Reactions of [Mo(≡CBr)(CO)$_2${HB(pzMe$_2$)$_3$}] (pz = pyrazol-1-yl) with Amines: Synthesis of Amino, Pyridinium, and Thiolato Carbyne Complexes

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Received May 26, 2008

The reactions of the bromocarbyne complex [Mo(≡CBr)(CO)$_2${HB(pzMe$_2$)$_3$}] (pz = pyrazol-1-yl) with a range of secondary and heterocyclic amines have been investigated and found in each case to proceed via simple nucleophilic halide substitution to provide N-functionalized carbyne derivatives, some of which are not available via conventional approaches. With diethylamine or piperazine the simple dialkyaminocarbyne complexes [Mo(≡CNEt$_2$)(CO)$_2${HB(pzMe$_2$)$_3$}] or [Mo{≡CN(C$_2$H$_4$)$_2$NH}(CO)$_2${HB(pzMe$_2$)$_3$}] were obtained. With 4-*N,N*-dimethylaminopyridine the pyridiniumcarbyne salt [Mo(≡CNC$_5$H$_4$NMe$_2$-4)(CO)$_2${HB(pzMe$_2$)$_3$}]Br was obtained; pyridine provided a complex intractable mixture and collidine failed to react. *N*-Methylimidazole provided the imidazolium derivative [Mo(≡CNC$_3$H$_3$NMe)(CO)$_2${HB(pzMe$_2$)$_3$}]Br, while *N*-(trimethylsilyl)imidazole gave the neutral imidazolyl derivative [Mo(≡CNC$_3$H$_3$N)(CO)$_2${HB(pzMe$_2$)$_3$}] and *N,N′*-bis(trimethylsilyl)imidazolium bromide. The sulfenamide HN(SPh)$_2$ afforded the thiolatocarbyne complex [Mo(≡CSPh)(CO)$_2${HB(pzMe$_2$)$_3$}] rather than the expected aminocarbyne complex [Mo{≡CN(SPh)$_2$}(CO)$_2${HB(pzMe$_2$)$_3$}], while HN(PPh$_2$S)$_2$ failed to react. The complex **1** is unreactive toward 1,8-diazabicycloundecene (DBU); however prolonged heating results in the formation of [DBUH][Mo(O)$_3${HB(pzMe$_2$)$_3$}] via base-induced hydrolysis/oxidation.

Introduction

Aminocarbynes L$_n$M≡CNR$_2$ in some respects represent a special case of alkylidyne complexes[1] in that the short C−N bond, comparatively long M≡C bond, and trigonal geometry typically observed at nitrogen are consistent with contributions from a 2-azavinylidene resonance description (Chart 1B).

Inferred chemical implications of such a bonding description include a generally reduced reactivity relative to hydrocarbon-substituted alkylidynes, e.g., the reticence toward the formation of ketenyl ligands via alkylidyne−carbonyl coupling, which is otherwise a comparatively general feature of low-valent group 6 alkylidynes.[2] Relative to hydrocarbon-substituted alkylidynes, spectroscopic ramifications include the observation of aminomethylidyne ^{13}C resonances to higher frequency of those for hydrocarbon alkylidynes and a shift to lower frequency of ν_{CO} for carbonyl co-ligands in otherwise analogous complexes, thereby indicating that the normally superlative π-acidity of the alkylidyne ligand is somewhat compromised by this pπ(N)−pπ(C) overlap. While all of these factors might make aminomethylidynes less interesting candidates for study from a chemical reactivity perspective, this extension of the M≡C π-system beyond the alkylidyne carbon might in principle offer some potential in the field of organometallic nonlinear optics,[3] although this has yet to be explored. In this respect the studies by H. Fischer of *imino*carbynes (2-aza-allenylidenes, L$_n$M≡C−N=CR$_2$) revealed unusual features.[4]

Synthetic routes to aminomethylidynes with comparatively general applicability include not only the classical Fischer approach of alkoxide abstraction from amino(alkoxy)carbene complexes[5] but also oxide abstraction from carbamoylates[6−10] and the N-alkylation of electron-rich isonitrile complexes (Scheme 1).[11−14] This latter approach adds further conceptual support to the azavinylidene description.

Each of these synthetic approaches has in common that either one or both of the amino substituents is installed early in the

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(6) Direct oxide abstraction was originally demonstrated by Fischer in the synthesis of the benzylidyne complex [W≡CPh)Br(CO)$_4$] using Br$_2$PPh$_3$ and the aminomethylidyne complex [W(≡CNEt$_2$)Cl(CO)$_4$] using thionyl chloride as the oxide-abstracting agent.[7] Subsequent refinement by Mayr established the effectiveness of (CF$_3$CO)$_2$O and oxalyl halides,[8] which we[9] and Filippou[10] have applied to aminomethylidyne syntheses.

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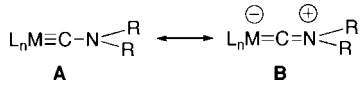
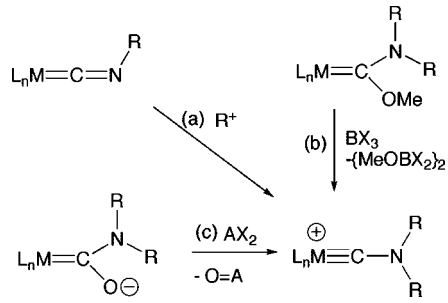
10.1021/om8004756 CCC: $40.75
Publication on Web 08/14/2008

Chart 1. Aminocarbyne (A) and 2-Azavinylidene (B) Canonical Forms



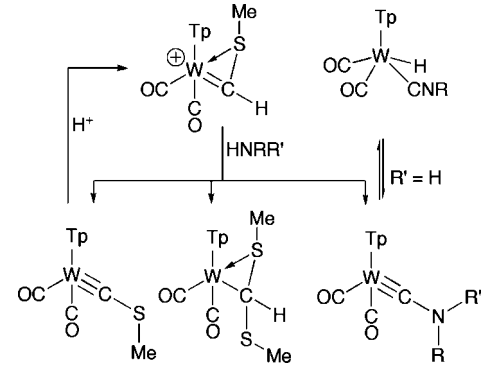
Scheme 1. Illustrative Generic Synthetic Routes to Aminocarbyne Complexes: (a) Isonitrile Alkylation; (b) Alkoxide Abstraction (X = F, Cl, Br); (c) Oxide Abstraction (AX_2 = Ph_3PBr_2, $OSCl_2$, $O{=}CCl_2$, $(OCCl)_2$, $(CF_3CO)_2O$



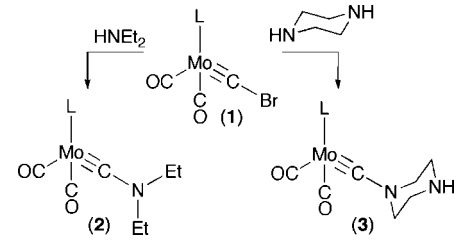
synthetic sequence. We considered that it might be expedient to develop synthetic protocols that allowed access to a wide range of aminocarbyne derivatives from a common intermediate that is late in the synthetic sequence. One such case is provided by the reactions of the thiolatocarbene complex $[W(\eta^2\text{-HCSMe})(CO)_2\{HB(pz)_3\}]^+$ (pz = pyrazolyl) with various amines, which were shown by Angelici (Scheme 2) to provide aminocarbyne complexes in addition to the bis(thiolato)alkyl complex $[W(\eta^2\text{-MeSCHSMe})(CO)_2\{HB(pz)_3\}]$.[15]

While important from an illustrative point of view and of fundamental interest, the synthetic utility of this protocol suffered from the numerous steps required to access $[W(\eta^2\text{-HCSMe})(CO)_2\{HB(pz)_3\}]^+$ from $[W(CO)_6]$ in addition to the side products $[W(\equiv CSMe)(CO)_2\{HB(pz)_3\}]$ and $[W\{\eta^2\text{-HC(SMe)}_2\}(CO)_2\{HB(pz)_3\}]$ that arise from a base-mediated

Scheme 2. Angelici's Aminomethylidyne Synthesis via Thiolatocarbene Aminolysis (Tp = $HB(pz)_3$)[15b]



Scheme 3. Synthesis of Simple Aminomethylidyne Complexes; L = $HB(pzMe_2)_3$



disproportionation of the precursor. We have therefore investigated the reactions of Lalor's bromocarbyne complex $[Mo(\equiv CBr)(CO)_2\{HB(pzMe_2)_3\}]$ (**1**, $pzMe_2$ = 3,5-dimethylpyrazol-1-yl)[16] with a range of amines. The complex **1** is readily available from $[Mo(CO)_6]$, and although the direct reactions of this complex with nucleophiles have not been reported, there is copious precedent involving the analogous chlorocarbyne complexes $[M(\equiv CCl)(CO)_2\{HB(pzMe_2)_3\}]$ (M = Mo, W)[17] and also of the palladium-catalyzed reactions of **1** with gold alkynyls.[18] None of these reports involve nitrogen-based nucleophiles.

