Synthesis and Reactivity of 16-Electron Cycloheptatrienyl-Molybdenum(0) Complexes with Bis(imidazolin-2-imine) Ligands

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The reaction of the ligands 1,2-bis(1,3-diisopropyl-4,5-dimethylimidazolin-2-imino)ethane (BL^{iPr}) and 1,2-bis(1,3,4,5-tetramethylimidazolin-2-imino)ethane (BL^{Me}) with the cycloheptatrienyl-molybdenum complex $[(\eta^7\text{-}C_7H_7)Mo(CH_3CN)_3]X$ ($X = BF_4$, PF_6) leads to acetonitrile substitution and formation of stable 16-electron half-sandwich complexes $(\eta^7\text{-}C_7H_7)Mo(BL^{iPr})]BF_4$, [**1**]$BF_4$, and $[(\eta^7\text{-}C_7H_7)Mo(BL^{Me})]X$, [**2**]X ($X = BF_4$, PF_6), two of which could be crystallographically characterized to reveal undistorted two-legged piano stool geometries. Cyclovoltammetric studies exhibit very negative redox potentials of $E° = -1.095$ V and $E° = -1.138$ V versus the ferrocene/ferrocenium couple (0 V), indicative of very electron-rich metal complexes. Oxidation of [**2**]X with $(\eta^7\text{-}C_7H_7)BF_4$ or $[Fe(\eta^5\text{-}C_5H_5)_2]PF_6$ furnished the Mo(I) complexes of general formula $[(\eta^7\text{-}C_7H_7)Mo(BL^{Me})(CH_3CN)]X_2$, [**3**]$X_2$ ($X = BF_4$, PF_6), which display a three-legged piano stool geometry in the solid state by coordination of one additional acetonitrile molecule to molybdenum. The same geometry is observed upon reaction of [**1**]BF_4 and [**2**]PF_6 with 2,6-dimethylphenyl isocyanide (XyNC) to afford the isocyanide complexes [**1**(CNXy)]BF_4 and [**2**(CNXy)]PF_6. Their CN stretching vibrations are observed at 2041 and 2030 cm^{-1}, confirming the electron richness and strong π-electron-releasing capability of the molybdenum-imine moiety.

Introduction

Coordinatively unsaturated organometallic complexes play a fundamental role as intermediates in homogeneous transition metal-catalyzed reactions, and their occurrence is rationalized by the 16- and 18-electron rule proposed by Tolman.[1] Numerous examples have been prepared to date, and their electronic and magnetic properties have been studied.[2] Among these systems, 16-electron ruthenium half-sandwich complexes containing cyclopentadienyl-ruthenium moieties $[(\eta^5\text{-}C_5R_5)Ru]$ have received considerable attention,[3–6] since complexes of this type can for instance be used for the stabilization of highly reactive species such as vinylidenes or allenylidenes by metal coordination.[7] In addition, these unsaturated complexes may serve as models for the active catalysts generated in ruthenium-catalyzed C−C bond forming reactions.[8]

Various factors can be responsible for the stabilization of these species, among which the introduction of π-donor ligands such as alkoxides, alkylthiolates, amides, or halides can be successfully employed for the creation of π-stabilized unsaturation.[9] Accordingly, the stabilization for instance of 16-electron half-sandwich ruthenium complexes of the type $[(\eta^5\text{-}C_5Me_5)Ru(PR_3)X]$ (X = OR, NHR, Cl, Br, I) can be achieved by electron donation from the heteroatomic anionic ligand.[10] Ligand π-coordination has also been suggested to exist in highly reactive ruthenium-amidinate complexes such as $[(\eta^5\text{-}C_5Me_5)Ru\{iPrNC(Me)NiPr\}]$.[11] In contrast, the cationic 16-electron tmeda complex $[(\eta^5\text{-}C_5Me_5)Ru(Me_2NCH_2CH_2NMe_2)]^+$ can be isolated despite the lack of nitrogen-to-metal π-donation. This complex, however, can only be stabilized by the use of the noncoordinating $[B\{3,5\text{-}C_6H_3(CF_3)_2\}_4]^-$ (BAr'_4) counteranion.[12] The same holds true for the rare 16-electron phosphane complexes $[(\eta^5\text{-}C_5Me_5)Ru(PP)]BAr'_4$ [PP = $(PEt_3)_2$, $iPr_2PCH_2CH_2PiPr_2$].[13]

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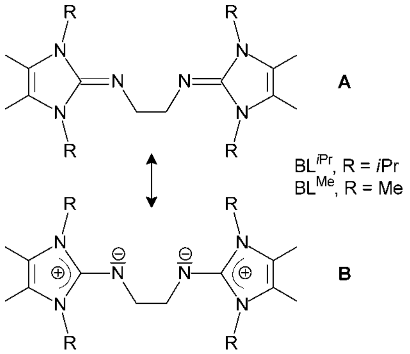
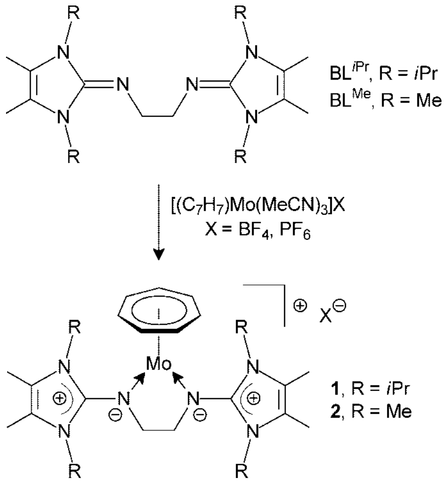
Scheme 1. Mesomeric structures for the bis(imidazolin-2-imine) ligands BL^R (R = Me, *i*Pr)



