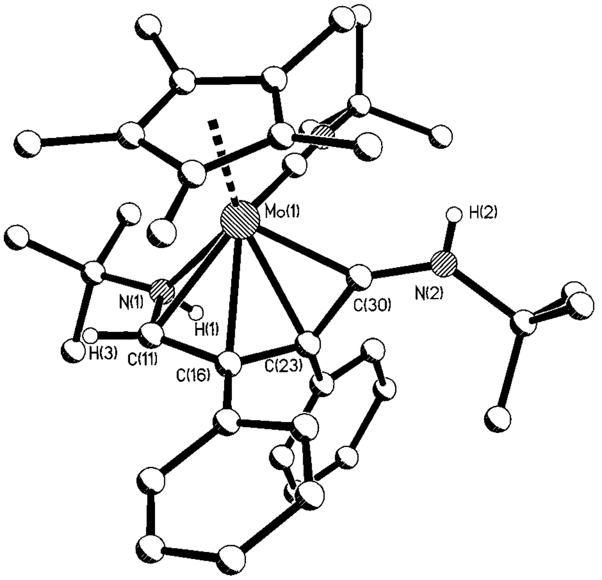


Figure 5. Structure of the cation of **7**. Most hydrogen atoms have been omitted for clarity.

Table 7. Bond Lengths (Å) and Angles (deg) for Compound 7

Mo(1)–C(30)	2.042(5)	N(1)–C(12)	1.508(6)
Mo(1)–C(16)	2.228(4)	N(2)–C(30)	1.305(6)
Mo(1)–C(23)	2.239(5)	N(2)–C(31)	1.504(6)
Mo(1)–N(1)	2.259(4)	C(11)–C(16)	1.403(6)
Mo(1)–C(11)	2.263(4)	C(16)–C(23)	1.475(6)
N(1)–C(11)	1.408(6)	C(23)–C(30)	1.423(6)
C(30)–Mo(1)–C(23)	38.49(16)	N(1)–C(11)–Mo(1)	71.7(3)
C(16)–Mo(1)–C(23)	38.57(15)	C(11)–C(16)–C(23)	115.6(4)
C(30)–Mo(1)–N(1)	109.56(16)	C(11)–C(16)–Mo(1)	73.1(3)
C(16)–Mo(1)–C(11)	36.39(16)	C(23)–C(16)–Mo(1)	71.1(2)
N(1)–Mo(1)–C(11)	36.28(15)	C(30)–C(23)–C(16)	111.5(4)
C(11)–N(1)–C(12)	124.3(4)	C(30)–C(23)–Mo(1)	63.2(2)
C(11)–N(1)–Mo(1)	72.0(2)	C(16)–C(23)–Mo(1)	70.3(2)
C(30)–N(2)–C(31)	133.5(4)	N(2)–C(30)–C(23)	135.0(4)
C(16)–C(11)–N(1)	116.6(4)	N(2)–C(30)–Mo(1)	144.6(4)
C(16)–C(11)–Mo(1)	70.5(3)	C(23)–C(30)–Mo(1)	78.3(3)

with the fragment bonding as an *N*-protonated η^4-monoazadiene. Attached to this unit by a single bond is another carbon atom, C(30), joined to the molybdenum atom by a double bond (of length 2.04 Å) and thus carbenoid in nature. The azadiene unit donates four electrons to the metal and the carbene two, making the positively charged ligand an overall six-electron donor. Two of the three added protons are attached to the nitrogen atoms of the isocyanide fragments involved in the ring, one of these nitrogen atoms now forming part of the diene; the third proton is, unusually, bonded to the carbon atom of one of these isocyanide moieties.

Other spectroscopic data are entirely consistent with this structure. The IR spectrum shows one ν(CN) band, at 2176 cm^{-1}, significantly higher than in **6** because of the extra positive charge on the metal. The ^1H NMR spectrum shows three distinct Bu^t environments and signals for two of the three added protons (the signal of the third is hidden by those of the phenyl rings) at 9.43 and 3.05 ppm. The latter, proton H(3), is split into a doublet ($^3J_{HH}$ = 8.8 Hz) by coupling to the neighboring amine proton. The ^{13}C spectrum has one carbene signal at 234 ppm and three signals in the range 65–96 ppm from the carbon atoms of the monoazadiene.

