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Supporting Information

Intermolecular C—H···O and n→π* and Short Intramolecular σ→π* Interactions in Molybdenum(0) Tetracarbonyl Complex of a very Twisted 14-membered Tetraazaannulene Macrocyclic Ligand: Structural and Computational Studies

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Synthesis and crystallization of 1

An equimolar quantity of molybdenum hexacarbonyl (0.132 g, 0.5 mmol) and $Me_2Ph_2H_2TAA$ (0.234 g, 0.5 mmol) were mixed and refluxed in a mixture of toluene (40 mL) and THF (10 mL) for 12 h. The pale-orange product was obtained by adding n-hexane to the concentrated. Single-crystals suitable for X-ray analysis were grown by vapour diffusion of *n*-hexane into dichloromethane solution of **1**. Different part of the single-crystal batch was selected, grinded and heated in vacuum oven for CHNO analysis. Elemental analyses: *Calc*. (%): C, 62.30; H, 3.85; N, 7.65; O, 13.10 *Found*: C, 62.31; H, 3.82; N, 7.68; O, 13.11. ^{1}H-NMR ($CDCl_3$, σ_{ppm}): 2.24 and 2.26 (singlet, CH_3, methyl protons), 4.21-4.38 (dd, methylene protons, CH_2, J = 10 Hz), 4.95 (singlet, olefinic proton, CH); 12.90 (singlet, NH). $^{13}C\{^{1}H\}$-NMR ($CDCl_3$, σ_{ppm}): 21.1, 23.8, 54.5, 101.1, 122.3, 122.5, 123.5, 124.5, 124.9, 125.2, 125.3, 125.9, 127.6, 127.8, 128.2, 128.5, 128.8, 129.0, 29.8, 130.2, 134.1, 135.6, 137.4, 144.9, 145.6, 157.3, 162.4, 175.2, 202.7, 209.7, 223.1. ATR, FT–IR (υ, cm^{-1}): 2003, 1976, 1860 and 1821 (four terminal CO); 1613 (imine, C=N). ESI-MS (positive mode) a base peak at *m/z* 469.2471 (Fig. S3) assignable to the mono-protonated macrocyclic ligand $[Me_2Ph_2H_3TAA]^{+}$ resulted by de-coordination of $Mo(CO)_4$.

Computational details

Density functional theory (DFT) calculations have been performed using the *Gaussian 09* package to perform geometry optimizations, the vibrational frequencies and the electronic structures of the complex (M. Frisch, *et al*., GAUSSIAN09. 2009. Gaussian Inc., Wallingford, CT, USA. http://www.gaussian.com). A frequency calculation after each geometry optimization ensured that the calculated structures are real minima in the potential energy surface of the molecules. The structure was optimized using the B3LYP exchange-correlation functionals with the LANL2DZ effective core pseudo-potential (ECP) and corresponding set of basic functions for Mo and 6-31G* (five pure d functions) for C, H, N and O (D. Andrae, U. Häußermann, M. Dolg, H. Stoll & H. Preuß, *Theor. Chim. Acta*, 1990, 77, 123–141.). The NBO program (K. L. Schuchardt, B. T. Didier, T. Elsethagen, L. Sun, V. Gurumoorthi, J. Chase, J. Li, & T. L. Windus, *J. Chem. Info. & Model*., 2007, 47, 1045–1052.) embedded in Gaussian 09 package used for calculations was done at B3LYP/LANL2DZ level of theory on optimized molecule. The natural bond orbital analysis emphasizes the role of intra- and intermolecular interaction or charge transfer in the title compound. It is performed by including all possible interaction between filled donor and empty acceptor NBOs and estimating the energetic importance by second-order perturbation theory. Molecular orbital (MO) compositions and the overlap populations were calculated using the AOMix *6.88* program (S. I. Gorelsky & A. B. P. Lever, *J. Organomet. Chem*., 2001, 635, 187–196). The analysis of the molecular orbital (MO) compositions in terms of the highest occupied orbitals (HOFO) and lowest unoccupied orbitals (LUFOs) of the fragment species F1 and F2 (F1 is $Mo(CO)_4$ and F2 is $Me_2Ph_2H_2TAA$) were performed by the AOMix *6.88* program. Charge decomposition analysis (CDA) implemented in AOMix *6.88* program was used to provide better qualitative and quantitative understanding of the nature of the chemical bonding in the complex based on the electron donation and back-donation between the metal and other fragments.