Recently, we have reported the isolation of very stable cationic 16-electron ruthenium complexes of the type $[(\eta^5\text{-}C_5Me_5)Ru(BL^R)]^+$ (R = *i*Pr, Me) containing the neutral 1,2-bis(imidazolin-2-imino)ethane ligands BL^{iPr} and BL^{Me}, in which the ruthenium atom even resists coordination by the chloride counterion.[14] This unusual stability can be ascribed to the strong π-basic nature of the novel bis(imidazoline) ligands, in which the ability of the imidazolium moiety to stabilize a positive charge leads to highly basic ligands with a strong electron-donating capacity (Scheme 1).[15–18] This behavior leads to a weak propensity of the Ru atom to coordinate other π-donor ligands such as chloride, whereas strong binding of σ-donor/π-acceptor ligands such as CO or isocyanides can be observed.[14]

In view of the growing number of well-characterized 16-electron cyclopentadienyl-ruthenium complexes, it is surprising that no analogous half-sandwich cycloheptatrienyl-molybdenum complexes have been reported to date, although the similarity between the isoelectronic and isolobal fragments $[(\eta^5\text{-}C_5R_5)Ru]$ and $[(\eta^7\text{-}C_7H_7)Mo]$ is well recognized.[19–22] The steric requirements of the C_7H_7 (Cht) ligand (cone angle ≈ 154°) make comparison with the C_5Me_5 (Cp*) system (cone angle ≈ 142°)[23] particularly appropriate, and it could clearly be demonstrated that complexes of the 16-electron $[(\eta^7\text{-}C_7H_7)MoL_2]$ auxiliary exhibit reactivity patterns analogous to those of $[(\eta^5\text{-}C_5Me_5)RuL_2]$ systems.[20,21] In this contribution, we present the synthesis and structural characterization of stable cationic 16-electron molybdenum complexes of the type $[(\eta^7\text{-}C_7H_7)Mo(BL^R)]^+$ (R = Me, *i*Pr) containing the neutral 1,2-bis(imidazolin-2-imino)ethane ligands BL^{Me} and BL^{iPr} and compare their properties with those of their $[(\eta^5\text{-}C_5Me_5)Ru(BL^R)]^+$ congeners.[14]

Scheme 2. Syntheses of 16-Electron Molybdenum(0) Complexes [1]X and [2]X (X = BF_4, PF_6)



Results and Discussion

Reactions of the Ligands BL^R with $[(\eta^7\text{-}C_7H_7)Mo(CH_3CN)_3]X$ (X = BF_4, PF_6). The synthesis of the ligands 1,2-bis(1,3-diisopropyl-4,5-dimethylimidazolin-2-imino)ethane (BL^{iPr}) and 1,2-bis(1,3,4,5-tetramethylimidazolin-2-imino)ethane (BL^{Me}) has been described elsewhere.[14] The reactions of these potentially bidentate ligands with the purple molybdenum(0) complexes $[(\eta^7\text{-}C_7H_7)Mo(CH_3CN)_3]X$ (X = BF_4, PF_6),[24] followed by precipitation with diethyl ether, afforded grass-green, extremely air-sensitive solids (Scheme 2). The ligands BL^{iPr} and BL^{Me} coordinate to molybdenum by substitution of the three acetonitrile molecules in the starting material to form stable 16-electron half-sandwich complexes $[(\eta^7\text{-}C_7H_7)Mo(BL^{iPr})]BF_4$, [**1**]$BF_4$, and $[(\eta^7\text{-}C_7H_7)Mo(BL^{Me})]X$, [**2**]X (X = BF_4, PF_6), respectively, which was confirmed by elemental analyses. The cations in [**1**]BF_4 and [**2**]X exhibit C_{2v} symmetry in solution according to their ^1H and ^{13}C NMR spectra in acetone-d_6. For instance, the ^1H NMR spectra of [**2**]BF_4 and [**2**]PF_6 each show one singlet for the NCH_2CH_2N unit together with two singlets for the two different types of methyl groups. In contrast, two doublets are observed in the ^1H NMR spectrum of [**1**]BF_4 for the diastereotopic isopropyl methyl groups, indicating a hindered rotation of the imidazoline moieties around the exocyclic C−N bonds at room temperature on the NMR time scale. The resonance for the η^7-coordinated cycloheptatrienyl ring appears as a broad signal at 4.90 ppm. Upon coordination of BL^{iPr}, the ^1H NMR resonance of the bridging ethylene hydrogen atoms is significantly shifted to higher field (from 3.47 to 2.18 ppm),

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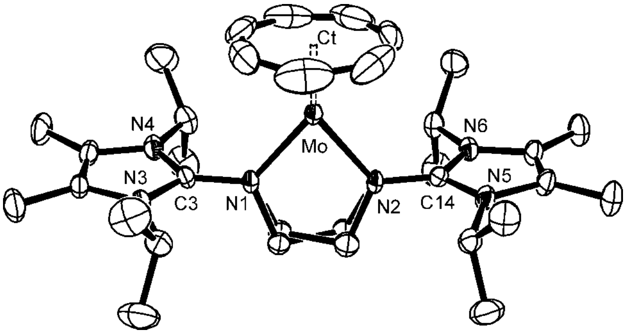

Figure 1. ORTEP drawing of the cation in [**1**]$BF_4 \cdot 2CH_3CN$ with thermal displacement parameters drawn at 50% probability. The ethylene bridge is disordered. Selected bond lengths [Å] and angles [deg]: Mo−N1 2.069(2), Mo−N2 2.073(2), Mo−C(Cht) 2.209(4)–2.280(4), N1−C3 1.358(3), N2−C14 1.353(3); N1−Mo−N2 77.83(9).