Results and Discussion

Heating a solution of **1** in benzene under reflux with an excess of diethylamine results in the formation of the aminomethylidyne complex $[Mo(\equiv CNEt_2)(CO)_2\{HB(pzMe_2)_3\}]$ (**2**, Scheme 3) in good yield (ca. 80%). The formulation of **2** follows from spectroscopic data and was confirmed by a crystallographic study, the results of which are summarized in Figure 1. The spectroscopic data may be compared with those for the

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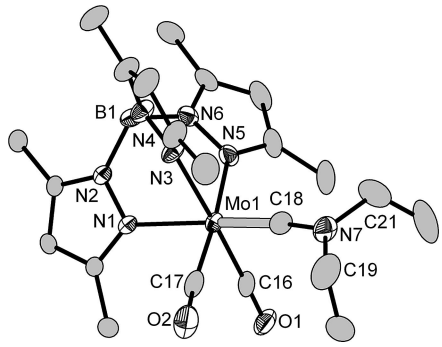

Figure 1. Molecular geometry of $[Mo(\equiv CNEt_2)(CO)_2\{HB(pzMe_2)_3\}]$ (**2**) in a crystal of $\mathbf{2}\cdot(Et_2O)_{0.5}$ (50% displacement ellipsoids, octant hatching for heteroatoms, hydrogen atoms omitted). Distances (Å) and angles (deg): Mo1−C18 1.853(3), Mo1−C16 1.962(3),Mo1−C17 1.986(3),Mo1−N5 2.241(2),Mo1−N3 2.245(2), Mo1−N1 2.286(2), N7−C18 1.316(4), N7−C21 1.458(5), N7−C19 1.467(4), C18−Mo1−C16 86.84(12), C18−Mo1−C17 82.40(12), C16−Mo1−C1783.94(12),C18−Mo1−N5 103.61(11),C16−Mo1−N5 95.28(10), C18−Mo1−N3 97.03(10), C17−Mo1−N3 97.48(11), N5−Mo1−N3 82.91(9), C16−Mo1−N1 95.50(9), C17−Mo1−N1 92.28(10), N5−Mo1−N1 81.77(8), N3−Mo1−N1 80.74(8), N7−C18−Mo1 172.2(3), C18−N7−C21 121.4(3), C18−N7−C19 121.1(3), C21−N7−C19 117.5(3).

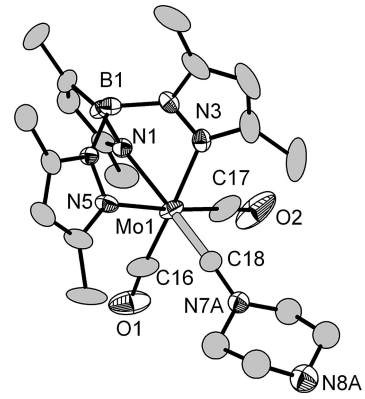

Figure 2. Molecular geometry of $[Mo\{\equiv CN(C_2H_4)_2NH\}(CO)_2\{HB(pzMe_2)_3\}]$ (**3**) in a crystal (50% displacement ellipsoids, octant hatching for heteroatoms, hydrogen atoms omitted, one of two independent molecules depicted with one of two positionally disordered piperazinyl rings). Selected bond distances (Å) and angles (deg): Mo1−C18 1.853(3), Mo1−N3 2.235(3), Mo1−N5 2.250(3), Mo1−N1 2.282(2), C18−N7A 1.324(4), C18−Mo1−C16 83.3(2), C18−Mo1−C17 85.3(2), C16−Mo1−C17 84.9(9), C18−Mo1−N3 99.0(9), C18−Mo1−N5 98.6(6).

analogous tungsten complexes $[W(\equiv CNEt_2)(CO)_2\{HB(pz)_3\}]$[15b] and $[W(\equiv CNEt_2)(CO)_2\{HB(pzMe_2)_3\}]$.[14i] Thus the presence of the aminoalkylidyne ligand follows from the observation of a low-field resonance (δ_C = 251.9) in the $^{13}C\{^1H\}$ NMR spectrum. Notably, two distinct pyrazolyl environments (2:1) are observed in both the ^1H and $^{13}C\{^1H\}$ NMR spectra, indicating that in contrast to the $HB(pz)_3$ ligand in Angelici's complex $[W(\equiv CNEt_2)(CO)_2\{HB(pz)_3\}]$,[15b] the Mo{HB(pz-$Me_2)_3$} cage is static on these NMR time scales, as is usually the case for the more bulky permethylated ligand.[1d]

Selected structural data for group 6 amino- and iminomethylidyne complexes are collated in Table S1. In the case of molybdenum and tungsten (r_{cov}(Mo) = 145, r_{cov}(W) = 146 pm) structural data for aminomethylidyne complexes span the ranges 1.801−1.903 and 1.282−1.369 Å for the M≡C and C−N bonds, respectively[1,19] within which lie the values for **2** (1.853(3) and 1.316(4) Å, respectively). Perhaps a feature more noteworthy than the individual Mo−C and C−N bond lengths is their sum. Thus, while the individual bond lengths vary for known complexes by 0.1 and 0.09 Å, respectively, their sum varies by only 0.04 (W, Mo)−0.05Å (Cr). Thus the aminomethylidyne ligand might be considered uniquely capable, among alkylidynes, of acting as an electroneutrality buffer in the way the more familiar carbonyl and isonitrile ligands can. Thus less π-basic metal centers have less effective M−C retrodonation (longer M−C bonds), which may be compensated for by more effective Nπ−Cπ donation (shorter bonds). We shall, however, return to this issue (vide infra) with a counter example. The geometry of the "$Mo(CO)_2\{HB(pzMe_2)_3\}$" fragment shows the typical features associated with alkylidyne coordination,[1d] i.e., acute N−Mo−N angles and an elongation (ca. 20 esd) of the Mo−N1 bond *trans* to the alkylidyne group, relative to those *trans* to carbonyl ligands. There is a modest deformation of the Mo1−C18−N7 spine away from linearity (172.2(3)°); however such bending is not uncommon in alkylidyne complexes.[1] The amino group in **2** aligns so as to eclipse one of the coordination axes (N5−Mo1−C17). This is in contrast to what is usually observed for arylmethylidyne complexes ligated by poly(pyrazolyl)boate ligands, in which the plane of the aryl substituent typically bisects the coordination axes, thereby minimizing steric interactions.[20,21] This behavior may be traced to the energy difference between the two alkylidyne acceptor orbitals, which is small in the case of benzylidyne ligands (effectively an axially symmetric pair of almost degenerate orbitals[22]) but significant for aminomethylidynes due to the strong conjugation of one of these with the π-donor amino group.

In a similar manner, the reaction of **1** with piperazine provides the mononuclear aminomethylidyne complex $[Mo\{\equiv CN(C_2H_4)_2NH\}(CO)_2\{HB(pzMe_2)_3\}]$ (**3**, Scheme 3). Despite considerable effort, we failed to identify conditions appropriate for the formation of a binuclear complex $(\mu\text{-}1,4\text{-}C_4H_8N_2)[-C\equiv Mo(CO)_2\{HB(pzMe_2)_3\}]_2$, although such a species appears entirely plausible. Spectroscopic data for **3** (δ_C(Mo≡C) = 247.7; $\nu_{CN}(CH_2Cl_2)$ = 1528 cm^{-1}) confirm the identity of the complex but otherwise call for little comment.