Discussion

Protonation of 1 and the Dealkylation of Coordinated Isocyanide. The protonation of metal–isocyanide compounds is well known to produce iminocarbene (alternatively, aminocarbyne) compounds through electrophilic addition to the nitrogen atom,[8] but protonation of a mixed alkyne–isocyanide complex such as **1** appears to be a new reaction. We therefore postulate that protonation of **1** leads initially to an iminocarbene, which then undergoes an intramolecular reaction with diphenylacetylene to form the observed product **4**. This is similar to a reaction reported by Geoffroy and co-workers, where a carbene (generated in situ) couples with diphenylacetylene to produce a vinylcarbene (Scheme 3).[9]

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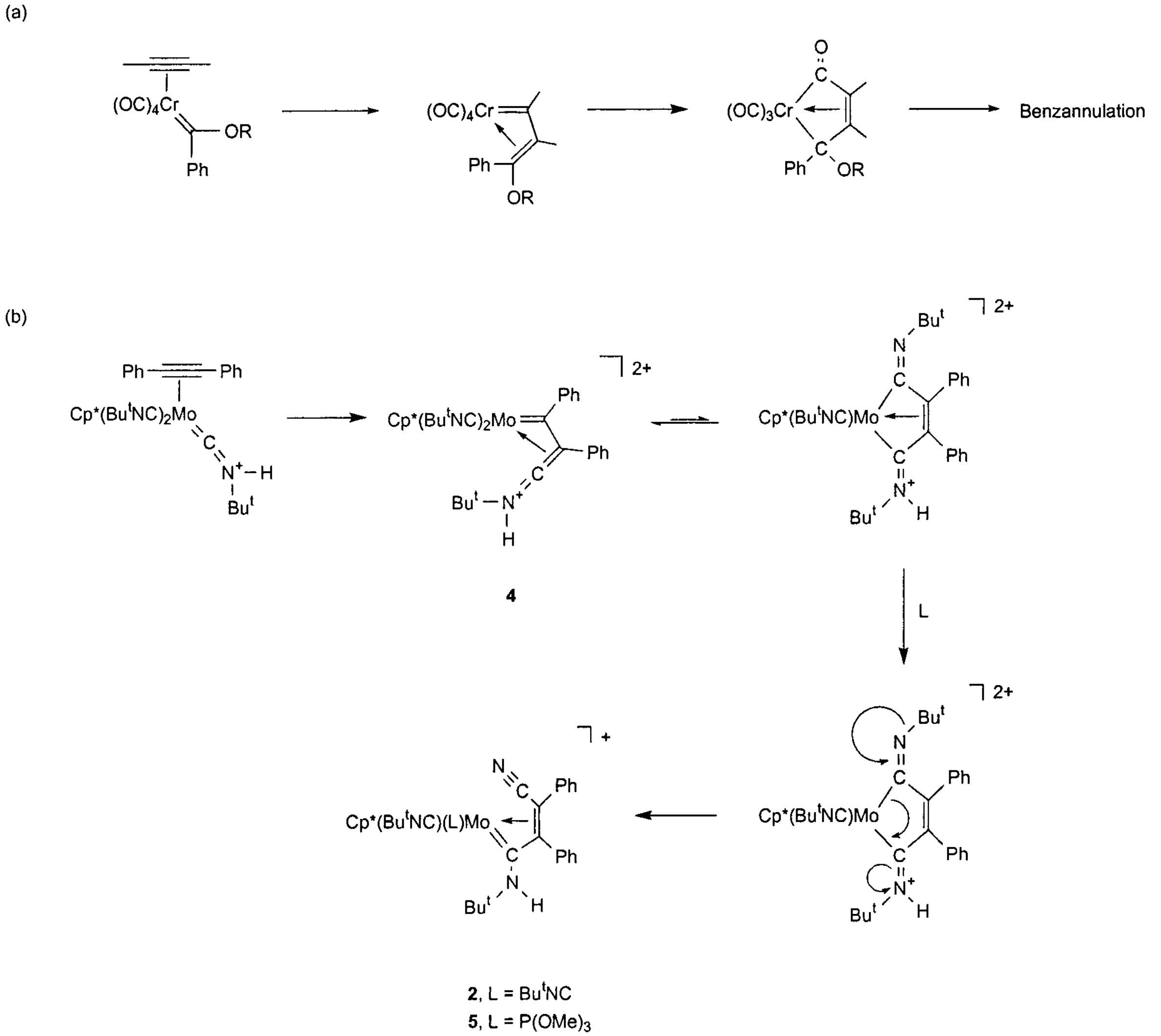
(8) Crociani, B. Reactions of Coordinated Isocyanides. In *Reactions of Coordinated Ligands*, Vol. 1; Braterman, P. S., Ed.; Plenum Press: New York, 1986.