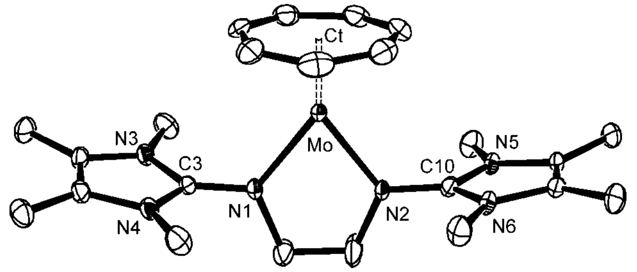

Figure 2. ORTEP drawing of the cation in [**2**]$BF_4 \cdot CH_3CN$ with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å] and angles [deg]: Mo−N1 2.076(3), Mo−N2 2.063(3), Mo−C(Cht) 2.226(4)–2.307(4), N1−C3 1.357(4), N2−C10 1.363(4); N1−Mo−N2 76.5(1).

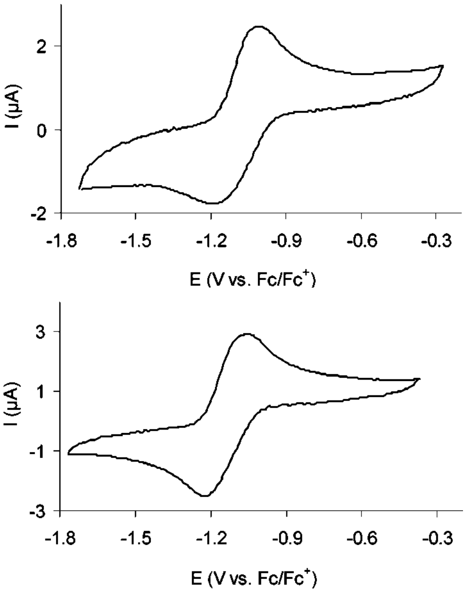

Figure 3. Cyclic voltammetric traces of [**1**]BF_4 (above) and [**2**]PF_6 (below), 1.0 mM solution in acetonitrile, (TBA)PF_6 (0.1 M), scan rate 0.1 V/s, $T = 25$ °C, against a Ag/AgCl reference electrode (3 M KCl), Pt working electrode; the ferrocene/ferrocenium couple displays a redox potential $E° = +476$ mV, and the values are referenced to $E°(Fc/Fc^+) = 0$ mV.

whereas downfield shifts are observed for all imine resonances. The same trends are observed upon coordination of BL^{Me}, where the resonance for the bridging ethylene hydrogen atoms is shifted from 3.63 to 2.23 ppm. Again, the remaining imine resonances are shifted to lower field, and a broad η^7-C_7H_7 signal is observed at 4.83 ppm.

Single crystals of [**1**]$BF_4 \cdot 2CH_3CN$ suitable for an X-ray diffraction analysis were obtained by crystallization from CH_3CN/Et_2O solution. The cationic half-sandwich complex exhibits a two-legged piano stool geometry with the η^7-C_7H_7 and the η^2-diimine ligand adopting a pseudo trigonal-planar coordination sphere around the molybdenum atom (Figure 1). Examination of the crystal packing reveals the absence of any relevant intermolecular contact between the cation and the tetrafluoroborate anion (shortest Mo•••F 4.64 Å). The atoms Mo, N1, and N2, together with Ct, the centroid of the Cht ring, are coplanar (mean deviation 0.02 Å), and the sum of the N1−Mo−N2 angle [77.83(9)°] and the two Ct−Mo−N angles is 359.7°. Consequently, the cation **1** can be regarded as being almost perfectly C_{2v} symmetric. Very short Mo−N bonds[25] in **1** [Mo−N1 2.069(2) Å, Mo−N2 2.073(2) Å] are in agreement with a strong electron-releasing capability of the BL^{iPr} ligand, which is implied by the ylidic resonance structure shown in Schemes 1 and 2. Charge separation in coordinated BL^{iPr} can also be clearly deduced from the observation of perpendicularly oriented imidazoline moieties with respect to the Mo−N−N coordination plane (interplanar angles 89.7° and 87.1°). This orientation rules out the possibility of π-interaction between the exocyclic nitrogen atoms and the imidazoline rings, leading to elongated C−N distances [N1−C3 1.358(3) Å, N2−C14 = 1.353(3) Å], much longer than expected for an N−C(sp^2) double bond (1.28 Å) and almost in the range of an N−C(sp^2) single bond (1.38 Å).[26]

Similarly to [**1**]$BF_4 \cdot 2CH_3CN$, single crystals of [**2**]$BF_4 \cdot CH_3CN$ were obtained from CH_3CN/Et_2O solution. Interestingly, even with decreased steric protection by substitution of the isopropyl groups in BL^{iPr} for the methyl groups in BL^{Me}, the molybdenum complex remains stable as a 16-electron species in the solid state, showing no tendency to coordinate acetonitrile. Any interaction between the cations **2** and the CH_3CN molecules or BF_4 anions can be excluded, since the shortest Mo•••N and Mo•••F separations are 4.80 and 5.39 Å, respectively (Figure 2). The structural parameters of the cation in [**2**]$BF_4 \cdot CH_3CN$ are very similar to those in [**1**]$BF_4 \cdot 2CH_3CN$; short Mo−N bonds [Mo−N1 2.076(3) Å, Mo−N2 2.063(3) Å] together with elongated exocyclic C−N bonds [N1−C3 1.357(4) Å, N2−C10 1.363(4) Å] are observed. Again, the imidazoline rings are almost perpendicularly oriented with respect to the Mo−N−N coordination plane (interplanar angles 80.3° and 88.3°). It should be noted that even though the complexes [**1**]BF_4 and [**2**]BF_4 crystallize as 16-electron species, the interaction with acetonitrile molecules in solution should be taken into account, in particular upon oxidation (*vide infra*).