The molecular structure of **3** was confirmed crystallographically (Figure 2); however considerable disorder was encountered, and since this is primarily associated with the piperazinylcarbyne ligand, i.e., the group of interest, it is inappropriate to interrogate the metrical parameters obtained in any depth. Suffice to say, the crystallographic study confirmed the gross

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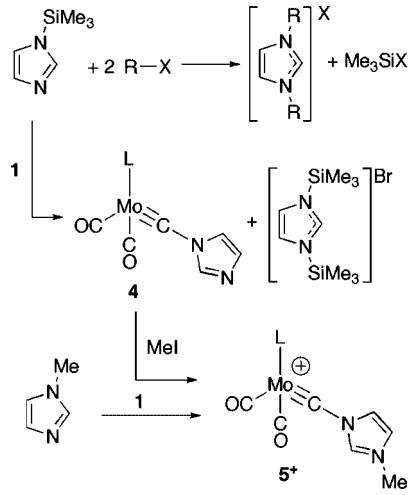
(22) A situation where the slight nondegeneracy of benzylidyne acceptor orbitals assumes considerable importance is in the field of electro-optical applications: Da Re, R. E.; Hopkins, M. D. *Coord. Chem. Rev.* **2005**, *249*, 1396.

Scheme 4. Synthesis of Imidazolyl and Imidazolium Carbine Complexes (R = Me, Et, Pr, CH_2CN, $CH_2C_6H_4Me$; X = Cl, Br)



topology, and despite the low precision, the geometric features are not dissimilar to those of **1**.

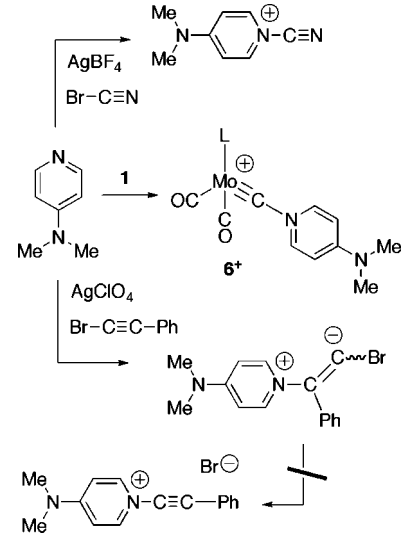
It has been previously shown that the reaction of *N*-trimethylsilylimidazole (TMS-Im) with alkyl halides provides a convenient route to *N,N′*-dialkylimidazolium halides.[23] It transpires that this is not an effective protocol for the synthesis of a bis(alkylidynyl)imidazolium salt from **1**. Rather, under the conditions so far explored, the sole product is the mononuclear *N*-imidazolylcarbyne **4** (Scheme 4).

Thus the reaction of **1** with an excess of TMS-Im provides a mixture of the compounds [Mo{≡C-*N*-Im}(CO)$_2${HB(pzMe_2)$_3$}] (**4**) and [*N,N′*-(TMS)$_2$Im]Br. The imidazolium salt has been previously reported[24] and was previously and also in this instance structurally characterized. This salt is however particularly easily hydrolyzed to organically soluble products (Him, TMS_2O), a feature that proved convenient in the purification of **4**. Complex **4** provides the first example of a carbyne complex in which the carbyne substituent is an N-bound aromatic heterocycle. Apart from this distinction, **4** is in other respects a conventional carbyne complex showing characteristic spectroscopic signatures, a comparatively high-field ^{13}C resonance (δ_C = 219.8), and ν_{CO} values in a region typical of hydrocarbon-substituted alkylidynes (CH_2Cl_2: 1997, 1911 cm^{-1}), suggesting little π-donation from the imidazolyl aromatic system in contrast to more conventional amino derivatives.

The synthesis of the imidazolylcarbyne complex **4** serves to illustrate a strength of this protocol in that such alkylidynes may not be accessed via any of the routes indicated in Scheme 1; that is, were the imidazolide anion sufficiently nucleophilic to attack a metal carbonyl, the subsequent steps (O-alkylation, oxide abstraction, or alkoxide abstraction) would not tolerate the presence of the second nucleophilic ring nitrogen. Complex **4** is also noteworthy in possessing a nucleophilic site remote from the Mo≡C bond, viz., the N-1 nitrogen that carries a lone pair.

Nucleophilic bromide displacement from **1** was also investigated with a range of aromatic N-heterocycles. Supportive precedent for the nucleophilic displacement of bromide from an sp-hybridized carbon by pyridines is somewhat ambivalent (Scheme 5). While cyanogen bromide reacts with 4-dimethylaminopyridine (DMAP) to provide a simple *N*-cyanopyridinium

Scheme 5. Reactions of DMAP with Br-Csp Compounds[25,26]



salt,[25] this reaction does not extend in a simple manner to 1-bromoalkynes. Rather, nucleophilic attack occurs at the 2-position of 1-bromo-2-phenylethyne to provide an adduct that does not undergo Fritsch−Buttenberg−Wiechel rearrangement,[27] while 1-bromo-2-mesitylethyne fails to react. The reactions of aromatic N-heterocycles with **1** were found to parallel those of cyanogen bromide rather than 1-bromoalkynes, though activation by silver salts was not necessary.

The *N*-methylimidazole (ImMe-3) reacted with **1** in refluxing benzene to provide the salt [Mo(≡C-ImMe-3)(CO)$_2${HB(pz)$_3$}]Br (**5**·Br). The spectroscopic data for **5**$^+$ are consistent with simple addition to the N-1 position of *N*-methylimidazole (Scheme 4). The connectivity could be further substantiated by unequivocal synthesis; the same complex (as the iodide salt **5**·I) results from the N-alkylation of **4** with excess iodomethane in a clean reaction that proceeds, albeit slowly, at room temperature (3−4 days). The reaction of **1** with pyridine required forcing conditions (toluene reflux), under which conditions the product was not sufficiently stable as to allow its isolation. The complex **1** was however unreactive toward collidine under these conditions. We consider this to be a kinetic problem deriving from the lower nucleophilicity of pyridine (pK_a 5.4),[28] cf. *N*-methylimidazole (pK_a 7.2)[28] requiring elevated temperatures to react, rather than any thermodynamic issues associated with the target complex. Accordingly, the reaction of **1** toward the more nucleophilic *N,N*-dimethylaminopyridine (pK_a 9.6)[28] was investigated and found to proceed readily in refluxing benzene with precipitation of the salt [Mo(≡CDMAP)(CO)$_2${HB(pzMe_2)$_3$}]Br (**6**·Br) occurring over 1 h.

The characterization of **6**·Br included a crystallographic study, the results of which are summarized in Figure 3. Together, **5**$^+$ and **6**$^+$ provide the first examples of carbyne complexes in which the carbyne substituent is a simple aromatic amine. Three canonical forms are depicted in Chart 2 to describe the bonding in **6**$^+$, the relevance of which may be questioned by interrogation of spectroscopic and structural data.

(23) Harlow, K. J.; Hill, A. F.; Welton, T. *Synthesis* **1966**, 697.
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(27) (a) Fritsch, P. *Ann.* **1894**, *279*, 319. (b) Buttenberg, W. P. *Ann.* **1894**, *279*, 327. (c) Wiechell, H. *Ann.* **1894**, *279*, 332.
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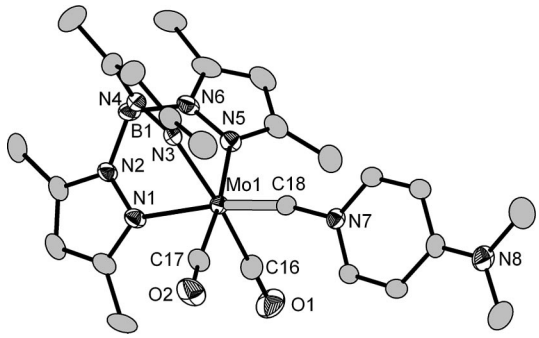
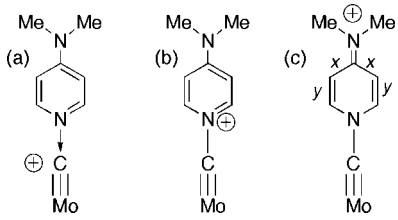