Scheme 4. (a) Initial Stages of the Dötz Reaction and (b) the Formation of 4 and Its Equilibrium with an Isomeric Metallacycle[a]



[a] This metallacycle may be trapped by addition of a ligand L, which causes rearrangement to give the observed product **2** or **5**.

It is also similar (Scheme 4) to one of the initial stages of the Dötz reaction,[10] a benzannulation that couples chromium-coordinated unsaturated (aryl or vinyl) alkoxycarbene ligands with alkynes and CO. One of the intermediates in the Dötz reaction is a vinylcarbene, an analogue of the iminiumvinylcarbene **4**, and it has been proposed that the next step in the Dötz reaction is an intramolecular insertion of carbon monoxide into the metal–carbene bond to give an η^4(4e)-vinylketene (Scheme 4).[11] We propose that the next step in the reaction of **4** with CNBu^t to form **2** is an analogous intramolecular insertion, that of CNBu^t into the M=C bond, producing an η^4(4e) metallacyclic intermediate (Scheme 4).

That this insertion reaction is intramolecular, rather than involving free isocyanide in the reaction mixture, is shown by the reaction of **4** with ligands other than CNBu^t. Thus, reaction of **4** with P(OMe)$_3$ produces [Mo{=C(NHBu^t)C(Ph)=C(Ph)CN}(CNBu^t){P(OMe)$_3$}(η^5-C$_5$Me$_5$)][BF$_4$], **5**, containing the same vinylcarbene ligand as **2**. The same vinylcarbene ligand is also formed when the two-electron donor cyclohexylisocyanide (CNCy) or chloride ion is added to a solution of **4** (respectively producing [Mo{=C(NHBu^t)C(Ph)=C(Ph)CN}(CNBu^t)(CNCy)(η^5-C$_5$Me$_5$)][BF$_4$] and [Mo{=C(NHBu^t)C(Ph)=C(Ph)CN}(CNBu^t)Cl(η^5-C$_5$Me$_5$)]). Therefore, it appears that in solution an equilibrium exists between **4** and a metallacyclic isomer that is trapped by addition of a two-electron donor ligand, L (Scheme 4). The metallacyclic species that is created is unstable toward loss of a *tert*-butyl cation, and the resulting elimination of [Bu^t]$^+$ and subsequent rearrangement generate the observed vinylcarbene products **2** (L = CNBu^t) and **5** {L = P(OMe)$_3$} (Scheme 4). We have recently reported the formation of a similar unstable metallacycle (containing CNxyl instead of CNBu^t).[1]

The elimination of the R group from a coordinated alkylisocyanide has been reported before.[12–14] In most cases the isocyanide involved is CNBu^t,[12,13] as in the present example, and normally the elimination is thermally induced;[12] for example, heating [Ru(CNBu^t)$_6$][PF$_6$]$_2$ under reflux in *n*-propanol for 12 h produces

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(9) Garrett, K. E.; Sheridan, J. B.; Porreau, D. B.; Feng, W. C.; Geoffroy, G. L.; Staley, D. L.; Rheingold, A. L. *J. Am. Chem. Soc.* **1989**, *111*, 8383.

(10) Dötz, K. H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 587.