On the basis of the structural results, it can be assumed that the unusual stability of the cationic complexes **1** and **2** stems from the strong π-electron releasing capability of the diimine ligands BL^{iPr} and BL^{Me}. Indeed, cyclic voltammetric studies on [**1**]BF_4 and [**2**]PF_6 in acetonitrile afford very negative redox potentials of $E° = -1.095$ V and $E° = -1.138$ V versus the ferrocene/ferrocenium couple, indicating a slightly stronger electron-releasing capability of the BL^{Me} ligand compared to BL^{iPr} (Figure 3). These potentials are much lower than usually observed for a reversible one-electron Mo(0)/Mo(I) oxidation

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(25) The Mo−N bonds in the cations **1** and **2** are shorter than any previously observed bond in (η^7-C_7H_7)Mo-N systems; see refs 20a, 21b, 21c, 27, and 29.

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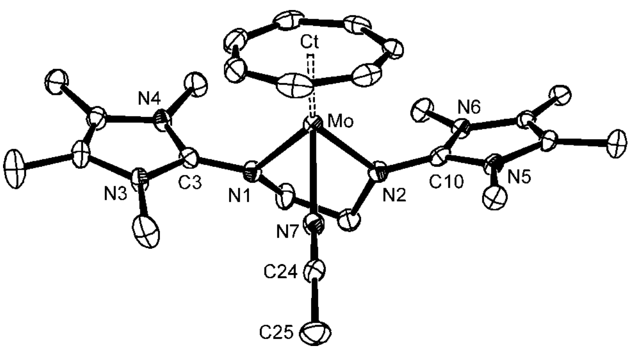

Figure 4. ORTEP drawing of the dication in $[(\eta^7\text{-}C_7H_7)Mo(BL^{Me})(CH_3CN)][PF_6]_2\cdot CH_3CN$, $[\mathbf{3}](PF_6)_2\cdot CH_3CN$, with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å] and angles [deg] in $[\mathbf{3}][BF_4]_2/[\mathbf{3}][PF_6]_2\cdot CH_3CN$: Mo−N1 2.164(2)/2.144(2), Mo−N2 2.127(2)/2.116(3), Mo−N7 2.227(2)/2.241(2), Mo−C(Cht) 2.246(3)–2.322(3)/2.243(3)–2.307(3), N1−C3 1.346(3)/1.350(4), N2−C10 1.350(3)/1.349(4), N7−C24 1.143(4)/1.131(4); N1−Mo−N2 76.55(8)/75.7(1), Mo−N7−C24 166.4(2)/169.0(3), N7−C24−C25 177.7(3)/178.6(3).

process in cycloheptatrienyl-molybdenum complexes of the general type $[(\eta^7\text{-}C_7H_7)MoL_2X]$.[20,27] The $E°$ values for $[\mathbf{1}]BF_4$ and $[\mathbf{2}]PF_6$ are also more negative than those of their ruthenium analogues $[(\eta^5\text{-}C_5Me_5)Ru(BL^R)]OTf$ (R = *i*Pr, Me; OTf = triflate), $E° = -569$ mV and $E° = -588$ mV.[14] This trend is in agreement with other comparative studies on $[(\eta^7\text{-}C_7H_7)Mo]$ and $[(\eta^5\text{-}C_5R_5)Ru]$ systems.[20a] Since the redox potentials observed for $[\mathbf{1}]BF_4$ and $[\mathbf{2}]PF_6$ lie far below $E°$ of the Fc/Fc$^+$ couple, their oxidation to dicationic complexes should easily be possible by chemical oxidation with ferrocenium salts, or even with much weaker oxidation agents such as tropylium salts, for which a redox potential of $E° = -650$ mV in acetonitrile versus the Fc/Fc$^+$ couple has been reported.[28] Consequently, treatment of a green solution of $[\mathbf{2}]BF_4$ in THF/CH_3CN with tropylium tetrafluoroborate, $(\eta^7\text{-}C_7H_7)BF_4$, afforded the Mo(I) complex $[(\eta^7\text{-}C_7H_7)Mo(BL^{Me})(CH_3CN)][BF_4]_2$, $[\mathbf{3}][BF_4]_2$ as an orange crystalline compound (eq 1), whereas the oxidation of $[\mathbf{2}]PF_6$ with $[Fe(\eta^5\text{-}C_5H_5)_2]PF_6$ furnished orange crystals of $[\mathbf{3}][PF_6]_2\cdot CH_3CN$ after diffusion of diethyl ether into an acetonitrile solution (eq 2).

$$[\mathbf{2}]BF_4 + (C_7H_7)BF_4 \xrightarrow[-1/2(C_7H_7)_2]{CH_3CN} [\mathbf{3}][BF_4]_2 \qquad (1)$$

$$[\mathbf{2}]PF_6 + (Fc)PF_4 \xrightarrow[-Fc]{CH_3CN} [\mathbf{3}][PF_6]_2 \qquad (2)$$

To unequivocally establish the formation of Mo(I) complexes, the molecular structures of $[\mathbf{3}][BF_4]_2$ and $[\mathbf{3}][PF_6]_2\cdot CH_3CN$ were established by X-ray diffraction analyses, and the dication in the latter complex is shown in Figure 4. In both cases, the dication $[(\eta^7\text{-}C_7H_7)Mo(BL^{Me})(CH_3CN)]^{2+}$ (**3**) contains a coordinated acetonitrile ligand and exhibits a three-legged piano stool geometry with elongated Mo−N(imine) bonds in comparison to the structure of $[\mathbf{2}]BF_4\cdot CH_3CN$. The Mo−N($CH_3CN$) bonds are significantly longer [Mo−N7 2.227(2) (BF_4 salt), 2.241(2) Å (PF_6 salt)]; they are also longer than the Mo−N distance of 2.166(3) Å observed for the Mo(I) acetonitrile complex $[(\eta^7\text{-}C_7H_7)Mo(CH_3CN)I_2]$.[29]