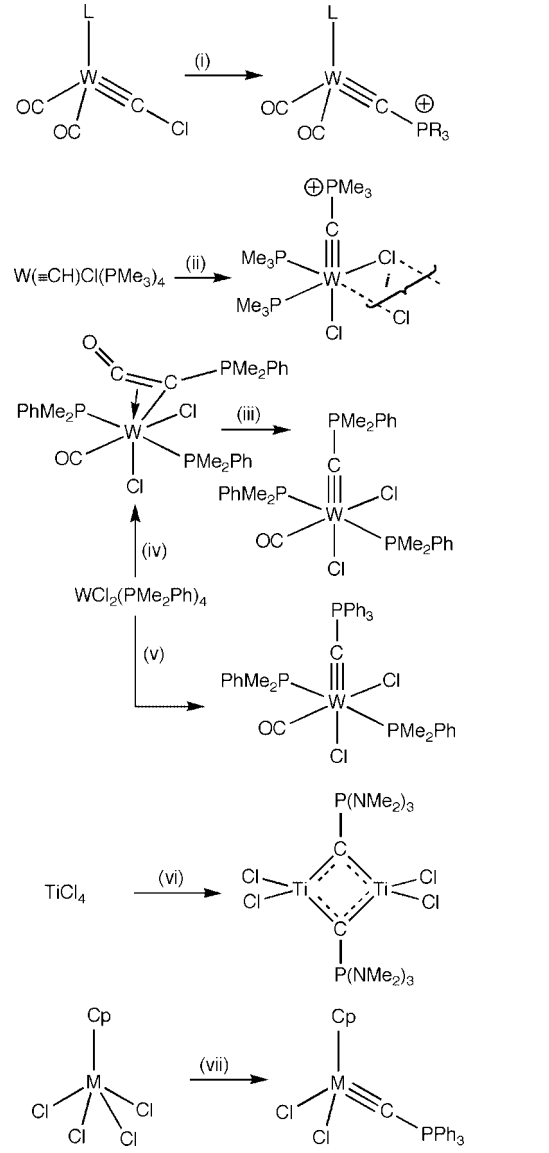
Figure 3. Molecular geometry of $[Mo(\equiv CNC_4H_4CNMe_2\text{-}4)(CO)_2\{HB(pzMe_2)_3\}]^+$ ($\mathbf{6}^+$) in a crystal of $\mathbf{6}\cdot Br\cdot(CHCl_3)_4$ (50% displacement ellipsoids, octant hatching for heteroatoms, hydrogen atoms omitted, one of two crystallographically independent molecules shown). Distances (Å) and angles (deg): Mo1−C18 1.807(4), Mo1−C17 1.997(4), Mo1−C16 2.015(4), Mo1−N5 2.208(3), Mo1−N3 2.215(3), Mo1−N1 2.268(30), N7−C23 1.366(4), N7−C19 1.373(5), N7−C18 1.394(5), N8−C21 1.327(5), N8−C25 1.454(6), N8−C24 1.468(6), C18−Mo1−C17 82.71(16), C18−Mo1−C16 85.20(15), C17−Mo1−C16 90.87(17), C18−Mo1−N5 103.24(14), C18−Mo1−N3 103.37(13), Mo1−C18−N7 166.9(3), C23−N7−C19 119.3(3), C23−N7−C18 120.2(3), C19−N7−C18 120.5(3).

Chart 2. Canonical Forms to Describe the Bonding in $\mathbf{6}^+$: (a) Base-Stabilized Carbynium; (b) Pyridinium; (c) Quinonoid



Form (a) depicts a base-stabilized carbynium situation, which has precedent in Templeton's phosphonio carbynes $[W(\equiv CPR_3)(CO)_2\{HB(pzMe_2)_3\}]PF_6$ ($PR_3 = PMe_2Ph$, PPh_3, PCy_3),[17g] which similarly derive from nucleophilic attack by phosphines upon the chlorocarbyne complex $[W(\equiv CCl)(CO)_2\{HB(pzMe_2)_3\}]$. These phosphoniocarbyne complexes give rise to comparatively high-frequency ^{13}C resonances (typically $\delta_C = 242-251$). Less directly analogous phosphoniocarbynes include those reported by Schrock,[29] Hillhouse,[30] Schmidbaur,[31] and Sundermeyer[32] (Scheme 6), none of which eventuate from synthetic routes that might be applicable to nitrogen analogues. The carbyne carbon chemical shifts for $\mathbf{5}^+$ and $\mathbf{6}^+$ (204.4 and 214.1 ppm, respectively) are moved significantly upfield from those for simple aminocarbynes (e.g., 251.9 ppm for **2**). Fischer's iminocarbynes

Scheme 6. Synthesis of Phosphoniocarbynes: (i) PR_3, $NaPF_6$;[17g] (ii) Al_2Cl_6, C_2Cl_6;[29] (iii) Δ;[30] (iv) O=C=C=C=O;[30] (v) Ph_3P=C=C=O;[30] (vi) $(Me_2N)_3P$=CH_2;[31] (vii) Ph_3P=CH_2, M = Nb, Ta[32]



("2-azaallenylidenes") are also similarly shifted to higher field (ca. 200 ppm).[4a] The degree of quinonoid contribution (Chart 2c) might be expected to be manifest as a partial localization of π-bonding within the ring. If we take the ratio of C−C bonds adjacent to the NMe_2 substituent (x, Chart 2c) to those once removed (y, Chart 2c), this takes the value 1.02 for free DMAP,[33a] 1.05 for [HDMAP],[+33b] and 1.04 for [F_3BDMAP];[33c] that is, a modest increase is observed for the formation of Lewis acid adducts with simple σ-bonding, hyperconjugation (BF_3) notwithstanding. Structural data for DMAP adducts with π-acidic N-substituents are somewhat sparse; however the acyl[33d] and benzoyl[33e] pyridinium cations show values of 1.06 and 1.05, respectively. In the case of $\mathbf{6}^+$ a value of 1.06 therefore suggests a degree of C−C multiple bond localization; that is, the quinonoid description would indeed appear to contribute to a valence bond picture. Benzoquinone and 4-nitroaniline, which might be considered benchmarks for quinone and "push−pull" systems, have values of 1.11 and 1.03, respectively.[34] However, the C18−N7 bond length of 1.394(5) Å is considerably longer than those found for **2** (1.316(4) Å) and **3** (1.324(4) Å), for which C−N multiple bonding was inferred. The Mo−C−N

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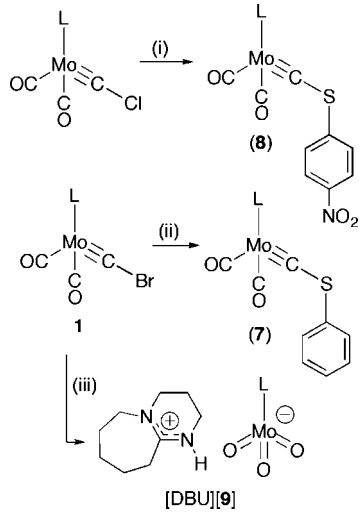
Scheme 7. (i) $NaBH_4$, $S_2(C_6H_4NO_2\text{-}4)_2$;[17c] (ii) $HN(SPh)_2$; (iii) DBU (H_2O)



angle is slightly bent at 166.9(3)° but remains within the spread of such angles for more conventional alkylidynes bound to the "$M(CO)_2\{HB(pzMe_2)_3\}$" fragment[1f] and is likely to be nothing more than a soft response to a combination of crystal-packing forces and nonbonded intramolecular interactions.

A couple of heteroatom-functionalized amines were briefly explored with mixed results. The phosphinamine $HN(PPh_2S)_2$ failed to react with **1** under mild conditions (refluxing THF or benzene). The sulfenamide $HN(SPh)_2$ also fails to react at room temperature; however addition of potassium hydride does induce a reaction. The product was not however the anticipated sulfenamido methylidyne $[Mo\{\equiv CN(SPh)_2\}(CO)_2\{HB(pzMe_2)_3\}]$ but rather the thiolatomethylidyne complex $[Mo(\equiv CSPh)(CO)_2\{HB(pzMe_2)_3\}]$ (**7**, Scheme 7) which was characterized on the basis of spectroscopic and crystallographic data. The mechanism by which **7** forms remains unclear. The fate of the missing phenylthionitrene fragment was not established, and the yield, being somewhat modest (ca. 40%), precludes detailed mechanistic discussion. Complex **7** has been previously claimed to result from the reaction of $[Mo(\equiv CCl)(CO)_2\{HB(pzMe_2)_3\}]$ with thiophenol under phase-transfer conditions; however no characterizational data were provided.[17c] The 4-nitrophenyl derivative (**8**) was similarly prepared, and although no spectroscopic data are available, the complex was structurally characterized. Accordingly, **7** has now been completely characterized, given that thiolatocarbyne complexes still remain comparatively rare,[17c,35] with most other known examples arising from the electrophilic alkylation/arylation of electron-rich thiocarbonyl precursors.[35]