(11) Dötz, K. H.; Tomuschat, P. *Chem. Soc. Rev.* **1999**, *28*, 187

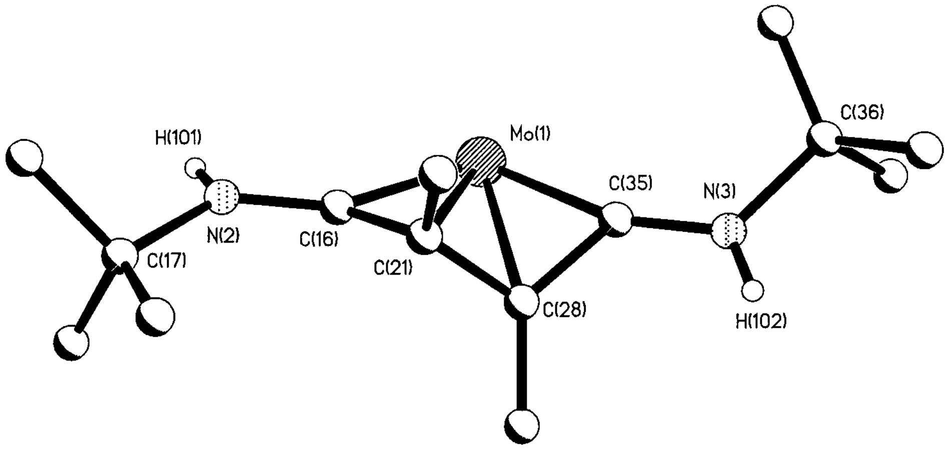

Figure 6. Metallacyclic core of **6**. One metallacyclopropene ring is formed by the atoms Mo(1)−C(35)−C(28) and the other by Mo(1)−C(16)−C(21), and the angle between the planes of these two rings is 35°.

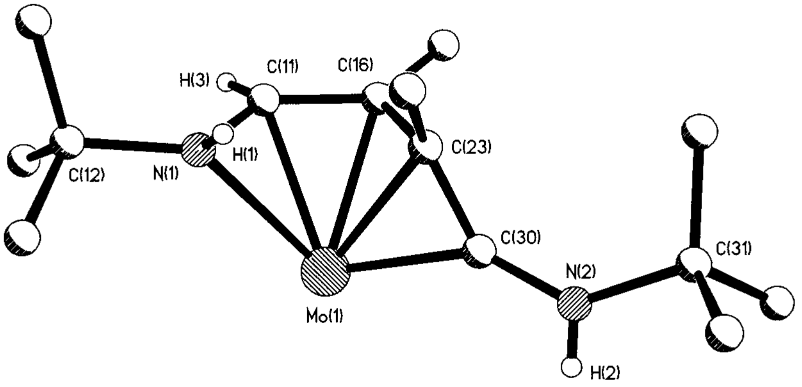

Figure 7. Metallacyclic core of **7**. The atoms N(1), C(11), C(16), and C(23) form the monoazadiene ring.

[Ru(CNBu^t)$_5$(CN)][PF$_6$]. However, in none of these prior reports has elimination been triggered by coordination of another ligand to the metal, and in none has the resulting cyano group not been directly coordinated to the metal.

Structures of 6 and 7. Complex **6** contains a metallacyclopentatriene, with an η^4(6e) ligand derived from the diphenylacetylene and two of the isocyanide ligands. Several metallacyclopentatrienes have been reported,[15] although only one system contains a six-electron donor ligand such as that in **6**.[16] In all previous studies the organic part of the ring is planar, giving the metallacycle either a planar or envelope configuration; in every case, each of the two terminal carbon atoms of the ring donates two electrons to the metal. In the example of six-electron metal-to-ligand donation, the π-bond between the two β-carbon atoms of the organic system is not conjugated with the rest of the metallacycle because the ring is folded. This π-bonding orbital constitutes the HOMO of the ligand and is able to π-donate two further electrons to the metal. An envelope configuration is adopted by the metallacycle in order that this is geometrically possible (Figure 8).

