Half-sandwich complex with intramolecular amino group coordination: synthesis of molybdenum iodide complexes

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Abstract

A half-sandwich molybdenum iodide complex with an intramolecular amino group coordination was obtained by irradiation of η^5-$C_5H_4CH_2CH_2N(CH_3)_2Mo(CO)_3I$. It crystallized as a violet triclinic, $a = 8.0910(9)$, $b = 13.4336(18)$, $c = 14.3033(9)$ Å, $\alpha = 116.655(9)$, $\beta = 90.813(7)$, and $\gamma = 104.715(10)°$. There are two essentially similar independent molecules within the unit cell. The geometry of the pseudo-square pyramidal is shown as cis orientation of the two carbonyl groups. Iodide abstraction by a silver ion generated a cationic molybdenum complex. Replacing the dimethylamino group with methyl α indicated a 2.5:1 diastereoselectivity ratio.

Introduction

One of the classic ligands of coordination chemistry is amine, but it has not often been used with organotransitionmetal compounds [1]. Without π-acceptor capability, amine coordinates only weakly to low-valent transition metals and forms relatively labile complexes [2]. However, the amine complex might be more stable if the amino group coordinated intramolecularly. In order to explore the nature of amine as a ligand of transition metals and in pursuit of our interest in half-sandwich complexes, we have prepared a stable half-sandwich manganese complex with intramolecular amino group coordination [3]. The structure has been fully characterized by spectroscopy and X-ray crystallography. Although transition metal complexes with substituted cyclopentadienes have been reported [4], the complexes with intramolecular ligation by a functionalized cyclopentadiene side chain have received only slight attention [5]. In this report, we want to extend our knowledge of this type of ligand in molybdenum complexes and to investigate a molybdenum cationic complex which might have applications in synthesis [6].

Results and discussion

The bidentate ligand, (dimethylaminoethyl)cyclopentadiene **2a** was prepared by reacting sodium cyclopentadienylide with 2-dimethylaminoethyl chloride in THF. Examination of the ^{1}H NMR spectrum showed two singlets in a ratio of 55:45, corresponding to the N,N-dimethyl resonances (δ 2.26 and 2.27 for R = H; δ 2.27 and 2.29 for R = CH$_3$). This suggests that two olefinic regioisomers were obtained. After deprotonation with ^{n}BuLi, both isomers gave an identical anion which was reacted with Mo(CO)$_6$. The resulting molybdenum anion [7] was treated with iodine, yielding a red liquid, complex **3a** (see Scheme 1). The molybdenum iodide **3a** showed typical tricarbonyl stretchings at 2036 cm^{-1} as a strong, sharp absorption, and at 1956 cm^{-1} as a very strong, broad absorption in the infrared spectrum.

Upon irradiation of **3a** in THF, the original red solution turned violet. After evaporation of solvent, a violet crystalline compound was obtained. Examination of the IR spectrum showed two carbonyl stretchings of equal intensity at 1961 and 1849 cm^{-1} [8]. This indicates carbon monoxide was liberated and a dicarbonyl compound was produced [9]. The ^{1}H NMR spectrum displayed nonequivalent resonances of the N,N-dimethyl protons at δ 2.94(s) and δ 2.76(s), compared to the solitary methyl singlet resonance of complex **3a** at δ 2.24. Four cyclopentadienyl protons were also revealed as non-equivalent resonances at δ 6.00–5.97(m), 5.77–5.74(m), 5.19–5.15(m) and δ 4.53–4.49(m), while the cyclopentadienyl protons of **3a** appeared at δ 5.55 (t, 2H, J = 2.2 Hz) and δ 5.41 (t, 2H, J = 2.2 Hz). This suggests the occurrence of intramolecular amino group coordination to form a relatively rigid molecule.