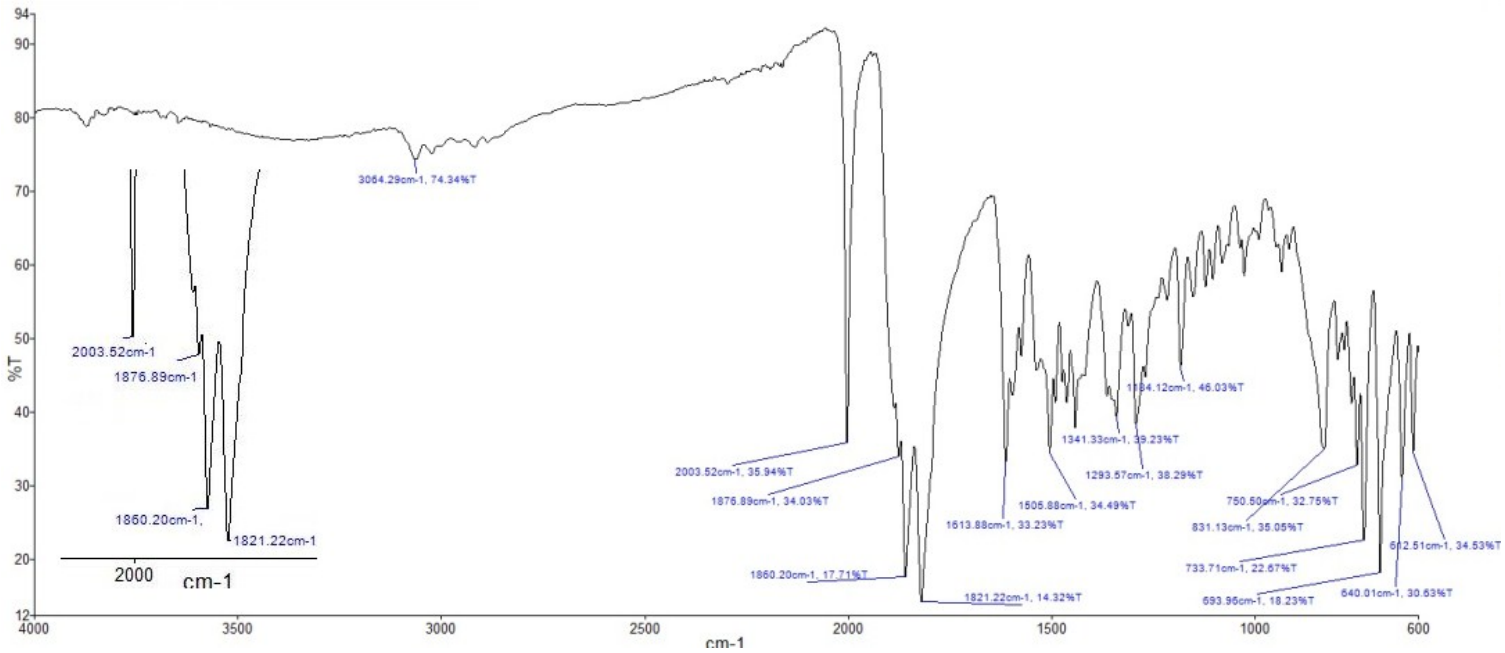

Fig. S1. The FT-IR (ATR) spectrum of **1**. The inset (left) shows the stretching region for $Mo(CO)_4$ segment.