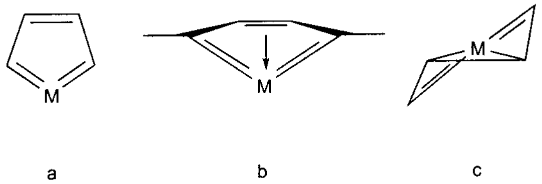

Figure 8. Planar (a), envelope (b), and twist (c) conformations adopted by metallacyclopentatriene.

The metallacycle in **6** is different from all previous examples in that it adopts a twist configuration, with a nonplanar organic fragment. Delocalization of the π-sys-

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(12) (a) Posznik, G.; Carroll, P. J.; Wayland, B. B. *Organometallics* **1993**, *12*, 3410. (b) Farr, J. P.; Abrams, M. J.; Costello, C. E.; Davison, A.; Lippard, S. J.; Jones, A. G. *Organometallics* **1985**, *4*, 139. (c) Tetrick, S. M.; Walton, R. A. *Inorg. Chem.* **1985**, *24*, 3363. (d) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Inorg. Chem.* **1984**, *23*, 1739. (e) Bell, A.; Walton, R. A. *J. Organomet. Chem.* **1984**, *263*, 359. (f) Bell, A.; Lippard, S. J.; Roberts, M.; Walton, R. A. *Organometallics* **1983**, *2*, 1562. (g) Giandomenico, C.; Hanau, L. H.; Lippard, S. J. *Organometallics* **1982**, *1*, 142.

(13) (a) Jones, W. D.; Kosar, W. P. *Organometallics* **1986**, *5*, 1823. (b) Crociani, B.; Nicoline, M.; Richards, R. L. *Inorg. Chim. Acta* **1975**, *12*, 53.

(14) (a) Werner, H.; Hörlin, G.; Jones, W. D. *J. Organomet. Chem.* **1998**, *562*, 45. (b) Evans W. J.; Drummond, D. K. *Organometallics* **1988**, *7*, 797. (c) Treichel, P. M.; Hess, R. W. *J. Chem. Soc., Chem. Commun.* **1970**, 1626.

(15) For metallacyclopentatriene complexes see: (a) Albers, M. O.; deWaal, D. J. A.; Liles, D. C.; Robinson, D. J.; Singleton, E.; Wiege, M. B. *J. Chem. Soc., Chem. Commun.* **1986**, 1680. (b) Gemel, C.; LaPensée, A.; Mauthner, K.; Mereiter, K.; Schmid, R.; Kirchner, K. *Monatsh. Chem.* **1997**, *128*, 1189. (c) Pu, L.; Hasegawa, T.; Parkin, S.; Taube, H. *J. Am. Chem. Soc.* **1992**, *114*, 2712. (d) Hirpo, W.; Curtis, M. D. *J. Am. Chem. Soc.* **1988**, *110*, 5218. (e) Hessen, B.; Meetsma, A.; van Bolhuis, F.; Teuben, J. H.; Helgesson, G.; Jagner, S. *Organometallics* **1990**, *9*, 1925. (f) Ernst, C.; Walter, O.; Dinjus, E.; Arzberger, S.; Görls, H. *J. Prakt. Chem.* **1999**, *341*, 801. (g) Rüba, E.; Mereiter, K.; Schmid, R.; Kirchner K. *J. Chem. Soc., Chem. Commun.* **2001**, 1996. (h) Becker, E.; Rüba, E.; Mereiter, K.; Schmid, R.; Kirchner K. *Organometallics* **2001**, *20*, 3851. (i) Curtis, M. D.; Real, J.; Hirpo, W.; Butler, W. M. *Organometallics* **1990**, *9*, 66.

(16) (a) Kerschner, J. L.; Fanwick, P. E.; Rothwell, I. P. *J. Am. Chem. Soc.* **1988**, *110*, 8235. (b) Kriley, C. E.; Kerschner, J. L.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1993**, *12*, 2051.

tem is therefore broken between the two β-carbon atoms C(21) and C(28), rather than between the α- and β-carbons as in the example discussed above. Thus, although formally a metallacyclopentatriene, the ligand may also be regarded as containing two metallacyclopropene fragments linked by a single bond, C(21)−C(28), of length 1.46 Å, and with an angle of 35° between them (Figure 6). On comparing these aminometallacyclopropene rings with other crystallographically characterized aminometallacyclopropenes,[17] features such as the short carbon−nitrogen bond length and the planarity of the nitrogen atom, commonly associated with heteroatom-substituted (Fischer-type) carbenes, become apparent. Previous metallacyclopentatrienes are all alkyl or aryl substituted at the α-carbon atoms (i.e., Schrock carbenes).