Two geometries of the pseudo-square pyramidal structure of this molybdenum dicarbonyl complex are possible [10]. One is the orientation of amine *cis* relative to iodide, and the other is trans orientation. The higher symmetric trans isomer would be expected to show ^{1}H and ^{13}C NMR spectra simpler than that of the cis isomer. Therefore, the irradiation product was assigned to the *cis* complex **4a** on the basis of the non-equivalency of the N,N-dimethyl protons and of the cyclopentadienyl protons.
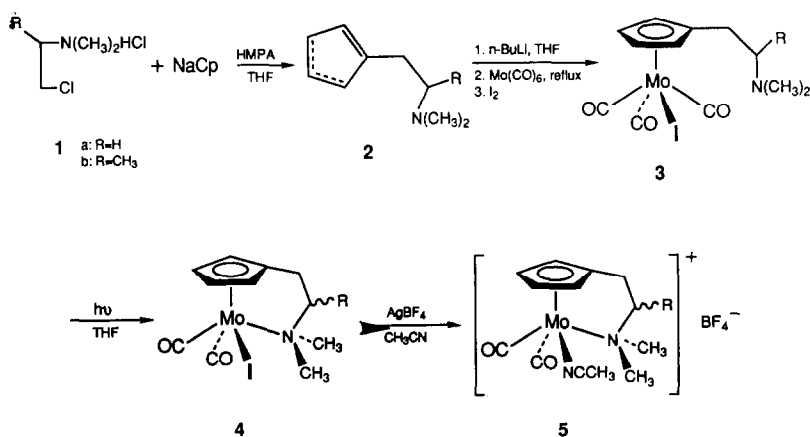
Scheme 1.

Table 1

Crystal data and refinement details for complex **4a**

Formula	$C_{11}H_{14}INO_2Mo$	Transmission factors max; min	0.99828, 0.79563
F.W.	415.08	2θ (max)	50°
Crystal system	triclinic	Octants	h, k, l
			$-9-9, 0-15, -16-15$
Space group	$P\bar{1}$	No. of data collected	5045
a (Å)	8.0910(9)	No. of unique data	4683; 4298 with $I > 2\sigma(I)$
b (Å)	13.4336(18)		
c (Å)	14.3033(9)	K	0.000100
V (Å^3)	1329.01(25)	R; R_w	0.028; 0.036
Z	4		
D_c (g cm^{-3})	2.075	G.O.F.	2.25
$F(000)$	791.76	maximum shift/σ ratio	0.032
Crystal dimension (mm)	$0.46 \times 0.31 \times 0.25$	ρ_{max} (e Å^{-3})	1.010

A single crystal of **4a** was grown by slow diffusion of a CH_2Cl_2 solution of **4a** into hexane at ambient temperature (Tables 1, 2). A triclinic violet crystal was subjected to X-ray diffraction study to show *cis* orientation of amino group and iodide (see Fig. 1). This result is in accord with our spectroscopic arguments (see above). Further crystal data show that the bond length (Table 3) of Mo(1)–N(1) (2.38 Å) lies between the covalent radius (2.05 Å) and the sum of the van der Waals radii (2.76 Å). Bond length of Mo(1)–I(1) (2.8509 Å) is similar to that reported in the literature [11]. A linear geometry of metal-carbonyl is consistent with the bond angles of Mo(1)–C(1)–O(1) (175.9°) and Mo(1)–C(2)–O(2) (176.2°). The torsion angle of 170.2° of C(4)–C(5)–C(9)–C(8), suggests the C(4)–C(5) bond is bent 10° away from the cyclopentadiene plane.

In order to test the effect of the α-alkyl substituent on the degree of diastereo-selectivity of the formation of the bidentate complex, the α-methyl amino compound **3b** was prepared. Irradiation of **3b** gave a 2.5:1 mixture of diastereomers **4b**. Both isomers showed in the ^{1}H NMR spectrum non-equivalent resonances of the cyclopentadienyl protons and the N,N-dimethyl protons, suggesting that the diastereomers are both of *cis* orientation. We were not able to separate these two isomers chromatographically or crystallographically. Therefore the relative stereo-chemistry of the methyl group to the metal centre is not yet defined.