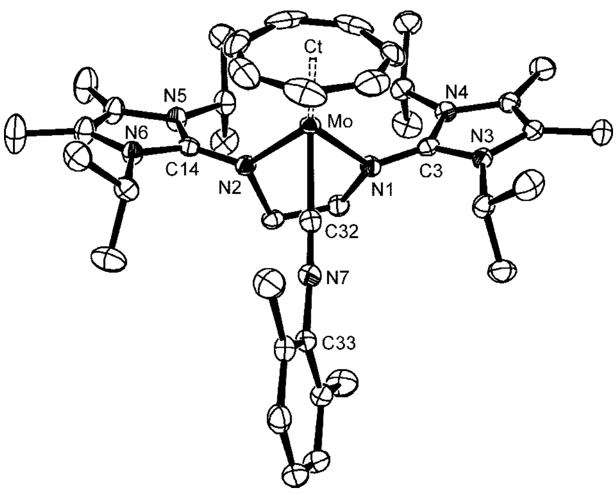

Figure 5. ORTEP drawing of the cation in $[\mathbf{1}(CNXy)]BF_4\cdot C_3D_6O$ with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å] and angles [deg]: Mo−N1 2.207(2), Mo−N2 2.143(2), Mo−C32 2.096(2), Mo−C(Cht) 2.251(2)–2.302(2), N1−C3 1.339(3), N2−C14 1.344(2), C32−N7 1.168(3); N1−Mo−N2 75.22(6), Mo−C32−N7 178.1(2), C32−N7−C33 175.7(2).

Isocyanide Adducts of $[\mathbf{1}]BF_4$ and $[\mathbf{2}]PF_6$. Reactions of $[\mathbf{1}]BF_4$ and $[\mathbf{2}]PF_6$ with 2,6-dimethylphenyl isocyanide (XyNC) in acetone afforded the isocyanide complexes $[\mathbf{1}(CNXy)]BF_4$ and $[\mathbf{2}(CNXy)]PF_6$ in good yields (eqs 3 and 4). The complexes were isolated as red crystals upon diffusion of diethyl ether into their acetone solutions. In the ^1H and ^{13}C NMR spectra, coordination of the isocyanides is clearly indicated by the observation of the expected isocyanide resonances together with significantly shifted resonances for the bidentate ligands compared to those observed for $[\mathbf{1}]BF_4$ and $[\mathbf{2}]PF_6$. The IR spectra exhibit strong CN stretching vibrations at 2041 cm^{-1} for $[\mathbf{1}(CNXy)]PF_6$ and at 2030 cm^{-1} for $[\mathbf{2}(CNXy)]PF_6$, which is strongly shifted to lower wavenumbers with respect to the uncoordinated isocyanide.[30] These values are in agreement with strong π-back-donation from molybdenum(0) to the isocyanide ligands, which is much more pronounced than in related Mo(0) complexes, e.g., $\nu_{CN} = 2161$ cm^{-1} (in CH_2Cl_2) for $[(\eta^7\text{-}C_7H_7)Mo(bipy)(CN\mathit{t}Bu)]PF_6$.[20d] As previously deduced from the cyclic voltammetric studies, the IR results also indicate a stronger electron-releasing capability of the BL^{Me} ligand compared to BL^{iPr}.

$$[\mathbf{1}]BF_4 + XyNC \rightarrow [\mathbf{1}(CNXy)]BF_4 \qquad (3)$$

$$[\mathbf{2}]PF_6 + XyNC \rightarrow [\mathbf{2}(CNXy)]PF_6 \qquad (4)$$

The isocyanide complexes could be crystallized from acetone/Et_2O solution, and the molecular structures of the cations in $[\mathbf{1}(CNXy)]BF_4\cdot d_6$-acetone and $[\mathbf{2}(CNXy)]PF_6$ are shown in Figures 5 and 6. Both complexes exhibit a three-legged piano stool geometry with significantly elongated Mo−N bonds compared to the starting materials [Mo−N1 2.207(2) Å, Mo−N2 2.143(2) Å and Mo−N1 2.252(3) Å, Mo−N2 2.189(3) Å]. In both cases, the aryl moieties of the isocyanide ligands adopt an approximately perpendicular orientation, and the six-membered benzene rings subtend angles of 19.8° and 17.0°, respectively, with the plane containing the Cht centroid, the Mo

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[30] Stephany, R. W.; de Bie, M. J. A.; Drenth, W. *Org. Magn. Reson.* **1974**, *6*, 45. In our hands, 2,6-dimethylphenyl isocyanide shows $\nu_{CN} = 2123$ cm^{-1} in KBr.

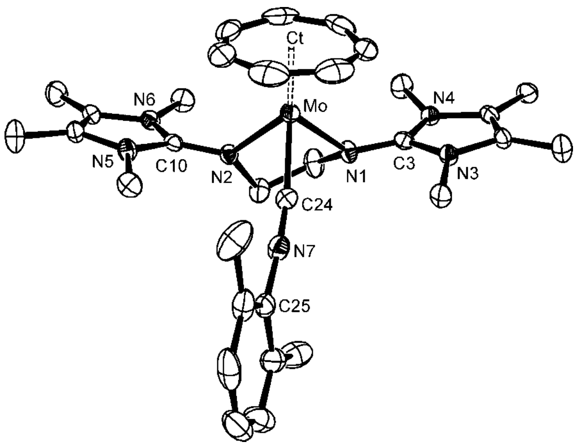

Figure 6. ORTEP drawing of the cation in [**2**(CNXy)]PF_6 with thermal displacement parameters drawn at 50% probability. Selected bond lengths [Å] and angles [deg]: Mo−N1 2.252(3), Mo−N2 2.189(3), Mo−C24 2.077(3), Mo−C(Cht) 2.271(4)–2.324(4), N1−C3 1.326(4), N2−C10 1.327(4), C24−N7 1.172(5); N1−Mo−N2 76.7(1), Mo−C24−N7 173.5(3), C24−N7−C25 174.3(4).