Overall, the metallacycle within **7** differs from that of **6** only by the addition of a proton to one of the α-carbon atoms of the ring, and therefore one end of the ligand is still a metallacyclopropene ring similar to those in **6**. However, as reported above, the rest of the ligand has become a protonated η^4-monoazadiene. The structure of a compound containing a similar fragment, namely, $[Mo(CO)_2(PBu_3)_2(\eta^4\text{-PhNH=CHCH=CHPh})]$,[18] has been reported, though this was synthesized from an unprotonated η^4-monoazadiene compound. Many more structures containing unprotonated analogues[19] show structural features also found in **7**, including the coplanarity not only of the four atoms of the diene but also of the atoms attached to the carbon atoms C(11) and C(16) of the ring (Figure 7).

Conclusions

The current paper reports the synthesis of the mixed alkyne−isocyanide compound **1**, which readily undergoes ligand-coupling reactions. We have shown before[1] that a similar alkyne−isocyanide system will react with further isocyanide to give ligand-coupled products, but whereas this only involved rearrangement of the moieties present, the current paper reports a much rarer isocyanide dealkylation reaction. Some understanding of this process has been gained through selectively protonating **1** and then introducing the additional ligand (which does not have to be an isocyanide); it appears that this additional ligand drives the dealkylation by trapping an unstable intermediate. Such a process is unprecedented: dealkylation reactions of coordinated isocyanides are normally thermally induced.

A second theme is the reductively induced coupling of the alkyne and isocyanide. Reduction and protonation of **1** causes the formation of an η^4(6e)-metallacyclopentatriene, **6**; this is the second such system known and the first metallacyclopentatriene to contain a nonplanar ligand. Consideration of the X-ray crystal structure suggests that it may be regarded as two linked Fischer-carbene type metallacyclopropenes. Further protonation of this metallacycle generates compound **7**, containing an unusual ligand formed from a protonated η^4-monoazadiene bonded to an aminocarbene functionality.

Experimental Section

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry dinitrogen using dried and deoxygenated solvents. All complexes are stable for short periods in air in the solid state. NMR spectra were recorded on a JEOL GX400 spectrometer with $SiMe_4$ as an internal standard. IR spectra were recorded on a Perkin-Elmer 1600 series FTIR spectrometer. Electrochemical studies were carried out as previously described.[20] Under the conditions employed, $E^{\circ\prime}$ for the one-electron oxidation of ferrocene, 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 at the University of Bristol.

Syntheses. $[Mo(CO)(PhC{\equiv}CPh)_2(\eta^5\text{-}C_5Me_5)][BF_4]$[2] was prepared by a modification of the published procedure. To a purple solution of $[MoMe(CO)_3(\eta^5\text{-}C_5Me_5)]$[21] (4.28 g, 12.9 mmol) and diphenylacetylene (15 g, 84 mmol) in CH_2Cl_2 (60 cm^3) was added HBF_4 (54% in Et_2O, 1.8 cm^3, 13.0 mmol), causing the solution to effervesce and become brown. Diethyl ether (60 cm^3) was then added, and the solution stored at 4 °C for 4 days. The resulting orange crystals were isolated by filtration and washed with diethyl ether, to give 4.30 g (6.1 mmol, 47%) of the desired product, suitable for synthetic use.