The violet crystalline complex **4a** did not decompose when kept overnight in air at room temperature. When it was treated with silver tetrafluoroborate in acetoni-trile, iodide was abstracted and a molybdenum cationic complex **5a**, with a mole of acetonitrile was obtained in nearly quantitative yield. The stretching of the coordinated nitrile appeared at 2044 cm^{-1}(m) suggesting that the acetonitrile is coordinated in a σ^1 fashion [12]. In the ^{1}H NMR spectrum, the four cyclopentadi-enyl protons revealed a similar pattern to that of the molybdenum iodide complex **4a**. The N,N-dimethyl protons also appeared as non-equivalent resonances at δ 2.77 and δ 2.58. The results indicate that the cationic complex **5a** retains the same *cis* orientation as the molybdenum iodide **4a**. The synthetic applicability of com-plex **5a** is under investigation.

Table 2

Atomic coordinates and B_{iso}

Atom	x	y	z	B_{iso}
I(1)	0.90048(4)	0.64388(3)	0.87879(2)	4.35(2)
I(2)	0.54798(4)	0.28969(2)	0.36025(2)	3.83(2)
Mo(1)	1.16583(4)	0.78322(3)	1.05690(2)	2.52(2)
Mo(2)	0.34932(4)	0.21840(3)	0.49394(3)	2.67(2)
N(1)	1.3106(4)	0.6388(3)	0.9748(2)	2.9(2)
N(2)	0.1200(5)	0.2643(3)	0.4303(3)	3.8(2)
O(1)	1.1662(5)	0.7268(3)	1.2445(2)	4.8(2)
O(2)	0.8427(5)	0.8389(4)	1.1608(3)	6.0(2)
O(3)	0.5886(6)	0.0562(4)	0.4200(4)	7.0(3)
O(4)	0.1177(5)	−0.0331(3)	0.4016(3)	6.4(2)
C(1)	1.1664(5)	0.7436(3)	1.1723(3)	3.1(2)
C(2)	0.9583(6)	0.8153(4)	1.1193(3)	3.9(2)
C(3)	1.3998(6)	0.6631(4)	0.8930(3)	3.7(2)
C(4)	1.5184(6)	0.7870(4)	0.9416(3)	3.8(2)
C(5)	1.4196(5)	0.8694(3)	1.0080(3)	3.4(2)
C(6)	1.4321(5)	0.9207(4)	1.1198(3)	3.5(2)
C(7)	1.2996(6)	0.9764(3)	1.1505(4)	4.3(2)
C(8)	1.2083(6)	0.9590(4)	1.0577(4)	4.4(3)
C(9)	1.2840(7)	0.8936(4)	0.9699(4)	4.4(3)
C(10)	1.2019(6)	0.5148(4)	0.9208(4)	3.9(2)
C(11)	1.4420(6)	0.6471(4)	1.0529(4)	3.9(2)
C(21)	0.5072(7)	0.1185(4)	0.4488(4)	4.7(3)
C(22)	0.1974(6)	0.0587(4)	0.4305(4)	4.3(3)
C(23)	0.0059(7)	0.2918(5)	0.5155(4)	6.1(3)
C(24)	0.1140(7)	0.3913(4)	0.6194(4)	4.9(3)
C(25)	0.2631(6)	0.3567(4)	0.6424(3)	3.6(2)
C(26)	0.4386(6)	0.4053(3)	0.6412(3)	3.7(2)
C(27)	0.5341(6)	0.3361(4)	0.6509(4)	4.2(2)
C(28)	0.4154(7)	0.2422(4)	0.6585(3)	4.5(3)
C(29)	0.2515(7)	0.2558(4)	0.6539(3)	4.1(2)
C(30)	0.1788(9)	0.3725(6)	0.4138(5)	6.5(4)
C(31)	0.0183(9)	0.1730(6)	0.3292(5)	8.3(4)