atom, and the isocyanide carbon atom. The molybdenum–carbon(isonitrile) bonds are short [Mo−C32 2.096(2) and Mo−C24 2.077(3) Å], confirming strong metal-to-ligand π-back-donation. For instance, these distances are considerably shorter than the corresponding distance of Mo−C 2.135(3) Å observed for the only related structurally characterized isocyanide complex $[(\eta^7\text{-}C_7H_7)Mo(N,N')(CN{t}Bu)]BF_4 \cdot CH_2Cl_2$ (*N,N′* = chiral iminopyridine ligand).[21b] As expected, cyclic voltammetric studies on [**2**(CNXy)]PF_6 in acetonitrile afford a considerably more positive redox potential of $E° = -941$ mV versus the Fc/Fc^+ couple in comparison with that of [**2**]PF_6 ($E° = -1.138$ V, *vide supra*), which can be ascribed to the better π-acceptor properties of the isocyanide ligand compared to CH_3CN. Nevertheless, the redox potential of this isocyanide complex is still far more negative than the potentials reported for other 18-electron cycloheptatrienyl-molybdenum isocyanide complexes, e.g., $[(\eta^7\text{-}C_7H_7)Mo(bipy)(CN{t}Bu)]PF_6$,[20d] giving further evidence for the extraordinary electron richness and donor properties of the BL^{Me} ligand.

Conclusions

In this contribution, we have presented 16-electron cycloheptatrienyl-molybdenum half-sandwich complexes of unusual stability, which can be ascribed to the strong π-basic nature of the bis(imidazolin-2-imine) ligands. Despite the presence of π-stabilization, these complexes still exhibit a strong propensity to bind σ-donor/π-acceptor ligands such as isocyanides. This behavior makes these highly stabilized yet reactive 16-electron complexes suitable systems for the activation of small molecules such as N_2 and H_2 and promising candidates for catalytic applications. These investigations are currently in progress in our laboratory.

Experimental Section

General Methods. All operations were performed in an atmosphere of dry argon by using Schlenk and vacuum techniques. All solvents were purified by standard methods and distilled prior to use. ^1H and ^{13}C NMR spectra were recorded on Bruker DPX 200, Bruker DPX 400, and Bruker AV 600 devices. The chemical shifts are given in ppm relative to TMS. The spin coupling patterns are indicated as s (singlet), d (doublet), m (multiplet), sept (septet), and br (broad, for unresolved signals). Elemental analysis (C, H, N) and IR spectroscopy analysis were performed on a Elementar Vario EL III CHNS elemental analyzer and on a Bruker Vertex 70. Mass spectrometry was performed with a Finnigan MAT 90 device. UV–vis spectra were recorded on a Varian Cary 50 device. Cyclic voltammetric traces have been measured on a Metrohm μAutolab type III device; complex concentrations were 1.0 mM in acetonitrile, $(TBA)PF_6$ (0.1 M), scan rate 0.1 V/s, $T = 25$ °C, against a Ag/AgCl reference electrode (3 M KCl) and using a Pt working electrode. The ferrocene/ferrocenium couple displays a redox potential $E° = +476$ mV; the values are referenced to $E°(Fc/Fc^+) = 0$ mV. $FcPF_6$ was obtained from Aldrich and used as received. BL^{iPr},[14] BL^{Me},[14] and $[(\eta^7\text{-}C_7H_7)Mo(CH_3CN)_3]X$ (X = BF_4, PF_6)[24] were prepared according to literature procedures.

$[(\eta^7\text{-}C_7H_7)Mo(BL^{iPr})]BF_4$, [1]$BF_4$. A solution of BL^{iPr} (112.6 mg, 0.27 mmol) in acetonitrile (10 mL) was added dropwise to a deep red solution of $[(\eta^7\text{-}C_7H_7)Mo(CH_3CN)_3]BF_4$ (102 mg, 0.257 mmol) in CH_3CN (5 mL) at room temperature. During the addition of the ligand, the reaction mixture turned green, and the solution was stirred for 16 h. The volume of CH_3CN was reduced to 5 mL, and the product was precipitated with a mixture of Et_2O and *n*-hexane (20 mL/20 mL). Filtration, washing with *n*-hexane (2 × 10 mL), and drying in vacuo afforded the product as a light green solid. Yield: 158 mg (89%). ^1H NMR (200 MHz, acetone-d_6): δ 5.03 (2 H, sept, NCH), 4.90 (7 H, br, C_7H_7), 2.50 (12 H, s, CCH_3), 2.18 (4 H, s, CH_2), 1.87 (12 H, d, $CHCH_3$) 1.42 (12 H, d, $CHCH_3$). ^{13}C NMR (50.32 MHz, acetone-d_6): δ 156.6 (NCN), 121.5 (N*C*CH_3), 81.4 (C_7H_7), 55.4 (*C*H_2), 49.4 (N*C*H), 22.8 (CH*C*H_3), 22.5 (CH*C*H_3), 10.4 (C*C*H_3). Anal. Calc for $C_{31}H_{51}N_6MoBF_4$: C, 53.92; H, 7.44; N, 12.17. Found: C, 53.58; H, 7.56; N, 12.31. UV–vis (CH_3CN): λ_{max}/nm 395 (ϵ, $dm^3\ mol^{-1}\ cm^{-1}$ 4900), 450sh (1130) and 748 (259).

$[(\eta^7\text{-}C_7H_7)Mo(BL^{Me})]BF_4$, [2]$BF_4$. A solution of BL^{Me} (150 mg, 0.493 mmol) in acetonitrile (10 mL) was added dropwise to a deep red solution of $[(\eta^7\text{-}C_7H_7)Mo(CH_3CN)_3]BF_4$ (186 mg, 0.469 mmol) in CH_3CN (5 mL) at room temperature. During the addition of the ligand, the reaction mixture turned green, and the solution was stirred for 4 h. The volume of CH_3CN was reduced to 5 mL, and the product was precipitated with a mixture of Et_2O and *n*-hexane (20 mL/20 mL). Filtration, washing with Et_2O (2 × 10 mL), and drying *in vacuo* afforded the product as a light green solid. Yield: 221 mg (81%). ^1H NMR (200 MHz, acetone-d_6): δ 4.83 (7 H, br, C_7H_7), 3.69 (12 H, s, NCH_3), 2.42 (12 H, s, CCH_3), 2.23 (4 H, s, CH_2). ^{13}C NMR (50.32 MHz, acetone-d_6): δ 158.4 (NCN), 121.5 (N*C*CH_3), 82.8 (C_7H_7), 53.9 (*C*H_2), 31.9 (N*C*H_3), 9.7 (C*C*H_3). Anal. Calc for $C_{23}H_{35}N_6MoBF_4$: C, 47.77; H, 6.10; N, 14.53%. Found: C, 47.10; H, 5.95; N, 14.53.