$[Mo(CNBu^t)_3(PhC{\equiv}CPh)(\eta^5\text{-}C_5Me_5)][BF_4]$, 1. To an orange solution of $[Mo(CO)(PhC{\equiv}CPh)_2(\eta^5\text{-}C_5Me_5)][BF_4]$ (1.51 g, 2.14 mmol) in CH_2Cl_2 (15 cm^3) was added $CNBu^t$ (0.73 cm^3, 6.42 mmol). The solution was stirred for 1 h, during which time it turned deep red. Diethyl ether (80 cm^3) was slowly added to give an orange microcrystalline solid, which was isolated by filtration, washed copiously with diethyl ether, and dried in vacuo, yield 1.49 g (93%).

$[Mo\{{=}C(NHBu^t)C(Ph){=}C(Ph)CN\}(CNBu^t)_2(\eta^5\text{-}C_5Me_5)][BF_4]$, 2. To a solution of $[Mo(PhC{\equiv}CPh)_2(CO)(\eta^5\text{-}C_5Me_5)]$ (0.500 g, 0.71 mmol) in thf (90 cm^3) was added $CNBu^t$ (0.322 cm^3, 2.84 mmol). This solution was heated under reflux for 16 h, cooled, filtered through Celite, and evaporated to dryness. The residue was redissolved in CH_2Cl_2 (10 cm^3), and the pale orange product precipitated by slow addition of *n*-hexane (100 cm^3), yield 0.409 g (75%). This solid is sufficiently pure for further experimental work, but may be recrystallized by storage of a CH_2Cl_2−*n*-hexane solution at 4 °C.

$[Mo\{C({=}NBu^t)C(Ph){=}C(Ph)CN\}(CNBu^t)_2(\eta^5\text{-}C_5Me_5)]$, 3. A 0.6 M solution of $NaN(SiMe_3)_2$ in toluene (0.9 cm^3, 0.54 mmol) was added to a suspension of **2** (0.40 g, 0.52 mmol) in thf (20 cm^3) and stirred for 20 min at room temperature. The slightly cloudy red solution was then evaporated to dryness and extracted with diethyl ether (4 × 20 cm^3). *n*-Hexane (100 cm^3) was added to the combined extracts, and the volume of the red solution reduced to about 50 cm^3 in vacuo. Storage overnight at −20 °C gave **3** as a red crystalline solid, yield 0.25 g (70%).

$[Mo\{{=}C(Ph)C(Ph){=}C{=}NHBu^t\}(CNBu^t)_2(\eta^5\text{-}C_5Me_5)][BF_4]_2$, 4. To a rapidly stirred solution of **1** (0.137 g, 0.183 mmol) in thf (10 cm^3) was added 4 drops of $HBF_4{\cdot}Et_2O$, causing the bottle-green product to precipitate. Stirring was continued for 1 min, and then the product was isolated by filtration, washed with diethyl ether (2 × 5 cm^3), and dried in vacuo, yield 0.118 g (77%).

$[Mo\{{=}C(NHBu^t)C(Ph)C(Ph)CN\}(CNBu^t)\{P(OMe)_3\}(\eta^5\text{-}C_5Me_5)][BF_4]$, 5. A solution of **4** (0.079 g, 0.094 mmol) and $P(OMe)_3$ (0.02 cm^3, 0.188 mmol) in CH_2Cl_2 (5 cm^3) was stirred for 30 min, producing a green-to-orange color change. *n*-

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Table 8. Crystal Data for Compounds 1−3, 6, and 7

	1	**2**	**3**	**6**·$CHCl_3$	**7**
formula	$C_{39}H_{52}N_3MoBF_4$	$C_{40}H_{53}N_4MoBF_4$	$C_{40}H_{52}N_4Mo$	$C_{40}H_{55}N_3MoBF_4Cl_3$	$C_{39}H_{55}N_3MoB_2F_8$
M	745.59	772.61	684.8	866.97	835.42
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2(1)/n$	$P2(1)/c$	$C2/c$	$P2(1)/n$	$P\bar{1}$
a/Å	13.9050(3)	10.9418(14)	11.5888(10)	10.566(2)	9.822(3)
b/Å	18.4722(3)	19.072(3)	16.8115(15)	16.005(3)	12.528(5)
c/Å	15.5330(3)	18.935(2)	39.321(3)	25.610(6)	17.506(6)
α/deg	90	90	90	90	84.74(4)
β/deg	97.2460(10)	91.666(2)	97.910(2)	94.337(14)	88.79(3)
γ/deg	90	18.935(2)	90	90	67.36(3)
U/Å^3	3957.88(13)	3949.7(9)	7587.8(11)	4318.3(16)	1979.5(12)
Z	4	4	8	4	2
μ/mm^{-1}	0.379	0.383	0.376	0.537	0.401
no. of reflns collected	20697	20683	15939	33718	17306
no. of ind reflns (R_{int})	6963 (0.0496)	6941 (0.0702)	4938 (0.0345)	6779 (0.2015)	6939 (0.0758)
goodness of fit on F^2	1.097	0.903	1.306	0.884	0.923
final R indices [$I > 2\sigma(I)$] $R1$, $wR2$	0.0465, 0.0931	0.0393, 0.0904	0.0606, 0.1290	0.0533, 0.1038	0.0524, 0.1023