Experimental section

All reactions were performed under an argon atmosphere with Schlenk techniques. Tetrahydrofuran (THF) and n-hexane were distilled from sodium benzophenone ketyls; methylene chloride (CH_2Cl_2) and hexamethylphosphoramide (HMPA) were distilled from CaH_2. Infrared solution spectra were recorded on a Perkin–Elmer 882 infrared spectrophotometer using 0.1 mm cells with CaF_2 windows. Melting points were determined by using a Yanaco model MP micro melting point apparatus and were uncorrected. ^{1}H NMR (200 MHz) and ^{13}C NMR (50 MHz) spectra were obtained with a Bruker AC-200 FT spectrophotometer. All chemical shifts are reported in parts per million (ppm) relative to Me_4Si. Elemental analyses were obtained on a Perkin–Elmer 2400 CHN elemental analyzer. High resolution and normal mass spectra were recorded on a VG 70-250S mass spectrophotometer at 70 eV mode unless otherwise indicated.
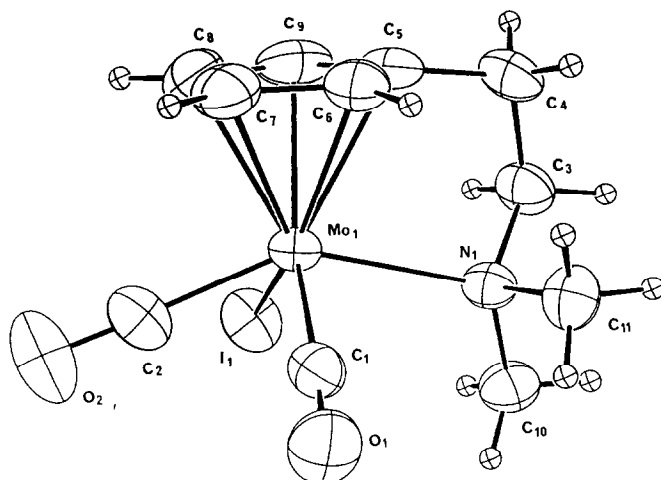
Fig. 1. Molecular structure of **4a**. There are two essentially similar independent molecules within the unit cell. Only one molecule is shown.

Preparation of (dimethylaminoethyl)cyclopentadiene (2a)

A THF solution of sodium cyclopentadienylide (2 *M*, 157 ml, 0.314 mol) was added to a stirred suspension of 2-dimethylaminoethyl chloride hydrochloride (18.1 g, 0.126 mol) in THF (100 ml) and HMPA (45 ml) at 0°C over 20 min. The resulting mixture was then refluxed for 4 h. The brown solution was concentrated under water aspirator pressure. Water (500 ml) was added to the residue which was then extracted with pentane (500 ml). The pentane layer was concentrated under water aspirator pressure and the residue distilled (Kugelrohr), using a dry ice cooling device at 0.5 Torr, 40°C. Colourless distillates were collected to give 14.3 g (83% yield) of **2a**. ^{1}H NMR (CDCl$_3$, 200 MHz): δ 6.48–6.06 (3H, m), 2.89–2.80 (2H, m), 2.62–2.45 (4H, m), 2.27 (6H, s, N(CH$_3$)$_2$, major), 2.26 (6H, s, N(CH$_3$)$_2$, minor). ^{13}C NMR (CDCl$_3$, 50 MHz): major, 145.0, 133.8, 132.5, 126.6,

Table 3

Selected bond lengths (Å) and bond angles (°) in complex **4a**

I(1)–Mo(1)	2.8509(6)	Mo(1)–N(1)	2.380(3)
Mo(1)–C(1)	1.949(4)	Mo(1)–C(2)	1.966(4)
Mo(1)–C(5)	2.367(4)	Mo(1)–C(6)	2.301(4)
Mo(1)–C(7)	2.261(4)	Mo(1)–C(8)	2.292(4)
Mo(1)–C(9)	2.373(4)	N(1)–C(3)	1.498(5)
O(1)–C(1)	1.152(5)	O(2)–C(2)	1.151(6)
C(3)–C(4)	1.518(6)	C(4)–C(5)	1.515(6)
I(1)–Mo(1)–N(1)	86.54(8)	I(1)–Mo(1)–C(1)	118.81(12)
I(1)–Mo(1)–C(2)	77.94(12)	N(1)–Mo(1)–C(1)	85.19(14)
N(1)–Mo(1)–C(2)	145.25(16)	N(1)–Mo(1)–C(5)	72.49(13)
Mo(1)–C(1)–O(1)	175.9(3)	Mo(1)–C(2)–O(2)	176.2(4)
C(1)–Mo(1)–C(2)	75.77(17)	Mo(1)–N(1)–C(3)	106.80(23)
Mo(1)–N(1)–C(10)	117.10(25)	Mo(1)–N(1)–C(11)	110.61(23)
C(3)–N(1)–C(10)	107.3(3)		