$[(\eta^7\text{-}C_7H_7)Mo(BL^{Me})]PF_6$, [2]$PF_6$. A solution of BL^{Me} (131 mg, 0.43 mmol) in acetonitrile (10 mL) was added dropwise to a deep red solution of $[(\eta^7\text{-}C_7H_7)Mo(CH_3CN)_3]PF_6$ (186 mg, 0.409 mmol) in CH_3CN (5 mL) at room temperature. During the addition of the ligand, the reaction mixture turned green and the solution was stirred for 4 h. The volume of CH_3CN was reduced to 5 mL, and the product was precipitated with a mixture of Et_2O and *n*-hexane (20 mL/20 mL). Filtration, washing with Et_2O (2 × 10 mL), and drying *in vacuo* afforded the product as a light green solid. Yield: 232 mg (89%). ^1H NMR (200 MHz, acetone-d_6): δ 4.83 (7 H, br, C_7H_7), 3.69 (12 H, s, NCH_3), 2.42 (12 H, s, CCH_3), 2.23 (4 H, s, CH_2). ^{13}C NMR (50.32 MHz, acetone-d_6): δ 158.4 (NCN), 121.5 (N*C*CH_3), 82.8 (C_7H_7), 53.9 (*C*H_2), 31.9 (N*C*H_3), 9.7 (C*C*H_3). Anal. Calc for $C_{23}H_{35}N_6MoPF_6$: C, 43.40; H, 5.54; N, 13.20. Found: C, 42.50; H, 5.47; N, 13.27. UV–vis (CH_3CN): λ_{max}/nm 392 (ϵ, $dm^3\ mol^{-1}\ cm^{-1}$ 5160), 440sh (1400) and 740 (217).

$[(\eta^7\text{-}C_7H_7)Mo(BL^{Me})(CH_3CN)][BF_4]_2$, [3][$BF_4$]$_2$. A solution of tropylium tetrafluoroborate, $(C_7H_7)BF_4$ (15.4 mg, 0.0865 mmol), in THF/acetonitrile (1 mL/2 mL) was added dropwise to a green solution of $[(\eta^7\text{-}C_7H_7)Mo(BL^{Me})]BF_4$ (50 mg, 0.0865 mmol) in

Table 1. Summary of Crystallographic Data for [1]$BF_4 \cdot 2CH_3CN$, [2]$BF_4 \cdot CH_3CN$, [3]$(PF_6)_2 \cdot CH_3CN$, [3]$(BF_4)_2$, [1(CNXy)]$BF_4 \cdot C_3D_6O$, and [2(CNXy)]PF_6

	[**1**]$BF_4 \cdot 2CH_3CN$	[**2**]$BF_4 \cdot CH_3CN$	[**3**]$[PF_6]_2 \cdot CH_3CN$	[**3**]$[BF_4]_2$	[**1**(CNXy)]$BF_4 \cdot C_3D_6O$	[**2**(CNXy)]PF_6
formula	$C_{35}H_{57}BF_4MoN_8$	$C_{25}H_{38}BF_4MoN_7$	$C_{27}H_{41}F_{12}MoN_8P_2$	$C_{25}H_{38}F_8MoN_7B_2$	$C_{43}H_{60}BD_6F_4Mo\ N_7O$	$C_{32}H_{44}F_6MoN_7P$
M	772.64	619.37	863.56	706.18	885.82	767.65
cryst size (mm)	0.24 × 0.20 × 0.19	0.24 × 0.19 × 0.15	0.16 × 0.12 × 0.07	0.30 × 0.15 × 0.08	0.37 × 0.29 × 0.28	0.25 × 0.17 × 0.08
crystal system	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P\bar{1}$	$Pbca$	$P2_1/n$	$P2_1/n$
a (Å)	10.8124(10)	14.507(3)	11.5973(14)	20.015(2)	15.5178(15)	8.0090(6)
b (Å)	31.337(3)	8.2464(16)	12.5314(14)	14.9142(14)	13.3193(14)	27.588(2)
c (Å)	12.0187(12)	23.934(4)	14.8528(18)	20.075(2)	21.697(2)	15.9818(12)
α (deg)	90.00	90.00	65.387(3)	90.00	90.00	90.00
β (deg)	107.634(3)	98.753(4)	70.003(3)	90.00	95.982(6)	100.119(2)
γ (deg)	90.00	90.00	66.079(3)	90.00	90.00	90.00
V (Å^3)	3880.9(6)	2829.9(9)	1754.5(4)	5992.5(10)	4460.0(8)	3476.3(4)
Z	4	4	2	8	4	4
D_{calcd} (g/cm^3)	1.322	1.454	1.635	1.565	1.319	1.467
μ (mm^{-1})	0.392	0.517	0.562	0.517	0.351	0.489
F(000)	1624	1280	878	2888	1856	1584
T/K	133	133	133	133	133	133
$2\theta_{max}$	56	56	56	56	56	56
no. of reflns measd	70496	50036	29964	98316	75034	64559
no. of indep reflns	9628	6981	8671	7433	11 069	8639
GOF	1.091	1.011	1.037	1.059	1.097	1.032
R_1	0.0532	0.0404	0.0434	0.0366	0.0346	0.0528
wR_2	0.1567	0.1140	0.1027	0.0990	0.0921	0.1428

THF/acetonitrile (2 mL/2 mL) at room temperature. During the addition, the reaction mixture turned orange, and the solution was stirred for 2 h. The product was precipitated with Et_2O (40 mL), filtered, washed with Et_2O (2 × 10 mL), and dried *in vacuo*. Yield: 56 mg (92%). Anal. Calc for $C_{25}H_{38}N_7MoB_2F_8$: C, 42.52; H, 5.42; N, 13.88. Found: C, 41.87; H, 5.56; N, 13.23.