Hexane (8 cm^3) was added and the resulting cloudy solution filtered through Celite. Overnight storage of the filtrate at 4 °C yielded **5** as a red crystalline solid, yield 0.047 g (61%).

[Mo{=C(NHBu^t)C(Ph)=C(Ph)C(NHBu^t)}(CNBu^t)(η^5-C_5Me_5)][BF_4], 6. A solution of **1** (0.200 g, 0.26 mmol) in thf (30 cm^3) was stirred over 10 cm^3 of a 0.5% sodium−mecury amalgam for 15 min to give a brown solution, which was decanted and evaporated to dryness. The resulting solid was redissolved in diethyl ether (20 cm^3), the solution was filtered through Celite, and then two drops of $HBF_4 \cdot Et_2O$ were added to the rapidly stirred solution to precipitate an orange solid. Brief treatment with ultrasound was used to promote solidification. This precipitate was isolated by filtration, redissolved in a mixture of thf (5 cm^3) and *n*-hexane (10 cm^3), and then filtered. Overnight storage of the filtrate at −10 °C gave the product as red-orange crystals, yield 0.060 g (30%). Crystals suitable for X-ray diffraction (as a $CDCl_3$ solvate) were grown from a $CDCl_3$ solution layered with *n*-hexane.

[Mo{=C(NHBu^t)C(Ph)C(Ph)CHNHBu^t}(CNBu^t)(η^5-C_5Me_5)][BF_4]$_2$, 7. A solution of **1** (0.100 g, 0.13 mmol) in thf (20 cm^3) was stirred over 10 cm^3 of a 0.5% sodium−mercury amalgam. The resulting orange-brown solution was filtered through Celite and protonated with a drop of $HBF_4 \cdot Et_2O$. The resulting cloudy orange solution was stirred for 5 min, before being evaporated to dryness and redissolved in CH_2Cl_2 (5 cm^3). This was again filtered through Celite, and then the crude product was precipitated by addition of an excess of diethyl ether. The resulting yellow powder was isolated by filtration and crystallized from a concentrated CH_2Cl_2 solution by inward vapor diffusion of diethyl ether to give **7** as yellow crystals, yield 0.042 g (37%).

Crystal Structure Determinations. The crystal structure determinations were carried out on a Bruker SMART diffractometer, that of **1** at 20 °C and those of **2**, **3**, **6**, and **7** in a nitrogen stream at −100 °C. In all cases graphite-monochromated Mo Kα radiation was used. Data correction was performed with the program SADABS.[22] The structures were solved by direct methods and refined by full-matrix least-squares techniques against F^2 using the programs SHELXS97 and SHELXL97.[23] The crystal and intensity data are given in Table 8. The structures of **1**, **6**, and **7** contain disordered $[BF_4]^-$ counterions, and that of **6** also has a disordered *tert*-butyl group. These disordered groups have all been modeled in two parts, with the sum of the occupancies of the parts constrained to 1.

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Supporting Information Available: Details of the structural determinations for complexes **1**, **2**, **3**, **6**, and **7**, including tables of crystal and intensity collection data, positional and anisotropic thermal parameters, and all of the bond distances and angles. This material is available free of charge via the Internet at http://pubs.acs.org.

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