59.1, 45.4 ($\times 2$), 41.3, 28.3 ppm; minor, 144.9, 134.6, 130.8, 126.9, 59.8, 45.4 ($\times 2$), 43.4, 29.1 ppm. High resolution mass. Found: 137.1225. $C_9H_{15}N$ calc.: 137.1204.

2b, R=CH$_3$; yield: 75%; colourless liquid, 0.5 Torr, 50°C. ^{1}H NMR (CDCl$_3$, 200 MHz): δ 6.44–6.05 (3H, m), 2.96–2.87 (2H, m), 2.83–2.72 (1H, m), 2.72–2.60 (1H, m), 2.35–2.23 (1H, m), 2.29 (6H, s, N(CH$_3$)$_2$, major), 2.27 (6H, s, N(CH$_3$)$_2$, minor), 0.96 (3H, d, J 6.5 Hz, CH$_3$, major), 0.95 (3H, d, J 6.5 Hz, CH$_3$, minor). High resolution mass. Found: 151.1350. $C_{10}H_{17}N$ calc.: 151.1361.

Preparation of η^5-$C_5H_4CH_2CH_2N(CH_3)_2Mo(CO)_3I$ (3a)

A hexane solution of ^{n}BuLi (1.6 M, 7.7 ml, 12.32 mmol) was added to a stirred solution of **2a** (1.683 g, 12.28 mmol) in THF (30 ml) at 0°C over 5 min. After stirring for another 10 min at 0°C, the resulting pale yellow solution was added via a double-tipped needle to a stirred suspension of Mo(CO)$_6$ (3.24 g, 12.28 mmol) in THF (50 ml). The mixture was then refluxed for 12 h. After the resulting orange solution was cooled in an ice-water bath a solution of iodine (3.12 g, 12.28 mmol) in THF (20 ml) was added over an hour. After stirring for 20 min, the solution was concentrated. The residue was then subjected to flash chromatography [13] through silica gel (230–400 mesh, 10% CH$_3$OH in CH$_2$Cl$_2$). The first red band was collected. After evaporation to dryness, a mixture of liquid and solids were obtained. The solid material was found to be the corresponding ammonium salt, generated due to the acidity of the silica gel. The mixture was dissolved with CH$_2$Cl$_2$ (200 ml) and washed once with aqueous potassium carbonate. After evaporation, **3a** was obtained as a red liquid, 4.12 g (75% yield). TLC (silica gel): $R_f = 0.39$ (10% CH$_3$OH in CH$_2$Cl$_2$). IR (THF): 2036(s), 1956(s) cm^{-1}. Mass spectra m/e (rel intensity (%)): 445 (M^+, 4), 417 (M^+ – CO, 17), 389 (M^+ – 2CO, 25). ^{1}H NMR (CDCl$_3$, 200 MHz): δ 5.55 (2H, t, J 2.2 Hz, Cp-H's), 5.41 (2H, t, J 2.2 Hz, Cp-H's), 2.68–2.59 (2H, m), 2.50–2.41 (2H, m), 2.24 (6H, s). ^{13}C NMR (CDCl$_3$, 50 MHz): 237.3, 220.9 ($\times 2$), 116.9, 95.1 ($\times 2$), 91.3 ($\times 2$), 60.2, 45.3 ($\times 2$), 27.1 ppm. Analysis. Found: C, 32.42; H, 3.25; N, 3.32. $C_{12}H_{14}INO_3Mo$ calc.; C, 32.53; H, 3.18; N, 3.16%.