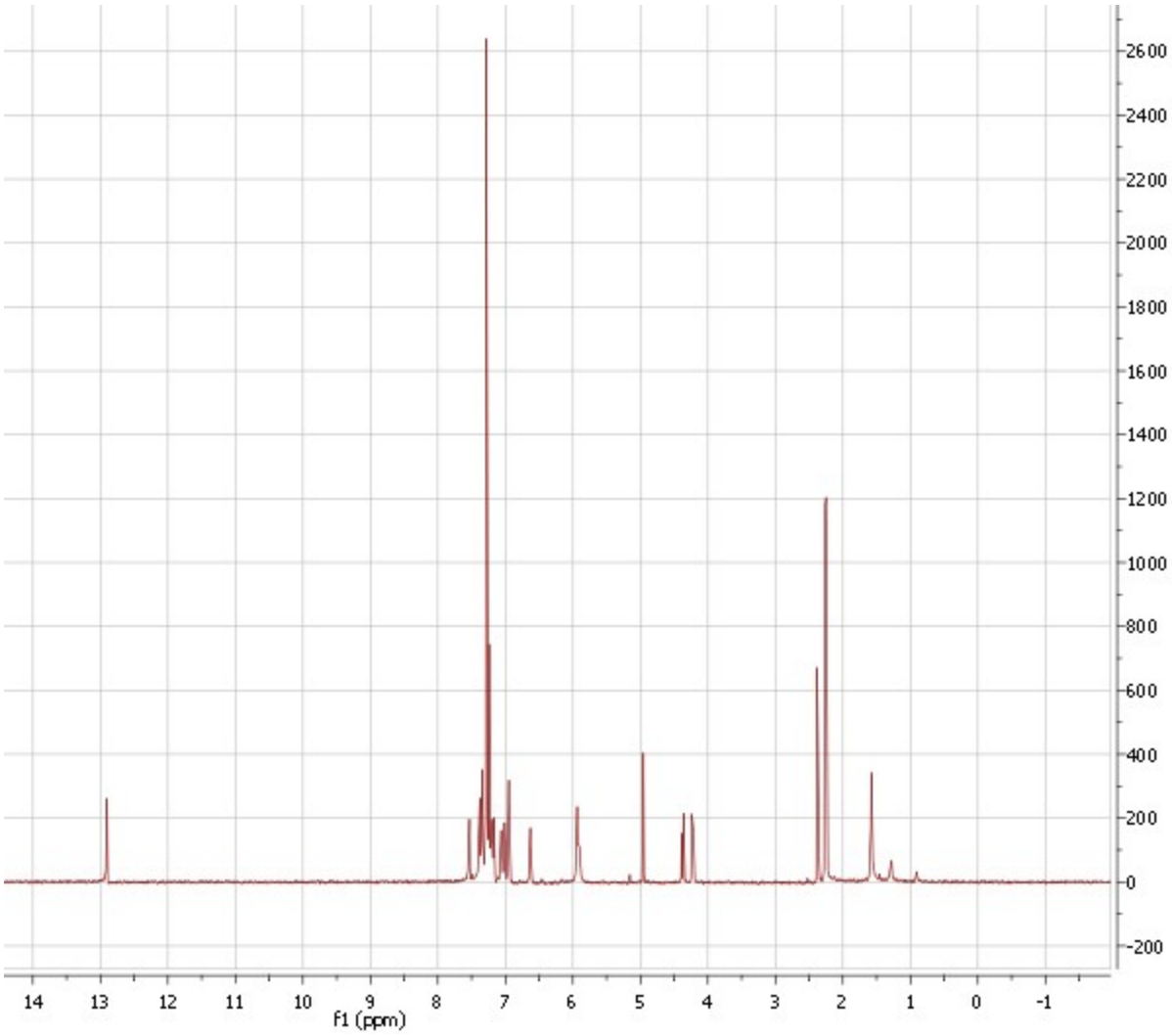

Figure S2. ^{1}H NMR (500 MHz), spectrum of the title compound in $CDCl_3$ at room temperature.