[(η^7-C_7H_7)Mo(BL^{Me})(CH_3CN)][PF_6]$_2$·CH_3CN, [3][PF_6]$_2$·CH_3CN. A deep blue solution of $FcPF_6$ (42 mg, 0.126 mmol) in THF/acetonitrile (5 mL/5 mL) was added dropwise to a green solution of [(η^7-C_7H_7)Mo(BL^{Me})]PF_6 (80 mg, 0.126 mmol) in THF/acetonitrile (5 mL/5 mL) at room temperature. During the addition, the reaction mixture turned orange, and the solution was stirred for 24 h. Diffusion of Et_2O afforded an orange crystalline material that was washed with Et_2O (2 × 10 mL) and dried *in vacuo*. Yield: 91 mg (84%). Anal. Calc for $C_{27}H_{41}N_8MoP_2F_{12}$: C, 37.55; H, 4.79; N, 12.98. Found: C, 37.17; H, 5.17; N, 12.83.

[1(CNXy)]BF_4. 2,6-Dimethylphenyl isocyanide (9.5 mg, 72.4 μmol) and [(η^7-C_7H_7)Mo(BL^{iPr})]BF_4 (50 mg, 72.4 μmol) were mixed together and dissolved in acetone (1 mL). Diffusion of Et_2O into acetone solution over several days yielded red crystals, which were isolated, washed with additional Et_2O (2 × 5 mL), and dried *in vacuo*. Yield: 51 mg (86%). ^{1}H NMR (400 MHz, acetone-d_6): δ 7.30–7.27 (3 H, mult, Xy-*H*), 4.97 (4 H, sept, NCH), 4.66 (7 H, s, C_7H_7), 2.93 (4 H, br, CH_2), 2.56 (6 H, s, Xy-CH_3), 2.39 (12 H, s, CCH_3), 1.75 (12 H, br, CHCH_3), 1.40 (12 H, br, CHCH_3). ^{13}C NMR (100.62 MHz, acetone-d_6): δ 159.0 (NCN), 134.8 (*o-C*) 129.5 (*p-C*), 129.3 (*m-C*), 121.2 (NCCH$_3$), 85.2 (C_7H_7), 57.8 (CH$_2$), 48.9 (NCH), 22.9 (CHCH$_3$), 22.2 (CHCH$_3$), 19.4 (*o*-CH_3), 10.4 (CCH$_3$). Anal. Calc for $C_{40}H_{60}N_7MoBF_4$: C, 58.47; H, 7.36; N, 11.93. Found: C, 57.48; H, 7.63; N, 11.24. IR (ATR/ cm^{-1}): 2041 ($\nu_{C\equiv N}$).

[2(CNXy)]PF_6. 2,6-Dimethylphenyl isocyanide (8.0 mg, 61 μmol) and [(η^7-C_7H_7)Mo(BL^{Me})]PF_6 (38.8 mg, 61 μmol) were mixed together and dissolved in acetone (1 mL). Diffusion of Et_2O into acetone solution over several days yielded red crystals, which were isolated, washed with additional Et_2O (2 × 5 mL), and dried *in vacuo*. Yield: 42 mg (90%). ^{1}H NMR (200 MHz, acetone-d_6): δ 7.28–7.15 (3 H, m, Xy-*H*), 4.66 (7 H, br, C_7H_7), 3.69 (12 H, s, NCH_3), 2.80 (4 H, br, CH_2), 2.48 (12 H, s, CCH_3), 2.24 (6 H, s, Xy-CH_3). ^{13}C NMR (50.32 MHz, acetone-d_6): δ 160.6 (NCN), 134.9 (*o-C*) 130.0 (*m-C*), 129.8 (*p-C*), 120.4 (NCCH$_3$), 88.2 (C_7H_7), 57.2 (CH$_2$), 33.0 (NCH$_3$), 20.0 (*o*-CH_3), 9.9 (CCH$_3$). Anal. Calc for $C_{32}H_{44}N_7MoPF_6$: C, 50.07; H, 5.78; N, 12.77. Found: C, 49.98; H, 6.27; N, 12.65. IR (ATR/ cm^{-1}): 2030 ($\nu_{C\equiv N}$).

Single-Crystal X-ray Structure Determinations. Numerical details are presented in Table 1. All X-ray data were collected with monochromated Mo Kα radiation (λ = 0.71073 Å) on a Bruker SMART 1000 CCD area detector. Absorption corrections were based on multiple scans (program SADABS). The structures were solved by direct methods and refined anisotropically by full-matrix least-squares on F^2 (Program SHELXTL: Prof. G. M. Sheldrick, Univ. of Göttingen). H atoms were included using a riding model (except methyl groups: refined as rigid groups). *Special features of refinement*: In [**1**]$BF_4 \cdot 2CH_3CN$, the acetonitriles of solvation could not be refined adequately and were therefore removed using the program SQUEEZE (A. L. Spek, University of Utrecht, Netherlands). For [**1**]$BF_4 \cdot 2CH_3CN$ and [**2**]$BF_4 \cdot CH_3CN$, the ethylene bridge C1−C2 is disordered over two positions, which were refined isotropically. Hydrogen positions of solvent methyls (acetonitrile, acetone) should be regarded as tentative.

Supporting Information Available: Crystal data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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