Spectroscopic data associated with the "$Mo(CO)_2\{HB(pzMe_2)_3\}$" group are unremarkable, while the alkylidyne ligand gives rise to a characteristic resonance at 258.0 ppm in its $^{13}C\{^1H\}$ NMR spectrum, somewhat downfield from those for the aminocarbyne complexes. The characterization of **7** included a crystallographic study, the results of which are summarized

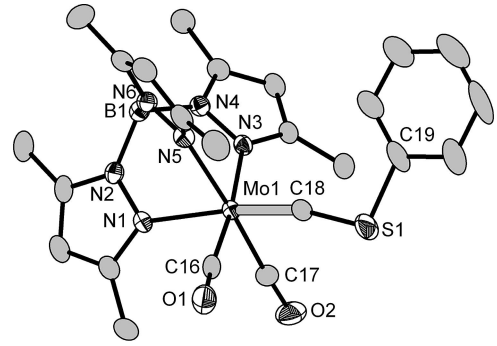


Figure 4. Molecular geometry of $[Mo(\equiv CSPh)(CO)_2\{HB(pzMe_2)_3\}]$ (**7**) in a crystal (one of two crystallographically independent molecules, 50% displacement ellipsoids, octant hatching for heteroatoms, hydrogen atoms omitted). Distances (Å) and angles (deg): Mo1−C18 1.820(3), Mo1−N3 2.218(2), Mo1−N5 2.225(2), Mo1−N1 2.297(2), S1−C18 1.697(3), S1−C19 1.794(3), C18−Mo1−C16 82.83(12), C18−Mo1−C17 82.08(13), C16−Mo1−C17 89.13(13), C18−Mo1−N3 102.41(11), C17−Mo1−N3 94.09(11), C18−Mo1−N5 103.83(11), N3−Mo1−N5 82.75(8), N3−Mo1−N1 81.90(8), N5−Mo1−N1 81.82(8), C18−S1−C19 102.94(15).

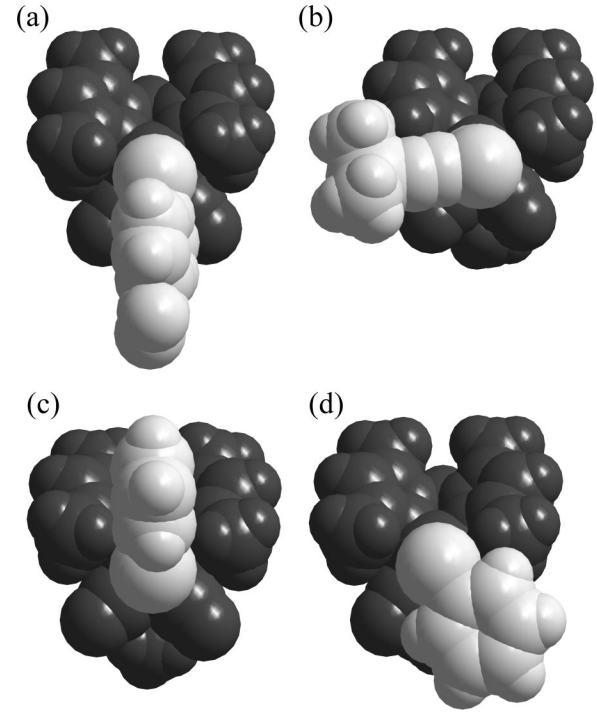


Figure 5. Views along the S···Mo or Se···Mo vectors of the molecular geometries of $[Mo(\equiv CR)(CO)_2\{HB(pzMe_2)_3\}]$: (a) R = $SC_6H_4NO_2$;[17c] (b) R = $SeC\equiv CSiMe_3$;[36] (c) R = SPh conformer based on Mo1; (d) R = SPh conformer based on Mo2.

in Figure 4. Structural data for mononuclear thiolatocarbyne complexes are limited to those for **8**,[17c] $[W(\equiv CSMe)(SMe)_2\{HB(pz)_3\}]$,[35a] and $[W(\equiv CSPh)(CO)(PPh_3)(\eta\text{-}C_5H_5)]$,[35e] the first of these being a direct analogue of **7**. The most striking feature of the crystal structure is that there are two crystallographically independent molecules, which show quite distinct conformations with respect to the orientation of the phenylthiolato substituent. One conformer (shown in Figure 4) has the SPh group nestled in the cleft provided by two of the pyrazolyl groups, while the second has this group eclipsing one of the Mo-CO groups but distal to the $HB(pzMe_2)_3$ group. Figure 5 depicts these two orientations in addition to those adopted by **8** and the recently

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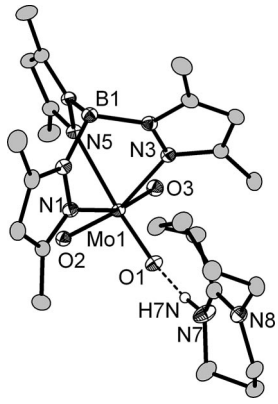

Figure 6. Molecular geometry of [DBUH][Mo(=O)$_3${HB(pzMe$_2$)$_3$}] ([DBUH][**9**]) in a crystal (50% displacement ellipsoids, octant hatching for heteroatoms, carbon-bound hydrogen atoms omitted). Distances (Å) and angles (deg): Mo1−O3 1.7299(11), Mo1−O2 1.7390(11), Mo1−O1 1.7647(11), Mo1−N5 2.3141(13), Mo1−N3 2.3373(13), Mo1−N1 2.3865(13), O1···H7N 1.79(2), O3−Mo1−O2 104.34(5), O3−Mo1−O1 105.65(5), O2−Mo1−O1 104.99(5), O3−Mo1−N5 88.25(5), O2−Mo1−N5 88.35(5), O3−Mo1−N3 86.62(5), O1−Mo1−N3 88.11(5), N5−Mo1−N3 74.58(5), O3−Mo1−N1 159.52(5), O2−Mo1−N1 87.61(5), O1−Mo1−N1 86.71(5), N5−Mo1−N1 75.33(4), N3−Mo1−N1 77.37(5).

reported alkynylselenolatoalkylidyne complex [Mo(≡CSeC≡CSiMe$_3$)(CO)$_2${HB(pzMe$_2$)$_3$}].[36]

All four molecules adopt distinct chalcogenolate conformations, and given the occurrence in equal amounts of both conformers of **7** in the crystal, we may safely assume that any conformational preference of the alkylidyne unit is very modest and less than the energy associated with crystal packing or intramolecular nonbonded interactions. Thus while aminocarbynes have a substantial degree of C−N multiple bonding, in the case of these thiolatocarbynes, any C−S hyperconjugation must be minimal and not result in any significant lifting of the degeneracy of the two carbyne acceptor orbitals. The disparity in SPh orientations is not reflected in variations to the geometrical parameters associated with the Mo−C−S−C linkage, these falling within the statistical precision limits for the two conformers. The exception is that in both conformers there is, as often observed, a modest bending at the carbyne carbon, which is marginally more pronounced for the Mo1 conformer (Mo1−C18−S1 166.9(2)°; Mo2−C42−S2 172.4(2)°). In both conformers, the Mo≡C bond is shorter (1.820(3), 1.828(3) Å) than observed for **2** (1.853(3) Å) but longer than found for **6**$^+$ (1.807(4) Å), further supporting the assumption that π-donation to the carbyne carbon is less effective for thiolato substituents than for amino groups.