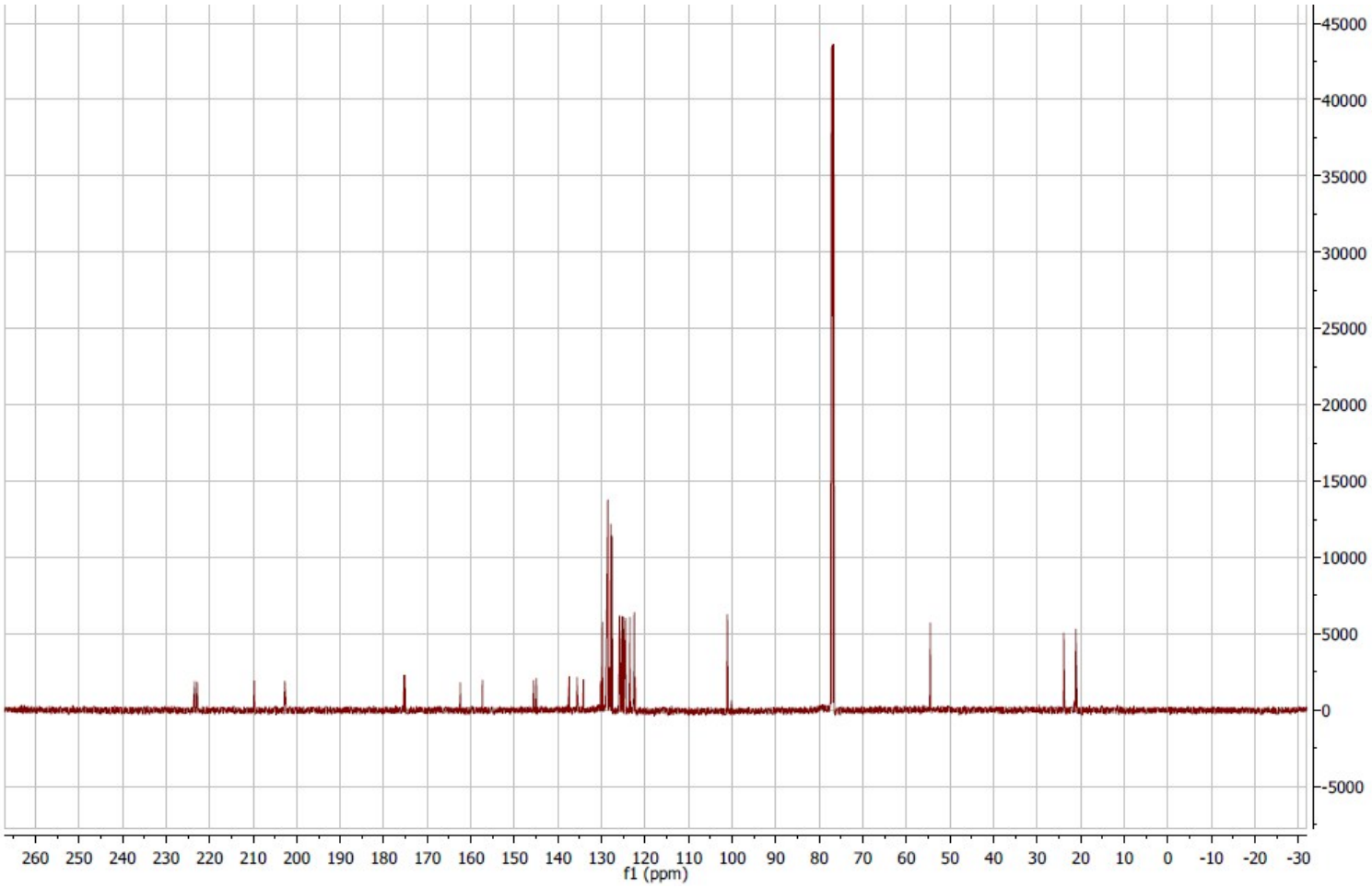

Figure S3. 13C{^{1}H} NMR (150 MHz), spectrum of **1** in $CDCl_3$ at room temperature.