η^5-$C_5H_4CH_2CH(CH_3)N(CH_3)_2Mo(CO)_3I$ (3b). Yield: 70%; red solid; m.p.: 35–36°C. IR (THF): 2035(s), 1953(s) cm^{-1}. Mass spectra at 20 eV, m/e (rel intensity (%)): 459 (M^+, 5), 431 (M^+ – CO, 12). ^{1}H NMR (CDCl$_3$, 200 MHz): δ 5.59–5.56 (1H, m, Cp-H), 5.54–5.51 (1H, m, Cp-H), 5.43–5.39 (2H, m, Cp-H), 2.74–2.60 (2H, m), 2.38–2.31 (1H, m), 2.26 (6H, s), 1.01 (3H, d, J 6.5 Hz, CH$_3$). ^{13}C NMR (CDCl$_3$, 50 MHz): 237.3, 220.8 ($\times 2$), 116.4, 95.8, 95.5, 91.1 ($\times 2$), 61.2, 40.2 ($\times 2$), 33.1, 13.2 ppm. Analysis. Found: C, 34.57; H, 3.73; N, 2.92. $C_{13}H_{16}INO_3Mo$ calc.: C, 34.16; H, 3.53; N, 3.06%.

Preparation of η^5-$C_5H_4CH_2CH_2\overline{N(CH_3)_2}Mo(CO)_2I$ (4a)

Into a borosilicate test tube was placed complex **3a** (1.20 g, 2.71 mmol). The open end was sealed with a rubber septum. The vessel was evacuated and then flushed with argon and THF (50 ml) added. The resulting deep red solution was cooled in a circulating ice-water bath and irradiated under an argon atmosphere, using a Hanovia 500W medium pressure Hg lamp for 2 h to allow the reaction to go to completion (monitored with IR until 2036 cm^{-1} band disappeared). The resulting violet solution was filtered through Celite. After concentration under reduced pressure, **4a** was obtained as violet crystals in 97% yield (1.10 g). M.p.:

134–136 °C. IR (THF): 1961(s), 1849(s) cm^{-1}. Mass spectra m/e (rel intensity (%)): 417 (M^+, 15), 389 ($M^+ - CO$, 20), 359(60). ^{1}H NMR (CDCl$_3$, 200 MHz): δ 6.00–5.97 (1H, m, Cp-H), 5.77–5.74 (1H, m, Cp-H), 5.19–5.15 (1H, m, Cp-H), 4.53–4.49 (1H, m, Cp-H), 3.79–3.66 (1H, m, C$_3$-H$_a$), 3.06–2.97 (1H, m, C$_3$-H$_b$), 2.94 (3H, s, NCH$_3$), 2.76 (3H, s, NCH$_3$), 2.62–2.40 (2H, m, C$_4$-H's). ^{13}C NMR (CDCl$_3$, 50 MHz): 262.1, 245.2, 133.6, 103.8, 89.4, 85.7, 80.9, 75.8, 56.4, 56.1, 25.1 ppm. Analysis. Found: C, 31.79; H, 3.45; N, 3.25. C$_{11}$H$_{14}$INO$_2$Mo calc.: C, 31.83; H, 3.40; N, 3.37%.

Crystal structure of η^5-C$_5$H$_4$CH$_2$CH$_2\overline{N(CH_3)_2}$Mo(CO)$_2$I (4a)

A single crystal of **4a** was obtained by slow diffusion of a CH$_2$Cl$_2$ solution of **4a** into hexane at 25 °C. Diffraction measurement was made on an Enraf-Nonius CAD-4 diffractometer by use of graphite monochromated Mo-K_α radiation (λ = 0.7093 Å) in the θ–2θ scan mode. Unit cell dimensions were obtained by least-squares refinement with use of 25 centred reflections for which $18.45 < 2\theta < 31.13°$. Other crystal data and refinement details are listed in Table 1.