Diazabicyclo[4.5.0]undecene (DBU) is popular as a comparatively strong but non-nucleophilic base, although on rare occasions it may also serve as a nucleophile. To establish whether DBU could be used as a sacrificial base in reactions of **1** with monobasic nucleophiles, the reaction of **1** with DBU alone was explored. Heating **1** with an excess of DBU in refluxing benzene failed to result in nucleophilic bromide substitution. Rather, over a period of 7 days, **1** was very slowly consumed with the only isolated product being small amounts of the salt [DBUH][Mo(=O)$_3${HB(pzMe$_2$)$_3$}] ([DBUH][**9**]), which was characterized crystallographically (Figure 6). The anion of this salt has been reported previously and is accessible via more strategic routes, e.g., oxidative decarbonylation of [Et$_4$N][Mo(CO)$_3${HB(pzMe$_2$)$_3$}] by dimethyldioxirane to provide [Et$_4$N][**9**].[37] Although salts of **9**$^-$ have not been structurally characterized, the related hydrated salt [Et$_4$N][Mo(=O)$_3$-{HB(pz)$_3$}](H$_2$O)$_2$ adopts a similar octahedral geometry[37] with molybdenum−oxo bond lengths of 1.725(6)−1.737(7) Å and angles between the oxo ligands of 104.6(3)−105.8(3)°. Notably in that structure, the two solvate water molecules are involved in hydrogen bonding to the oxo ligands. In the case of [DBUH][**9**], one oxo ligand is hydrogen bonded to the N−H of the [DBUH]$^+$ cation in such a way that the seven-membered ring of the DBUH$^+$ fits into the cleft provided by two pyrazolyl groups. This hydrogen bonding results in a very substantial lengthening of the "Mo=O1" bond (1.7647(11) Å) relative to the remaining oxo ligands (1.7390(11), 1.7299(11) Å), although the bond length still falls within the range typical of terminal oxo complexes of molybdenum(VI). Notably, aryloxides of the form [Mo(OAr)(=O)$_2${HB(pz^{i}Pr)$_3$}] have Mo−O "single" bond lengths in the range 1.866−1.931 Å.[38] Thus it would appear that DBU is insufficiently nucleophilic to react with **1** and that the eventual formation of [DBUH][**9**] is a result of the slow accumulation of traces of air and moisture during prolonged reflux. Moisture under these basic conditions would be expected to generate [DBUH][Mo(CO)$_3${HB(pzMe$_2$)$_3$}] via hydrolysis of the bromocarbyne ligand, followed by aerial oxidative decarbonylation. In the absence of DBU, complex **1** is stable under these conditions.

Concluding Remarks

A new synthetic route to aminocarbyne complexes has been demonstrated. Involving, as it does, the late installation of the carbyne substituent, this approach offers a degree of generality not available to more classical routes that require either the generation of lithium amides (functional group intolerance) or the electrophilic alkylation of previously synthesized and coordinated isonitriles. This has been illustrated by the syntheses of examples of novel types of aminomethylidynes, e.g., **3**−**6**$^+$, which are not accessible via more conventional routes. A tangential observation is that in the solid state structures of both **3** and **7** four or two conformations, respectively, are adopted for the alkylidyne ligand in the same crystal, providing circumstantial evidence that barriers to alkylidyne rotation and conformational preferences are at best modest and overcome by solid state effects.

Experimental Section

General Considerations. All manipulations involving **1** and its derivatives were routinely carried out under a dry and oxygen-free nitrogen atmosphere using standard Schlenk, vacuum line, and inert atmosphere drybox techniques, with dried and degassed solvents, which were distilled from sodium benzophenone ketyl (ethers, paraffins) or calcium hydride (dichloromethane). However, once isolated, the derivatives were in general air stable as crystalline solids. ^{1}H NMR spectra were obtained at 25 °C using Varian Mercury 300 (^{1}H: 300.066 MHz) or Inova 300 (^{1}H: 299.944 MHz) spectrometers. ^{13}C{^{1}H} spectra were performed on a Varian Inova 300 (^{13}C{^{1}H}: 75.421 MHz) spectrometer. Chemical shifts (δ, ^{1}H, ^{13}C) are given relative to internal SiMe$_4$ with coupling constants given in Hz. Elemental microanalysis (C, H, and N) was carried out by the microanalytical service of the Research School of Chemistry. Electrospray mass spectrometry (ESI) was performed

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by the Research School of Chemistry mass spectrometry service. Samples for ESI were prepared by dissolving a solid in a small amount of CH_2Cl_2 and diluting with methanol. Infrared spectra were obtained from CH_2Cl_2 solutions and Nujol mulls using a Perkin-Elmer Spectrum One FT-IR spectrometer. Single-crystal X-ray structure analyses were carried out on a Nonius KappaCCD-diffractometer using Mo Kα radiation (λ = 0.71073 Å). The structures were solved by direct methods (SHELXS-97) and refined with full-matrix least-squares method (refinement of F^2 against all reflections with SHELXL-97). All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were placed in idealized positions (riding model) and refined isotropically, except the N-bound hydrogen atom of the $[DBUH]^+$ cation of [DBUH][**9**], which was located from residual electron density and refined isotropically without restraints. The compound [Mo(≡CBr)-$(CO)_2${$HB(pzMe_2)_3$}] (**1**) was prepared according to the published procedure.[16]

Synthesis of [Mo(≡CNEt$_2$)(CO)$_2${HB(pzMe$_2$)$_3$}] (2). A solution of [Mo(≡CBr)$(CO)_2${$HB(pzMe_2)_3$}] (**1**; 500 mg, 0.92 mmol) in benzene (30 mL) was treated with dry diethylamine (2 mL, 20 equiv) and the mixture heated under reflux for 2 h. After this time the resultant suspension was filtered through diatomaceous earth to remove the precipitated $[Et_2NH_2]Br$. The solvent was removed from the filtrate under reduced pressure to afford a pale yellow powder, which was recrystallized from a mixture of dichloromethane and hexane to provide pale yellow crystals of **2**. Yield: 387 mg (79%). Crystals of a diethyl ether hemisolvate suitable for X-ray diffractometry were obtained by slow evaporation of a solution of **2** in Et_2O. IR (CH_2Cl_2): 1949s, 1850s (ν_{CO}), 1526m ($\nu_{C=N}$) cm^{-1}. IR (Nujol): 1938s, 1843s (ν_{CO}), 1520m ($\nu_{C=N}$) cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C): δ_H 1.31 (t, 6 H, NCH_2CH_3), 2.34 (s, 3 H, pzCH_3) 2.36 (s, 6 H, pzCH_3), 2.44 (s, 3 H, pzCH_3), 2.49 (s, 6 H, pzCH_3), 3.47 (q, 4 H, NCH_2), 5.73 (s, 1 H, pz*H*); 5.79 (s, 2H, pz*H*). $^{13}C\{^1H\}$ NMR: δ_C 251.9 (Mo≡C), 228.3 (CO), 151.3, 150.6, 144.0, 143.9, 105. 9, 105.8 (pz), 43.97 (NCH_2), 15.60, 14.78 (pzCH_3), 14.30 (NCH_2CH_3), 12.68, 12.53 (pzCH_3). MS-ESI(+): *m*/*z* 556 $[M + Na]^+$; 528 $[M + Na - CO]+$, 478 $[M + H - 2CO]^+$. Anal. Found: C, 47.81; H, 6.24; N, 17.67. Calcd for $C_{22}H_{32}BMoN_7O_2.H_2O$: C, 47.93; H, 6.22; N, 17.40. (H_2O of solvation confirmed by ^1H NMR integration.) Crystal data for **2**·$(OEt_2)_{0.5}$: $C_{22}H_{32}BMoN_7O_2.0.5(O(C_2H_5)_2)$, M_w = 570.35, monoclinic, $P2_1/c$, a = 8.05300(10) Å, b = 17.1793(3) Å, c = 19.9944(4) Å, β = 101.063(1)°, V = 2714.72(8) Å^3, Z = 4, D_{calcd} = 1.396 Mg m^{-3}, μ(Mo Kα) = 0.519 mm^{-1}, T = 100(2) K, 6241 independent reflections. F^2 refinement, R = 0.039, wR = 0.084 for 5198 reflections, [$I > 2\sigma(I)$, $2\theta_{max}$ = 55°], 345 parameters, CCDC 687811.