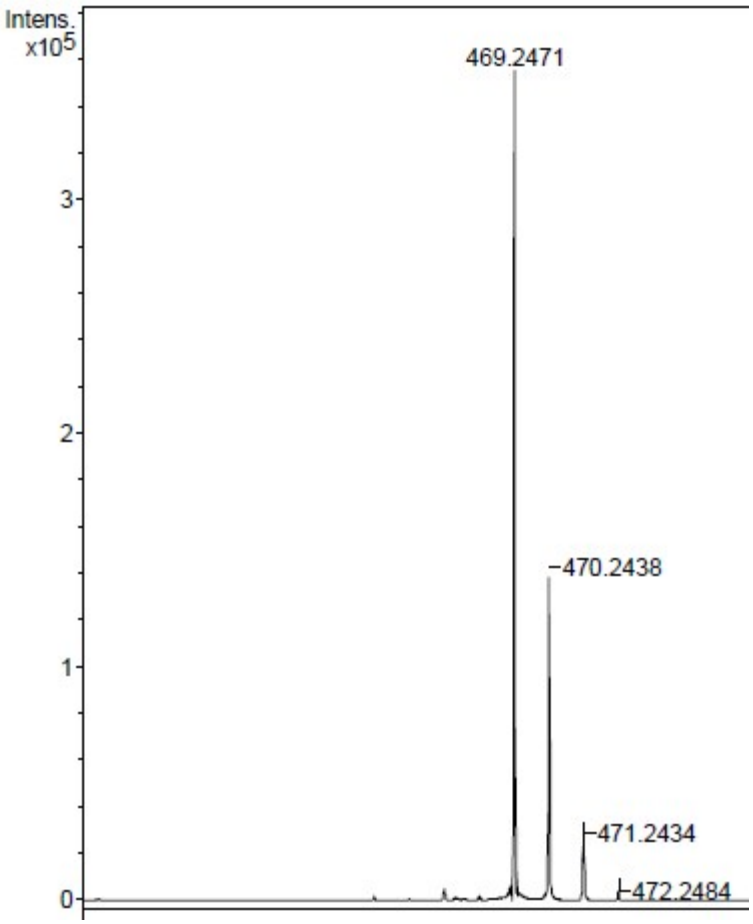

Fig. S4. Expanded ESI-MS spectrum of **1** in base peak position.

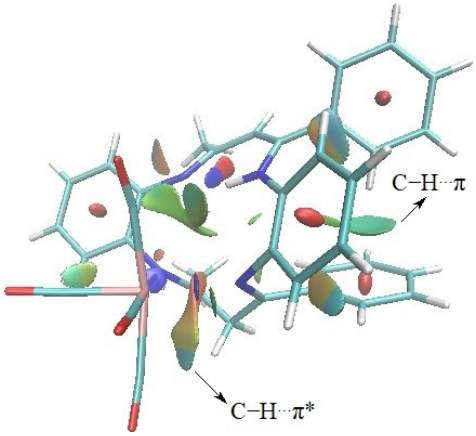

Fig. S5. The isosurface of the intramolecular C–H···CO and C–H···π interactions with pale-blue green colour with arrows.

Table S1. Crystal data and structure refinement for **1**.

Identification code	1	
Empirical formula	C36 H28 Mo N4 O4. CH_2Cl_2	
Formula weight	761.49	
Temperature	150(2) K	
Wavelength	0.71073Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 18.659(7) Å	α= 90°
	b = 9.1804(8) Å	β= 99.310(18)°
	c = 20.117(3) Å	γ = 90°
Volume	3400.6(14) $Å^3$	
Z	4	
Density (calculated)	1.487 Mg/m^3	
Absorption coefficient	0.589 mm^{-1}	
F(000)	1552	
Crystal size	0.300 x 0.100 x 0.050 mm^3	
Theta range for data collection	3.022 to 29.607°	
Index ranges	-23<=h<=23, -12<=k<=12, -27<=l<=26	
Reflections collected	29588	
Independent reflections	8341 [R(int) = 0.0680]	
Completeness to theta = 25.242°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.77769	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8341 / 1 / 438	
Goodness-of-fit on F^2	1.060	
Final R indices [I>2sigma(I)]	R1 = 0.0713, wR2 = 0.1607	
R indices (all data)	R1 = 0.0977, wR2 = 0.1777	
Largest diff. peak and hole	1.814 and -1.604 e. $Å^{-3}$	

Table S1. Bond lengths [Å] and angles [°] for **1**.

C(1)-O(1)	1.143(7)
C(1)-Mo(1)	2.033(5)
C(2)-O(2)	1.141(6)
C(2)-Mo(1)	2.040(5)
C(3)-O(3)	1.156(6)
C(3)-Mo(1)	1.962(5)
C(4)-O(4)	1.178(6)
C(4)-Mo(1)	1.949(5)
C(5)-C(6)	1.395(7)
C(5)-C(10)	1.396(7)
C(5)-N(1)	1.442(6)
C(6)-C(7)	1.390(7)
C(6)-H(6)	0.9300
C(7)-C(8)	1.387(9)
C(7)-H(7)	0.9300
C(8)-C(9)	1.371(8)
C(8)-H(8)	0.9300
C(9)-C(10)	1.403(7)
C(9)-H(9)	0.9300
C(10)-N(3)	1.409(6)
C(11)-N(3)	1.302(7)
C(11)-C(12)	1.434(7)
C(11)-C(23)	1.520(8)
C(12)-C(13)	1.368(7)
C(12)-H(12)	0.9300
C(13)-N(4)	1.354(6)
C(13)-C(24)	1.498(7)
C(14)-C(19)	1.383(6)
C(14)-C(15)	1.407(6)
C(14)-N(4)	1.410(6)
C(15)-C(16)	1.379(7)
C(15)-H(15)	0.9300
C(16)-C(17)	1.380(8)
C(16)-H(16)	0.9300