η^5-C$_5$H$_4$CH$_2$CH(CH$_3$)$\overline{N(CH_3)_2}$Mo(CO)$_2$I (4b). Yield: 93%; violet liquid. IR (THF): 1961(s), 1849(s) cm^{-1}. Mass spectra m/e (rel intensity (%)): 431 (M^+, 55), 403 ($M^+ - CO$, 100), 375 ($M^+ - 2CO$, 45), 72(46). High resolution mass. Found: 430.9272. C$_{12}$H$_{16}$INO$_2$Mo calc.: 430.9280.

Major isomer: ^{1}H NMR (CDCl$_3$, 200 MHz): δ 6.03–6.00 (1H, m, Cp-H), 5.67–5.64 (1H, m, Cp-H), 5.03–5.00 (1H, m, Cp-H), 4.64–4.61 (1H, m, Cp-H), 4.51–4.36 (1H, m), 2.87 (3H, s), 2.69 (3H, s), 2.53–2.47 (2H, m), 0.96 (3H, d, J 6.5 Hz). ^{13}C NMR (CDCl$_3$, 50 MHz): 263.7, 246.7, 129.4, 107.0, 89.0, 85.0, 81.6, 76.1, 53.9, 47.3, 32.4, 11.6 ppm.

Minor isomer: ^{1}H NMR (CDCl$_3$, 200 MHz): δ 5.87–5.84 (1H, m, Cp-H), 5.82–5.79 (1H, m, Cp-H), 5.45–5.42 (1H, m, Cp-H), 4.22–4.19 (1H, m, Cp-H), 3.63–3.48 (1H, m), 2.93 (3H, s), 2.67 (3H, s), 2.48–2.41 (2H, m), 1.04 (3H, d, J 6.5 Hz). ^{13}C NMR (CDCl$_3$, 50 MHz): 261.0, 242.2, 128.8, 99.0, 89.9. 88.8, 80.5, 78.8, 52.8, 45.5, 32.9, 12.0 ppm.

Preparation of [η^5-C$_5$H$_4$CH$_2$CH$_2\overline{N(CH_3)_2}$Mo(CO)$_2$CH$_3$CN]$^+$BF$_4^-$ (5a)

An acetonitrile solution of silver tetrafluoroborate (0.2 M, 35 ml) was added to a stirred solution of **4a** (2.89 g, 6.96 mmol) in acetonitrile (35 ml) at 0 °C over 30 min. Stirring was continued for 20 min. The mixture was then filtered through Celite and concentrated. The residue was dissolved with CH$_2$Cl$_2$ (20 ml). Diethyl ether (50 ml) was then added with swirling to allow for precipitation to occur. Solvents were then decanted and solids were dried under vacuum to give 2.82 g (97% yield) of **5a**. IR (CH$_2$Cl$_2$): 2044(m), 2001(s), 1889(s) cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$, 200 MHz): δ 6.40–6.37 (1H, m, Cp-H), 5.76–5.73 (1H, m, Cp-H), 5.55–5.51 (1H, m, Cp-H), 4.67–4.63 (1H, m, Cp-H), 3.56–3.43 (1H, m), 3.28–3.15 (1H, m), 2.75–2.52 (2H, m), 2.77 (3H, s, NCH$_3$), 2.70 (3H, s, CH$_3$CN), 2.58 (3H, s, NCH$_3$). ^{13}C NMR (CD$_2$Cl$_2$, 50 MHz): 253.9, 247.8, 150.0, 140.3, 102.4, 88.2, 86.6, 84.5, 79.6, 57.8, 53.5, 25.7, 5.5 ppm. Analysis. Found: C, 37.82; H, 4.10; N, 7.01. C$_{13}$H$_{17}$N$_2$O$_2$MoBF$_4$ calc.: C, 37.60; H, 4.13; N, 6.75%.

Supplementary material available. Lists of crystal data and refinement details (1 page), atomic coordinates and B_{iso} (1 page) and bond lengths and angles of **4a** (3 pages) are available from T.-F.W.

Acknowledgement

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