Synthesis of [Mo(≡CNC$_4$H$_8$NH)(CO)$_2${HB(pzMe$_2$)$_3$}] (3). A solution of [Mo(≡CBr)$(CO)_2${$HB(pzMe_2)_3$}] (**1**; 500 mg, 0.92 mmol) in benzene (30 mL) was treated with piperazine (174 mg, 2.02 mmol) and heated under reflux for 3.5 h, during which time a fine precipitate formed. The cooled yellow solution was filtered through diatomaceous earth, and the solvent was removed from the filtrate under reduced pressure to afford a bright yellow powder. The crude material was recrystallized from a mixture of dichloromethane and hexane to afford **3** as orange crystals. Yield: 320 mg (64%). IR (CH_2Cl_2): 1951s, 1852s (ν_{CO}), 1528m ($\nu_{C=N}$) cm^{-1}. IR (Nujol): 1935s, 1830s (ν_{CO}), 1524m ($\nu_{C=N}$) cm^{-1}. ^1H NMR ($CDCl_3$, 25 °C): δ_H 1.81 (s br, 1 H, NH), 2.33 (s, 3 H, pzCH_3), 2.35 (s, 6 H, pzCH_3), 2.43 (s, 3 H, pzCH_3), 2.46 (s, 6 H, pzCH_3), 3.08 (t, 4 H, $MoCNCH_2$, $^3J_{HH}$ = 5.1), 3.67 (t, 4 H, $HNCH_2$, $^3J_{HH}$ = 5.1); 5.73 (s, 1 H, pz*H*), 5.79 (s, 2 H, pz*H*). $^{13}C\{^1H\}$ NMR: δ_C 247.72 (Mo≡C), 227.9 (CO), 151.4, 150.5, 144.1, 144.0, 106.0, 105.9 (pz), 48.3, 45.8 (NC_4H_8NH), 15.9, 14.8, 12.6, 12.5 (pzCH_3). MS-ESI(+): *m*/*z* 569 $[M + Na]^+$, 547 $[M + H]^+$; 519 $[M + H - CO]^+$. Anal. Found: C, 47.47; H, 5.90; N, 18.76. Calcd for $C_{22}H_{31}BMoN_8O_2$·$0.25CH_2Cl_2$: C, 47.09; H, 5.59; N, 19.74 (CH_2Cl_2 of solvation confirmed by ^1H NMR integration). Crystals suitable for diffractometry were grown by slow diffusion of hexane into a concentrated solution of the complex in diethyl ether. Crystal data for [Mo(≡CNC_4H_8NH)$(CO)_2${$HB(pzMe_2)_3$}] (**3**): $C_{22}H_{31}BMoN_8O_2$·$0.5(O(C_2H_5)_2)$, M_w = 546.29, orthorhombic, $P2_12_12_1$, a = 9.9952(2) Å, b = 15.9318(3) Å, c = 31.2340(6) Å, V = 4973.75(17) Å^3, Z = 8, D_{calcd} = 1.459 Mg m^{-3}, μ(Mo Kα) = 0.563 mm^{-1}, T = 100(2) K, 10 816 independent reflections. F^2 refinement, R = 0.033, wR = 0.075 for 10 185 reflections, [$I > 2\sigma(I)$, $2\theta_{max}$ = 54°], 632 parameters. A considerable degree of disorder became apparent during the refinement. Primarily this disorder involves two crystallographically independent molecules, each with two distinct orientations for the piperazinyl ring (Figure 7). For the molecule based on "Mo1" the two orientations involve rotation of the entire alkylidyne group about the Mo≡C bond (Figure 7a,b; cf. Figure 5). For the molecule based on "Mo2" the two conformers correspond to bending of the $CN(CC)_2N$ ring (Figure 7c,d).

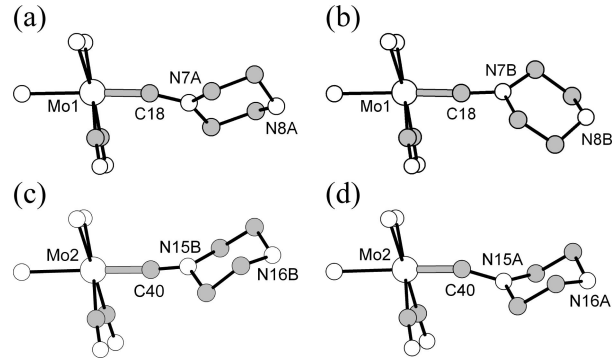

Figure 7. Conformational disorder in the piperazinylmethylidyne ligands of **3**.

Synthesis of [Mo(≡C−N−Im)(CO)$_2${HB(pzMe$_2$)$_3$}] (4). An oven-dried, one-necked, 100 mL Schlenk flask was cooled under nitrogen and charged with [Mo(≡CBr)$(CO)_2${$HB(pzMe_2)_3$}] (**1**; 500 mg, 0.92 mmol) and *N*-(trimethylsilyl)imidazole (TMS-Im, 0.35 mL, 2.30 mmol) in 30 mL of dry benzene, and the resultant yellow solution was heated at reflux for 90 min, after which time a fine white precipitate* had formed in a yellow solution. The solution was filtered through diatomaceous earth and the solvent removed to afford **4** as a bright yellow powder, which was recrystallized from a mixture of dichloromethane and hexane. Yield: 408 mg (84%). IR (CH_2Cl_2): 1997s, 1911s (ν_{CO}) cm^{-1}. IR (Nujol): 1986s, 1910s (ν_{CO}) cm^{-1} (ν_{CN} not unambiguously identified). ^1H NMR ($CDCl_3$, 25 °C): δ 2.28 (s, 3 H, pzCH_3), 2.30 (s, 6 H, pzCH_3), 2.33 (s, 3 H, pzCH_3), 2.36 (s, 6 H, pzCH_3), 5.71 [s, 1 H, pz*H*], 5.78 [s, 2 H, pz*H*]; 6.86, 7.27 [AB, 2 H, $H^{4,5}$(Im), $^3J_{AB}$ = 1.7 Hz], 7.90 [s, 1 H, H^2(Im)]. $^{13}C\{^1H\}$ NMR: δ_C 224.2 (CO), 219.8 (Mo≡C), 151.3, 150.8, 145.1, 144.6 [$C^{3,5}$(pz)], 137.7 [C^2(Im)], 127.8 [C^5(Im)], 118.9 [C^4(Im)], 106.5, 106.3 [C^4(pz)], 15.7, 14.7, 12.6 (br, pzCH_3). MS-ESI(+): (*m*/*z*) 551, $[M + Na]^+$, 529 $[M + H]^+$, 501 $[M + H - CO]^+$, 473 $[M + H - 2CO]^+$. Anal. Found: C, 47.55; H, 4.95; N, 21.00. Calcd for $C_{21}H_{25}BMoN_8O_2$: C, 47.75; H, 4.77; N, 21.21. *The white precipitate that was removed in the filtration step was recrystallized and identified on the basis of X-ray crystallography as the salt [*N*,*N*′-$(Me_3Si)_2$Im]Br.[24]

Synthesis of [Mo(≡C-ImMe-3)(CO)$_2${HB(pzMe$_2$)$_3$}]·Br (5·Br). An oven-dried, one-necked, 100 mL Schlenk flask was allowed to cool under nitrogen and charged with [Mo(≡CBr)-$(CO)_2${$HB(pzMe_2)_3$}] (**1**; 500 mg, 0.92 mmol), *N*-methylimidazole (0.18 mL, 2.3 mmol), and dry benzene (30 mL) and heated under reflux for 1 h. The resulting red suspension was allowed to cool, and the orange precipitate was isolated by filtration, washed with hexane (2 × 20 mL), and dried in vacuo. Recrystallization from a mixture of dichloromethane and hexane afforded orange crystals. Yield: 520 mg (90%). IR (CH_2Cl_2): 2017s, 1933s ν_{CO} cm^{-1}, 1583m

$\nu_{C\equiv N}$ cm^{-1}. IR (Nujol): 2006s, 1918s ν_{CO} cm^{-1}, 1580m $\nu_{C\equiv N}$ cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 °C): δ_H 2.34 (s, 3 H, pzCH_3), 2.36 (s, 9 H, pzCH_3), 2.42 (s, 6 H, pzCH_3) 18H, pzCH_3), 4.34 (s, 3 H, ImCH_3), 5.79 [s, 1H, H^4(pz)], 5.87 [s, 2 H, H^4(pz)], 7.52 [br, 1 H, H^4(Im)], 7.83 [br, 1 H, H^5(Im)], 10.34 [s, 1H, H^2(Im)]. ^{13}C{^{1}H} NMR: δ_C 223.0 (CO), 204.4 (Mo≡C), 151.4, 150.8, 145.6, 145.0 [C^{3,5}(pz)], 128.2 [C^5(Im)], 124.3 [C^2(Im)], 121.6 [C^4(Im)], 106.9, 106. Six [C^4(pz)], 37.3 (NCH_3), 16.4, 14.7, 12.7, 12.8 (CCH_3). ESI(+)-MS: *m*/*z* 543 [M]$^+$, 515 [M − CO]$^+$, 487 [M − 2CO]$^+$. Anal. Found: C, 41.26; H, 4.60; N, 17.43. Calcd for $C_{22}H_{28}BN_8MoO_2Br\cdot 0.25CH_2Cl_2$: C, 41.47; H, 4.46; N, 17.39 (CH_2Cl_2 of solvation confirmed by ^{1}H NMR integration).

Synthesis of [Mo(≡CNC$_5$H$_4$NMe$_2$-4)(CO)$_2${HB(pzMe$_2$)$_3$}]·Br (6·Br). An oven-dried, one-necked, 100 mL Schlenk flask was allowed to cool under nitrogen and charged with [Mo(≡CBr)(CO)$_2${HB(pzMe$_2$)$_3$}] (**1**; 500 mg, 0.92 mmol), 4-(dimethylamino)pyridine (282 mg, 2.30 mmol), and dry benzene (30 mL) and heated under reflux for 1 h. The resulting red suspension was allowed to cool, and the salmon precipitate was isolated by filtration, washed with hexane (2 × 20 mL), and dried in vacuo. Recrystallization from a mixture of dichloromethane and hexane afforded orange crystals. Yield: 571 mg (93%). Crystals suitable for X-ray diffraction were obtained from a slow diffusion of diethyl ether into a solution of **6**·Br in $CHCl_3$. IR (CH_2Cl_2): 2012s, 1929s ν_{CO}, 1574m $\nu_{C\equiv N}$ cm^{-1}. IR (Nujol): 1992s, 1904s ν_{CO}, 1565m $\nu_{C\equiv N}$ cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 °C): δ_H 2.33 (s, 9 H, pzCH_3), 2.34 (s, 3 H, pzCH_3), 2.35 (s, 6 H, pzCH_3), 3.50 (s, 6 H, N(CH_3)$_2$); 5.77 (s, 1 H, pz*H*); 5.85 (s, 2 H, pz*H*); 7.38 (d, 2 H$_{meta}$ NC_5H_4-4-NMe_2); 8.14 (d, 2 H$_{ortho}$ NC_5H_4-4-NMe_2). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 223.52 (s, CO); 214.06 (s, Mo≡C); 155.78 (s, C$_3$, NC_5H_4-4-NMe_2); 151.68 (s, *pz*CH_3); 150.90 (s, *pz*CH_3); 145.95 (s, *pz*CH_3); 145.387 (s, *pz*CH_3); 138.93 (s, C$_1$, NC_5H_4-4-NMe_2); 109.53 (s, C$_2$, NC_5H_4-4-NMe_2); 107.15 (s, *pz*H); 106.90 (s, *pz*H); 42.39 (s, NMe_2); 16.28 (s, pzCH_3); 15.04 (s, pzCH_3); 13.02 (s, pzCH_3), 12.94 (s, pzCH_3). ES(+)-MS (*m*/*z*): 583.3 [M]$^+$; 555.3 [M − CO]$^+$; 527.3 [M − 2CO]$^+$. Found: C, 42.86; H, 4.95; N, 15.57. Calcd for $C_{25}H_{32}N_8BMoO_2Br\cdot 0.5CH_2Cl_2$: C, 43.40; H, 4.71; N, 15.88 (CH_2Cl_2 of solvation confirmed by ^{1}H NMR integration). Crystal data for **6**·Br($CHCl_3$)$_4$: $C_{25}H_{32}BMoN_8O_2.(CHCl_3)_4$, M_w = 1140.72, monoclinic, $P2_1$, a = 14.9825(3) Å, b = 15.8754(3) Å, c = 19.5854(4) Å, β = 93.752(1)°, V = 4648.5(2) Å^3, Z = 4, D_{calcd} = 1.630 Mg m^{-3}, μ(Mo Kα) = 1.869 mm^{-1}, T = 100(2) K, 34 623 independent reflections. F^2 refinement, R = 0.039, wR = 0.084 for 27 597 reflections, [$I > 2\sigma(I)$, $2\theta_{max}$ = 66°], 1053 parameters, CCDC 687810. The structure exhibits 86% $P2_1/c$ pseudosymmetry. Structure refinement in $P2_1/c$, however, results in notably larger anisotropic thermal parameters for the atoms of the main molecule (cation) as well as severely increased disorder of the chloroform molecules. The data set bears about 1000 systematic absence violations against space group $P2_1/c$. The structure has been refined using a racemic twin model, and the relative twin ratio 0.573: 0.427 has been found. The two crystallographically independent bromide ions are surrounded by four chloroform molecules each. Five of these solvent molecules are disordered (2-fold each).

Synthesis of [Mo(≡CSPh)(CO)$_2${HB(pzMe$_2$)$_3$}] (7). To a solution of [Mo(≡CBr)(CO)$_2${HB(pzMe$_2$)$_3$}] (**1**; 200 mg, 0.37 mmol) in THF (20 mL) was added $HN(SPh)_2$ (0.096 g, 0.41 mmol), with no apparent reaction being observed. Addition of potassium hydride (0.02 g, 0.8 mmol) resulted in a small degree of effervescence and the disappearance of carbonyl stretches corresponding to **1** in the IR spectrum. The solvent was removed in vacuo and the residue recrystallized from a mixture of dichloromethane and diethyl ether to afford **7** as red crystals (62 mg, 40%). NB: This compound has been previously reported;[17c] however characterizational data have yet to appear. Crystals suitable for diffractometry were obtained by slow diffusion of diethyl ether into a solution of **7** in dichloromethane. IR (CH_2Cl_2): 1989s, 1905s (ν_{CO}) cm^{-1}. IR (Nujol): 1989s, 1887s (ν_{CO}) cm^{-1}. ^{1}H NMR ($CDCl_3$, 25 °C): δ_H 2.32 (s, 3 H, pzCH_3) 2.35 (s br, 15 H, pzCH_3), 5.72 (s, 1H, pz*H*), 5.81 (s, 2 H, pz*H*); 7.27−7.59 (m, 5 H, C_6H_5). ^{13}C{^{1}H} NMR: δ_C 258.0 (Mo≡C), 226.4 (CO), 151.4, 151.3, 145.0, 144.4 [C^{3,5}(pz)], 130.0 [C^1(C_6H_5)], 129.3[C^{3,5}(C_6H_5)], 128.0 [C^{2,6}(C_6H_5)], 126.1 [C^4(C_6H_5)], 106.4, 106.2 [C^4(pz)], 15.56, 14.65, 12.68, 12.62 (pzCH_3). ESI(+)-MS: *m*/*z* 595 [M + Na]$^+$, 517 [M + H − 2CO]$^+$, 501 [M − Ph]$^+$. Crystal data for **7**·$(OEt_2)_{0.5}$: $C_{24}H_{27}BMoN_6O_2S$, M_w = 570.33, triclinic, $P\bar{1}$ (No. 2), a = 10.7556(2) Å, b = 14.7960(3) Å, c = 17.6052(3) Å, α = 108.689(1)°, β = 90.741(1)°, γ = 103.944(1)°, V = 2563.34(9) Å^3, Z = 4, D_{calcd} = 1.478 Mg m^{-3}, μ(Mo Kα) = 0.626 mm^{-1}, T = 100(2) K, 11 745 independent reflections. F^2 refinement, R = 0.041, wR = 0.094 for 9455 reflections, [$I > 2\sigma(I)$, $2\theta_{max}$ = 60°], 631 parameters, CCDC 687812.

Crystal structure determination of [DBUH][Mo(O)$_3${HB(pzMe$_2$)$_3$}] [DBUH][**9**]: $C_{24}H_{39}BMoN_8O_3$, M_w = 594.38, monoclinic, $P2_1/c$, a = 9.9520(2) Å, b = 16.9385(2) Å, c = 15.9761(2) Å, β = 92.829(1), V = 2689.84(7) Å^3, Z = 4, D_{calcd} = 1.468 Mg m^{-3}, μ(Mo Kα) = 0.530 mm^{-1}, T = 100(2) K, 7830 independent reflections. F^2 refinement, R = 0.029, wR = 0.070 for 6646 reflections, [$I > 2\sigma(I)$, $2\theta_{max}$ = 60°], 351 parameters, CCDC 688451.

Acknowledgment. We thank the Australian Research Council (ARC) for financial support (Grant No. DP0556236) and the Deutscher Akademsicher Austauschdienst (DAAD) for the award of a postdoctoral fellowship (to J.W.).

Supporting Information Available: Full details of the crystal structure determinations of **2**.$(OEt_2)_{0.5}$ (CCDC 687811), **3**, **6**·Br($CHCl_3$)$_4$ (CCDC 687810), **7** (CCDC 687812), and [DBUH][**9**] (CCDC 688451) in CIF format, and Table S1, collating selected structural data for group 6 aminocarbyne complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

OM8004756