C(17)-C(18)	1.380(7)
C(17)-H(17)	0.9300
C(18)-C(19)	1.392(6)
C(18)-H(18)	0.9300
C(19)-N(2)	1.447(5)
C(20)-N(2)	1.292(6)
C(20)-C(30)	1.490(6)
C(20)-C(21)	1.513(6)
C(21)-C(22)	1.513(6)
C(21)-H(21A)	0.9700
C(21)-H(21B)	0.9700
C(22)-N(1)	1.294(6)
C(22)-C(36)	1.490(7)
C(23)-H(23A)	0.9600
C(23)-H(23B)	0.9600
C(23)-H(23C)	0.9600
C(24)-C(25)	1.365(8)
C(24)-C(29)	1.376(7)
C(25)-C(26)	1.396(8)
C(25)-H(25)	0.9300
C(26)-C(27)	1.373(9)
C(26)-H(26)	0.9300
C(27)-C(28)	1.367(9)
C(27)-H(27)	0.9300
C(28)-C(29)	1.382(8)
C(28)-H(28)	0.9300
C(29)-H(29)	0.9300
C(30)-C(35)	1.388(7)
C(30)-C(31)	1.406(6)
C(31)-C(32)	1.390(7)
C(31)-H(31)	0.9300
C(32)-C(33)	1.389(8)
C(32)-H(32)	0.9300
C(33)-C(34)	1.391(7)
C(33)-H(33)	0.9300
C(34)-C(35)	1.383(7)

C(34)-H(34)	0.9300
C(35)-H(35)	0.9300
C(36)-H(36A)	0.9600
C(36)-H(36B)	0.9600
C(36)-H(36C)	0.9600
N(1)-Mo(1)	2.266(4)
N(2)-Mo(1)	2.258(4)
N(4)-H(1N4)	0.850(10)
Cl(1)-C(1S)	1.820(15)
Cl(2)-C(1S)	1.827(11)
C(1S)-H(1S1)	0.9700
C(1S)-H(1S2)	0.9700

O(1)-C(1)-Mo(1)	167.7(5)
O(2)-C(2)-Mo(1)	170.2(5)
O(3)-C(3)-Mo(1)	178.0(5)
O(4)-C(4)-Mo(1)	177.1(4)
C(6)-C(5)-C(10)	121.7(4)
C(6)-C(5)-N(1)	119.7(5)
C(10)-C(5)-N(1)	118.6(4)
C(7)-C(6)-C(5)	118.8(5)
C(7)-C(6)-H(6)	120.6
C(5)-C(6)-H(6)	120.6
C(8)-C(7)-C(6)	120.7(5)
C(8)-C(7)-H(7)	119.7
C(6)-C(7)-H(7)	119.7
C(9)-C(8)-C(7)	119.7(5)
C(9)-C(8)-H(8)	120.2
C(7)-C(8)-H(8)	120.2
C(8)-C(9)-C(10)	121.7(6)
C(8)-C(9)-H(9)	119.1
C(10)-C(9)-H(9)	119.1
C(5)-C(10)-C(9)	117.4(5)
C(5)-C(10)-N(3)	117.8(4)
C(9)-C(10)-N(3)	124.4(5)
N(3)-C(11)-C(12)	119.7(5)

N(3)-C(11)-C(23)	125.5(5)
C(12)-C(11)-C(23)	114.7(5)
C(13)-C(12)-C(11)	126.1(5)
C(13)-C(12)-H(12)	116.9
C(11)-C(12)-H(12)	116.9
N(4)-C(13)-C(12)	121.8(4)
N(4)-C(13)-C(24)	120.8(4)
C(12)-C(13)-C(24)	117.2(5)
C(19)-C(14)-C(15)	118.2(4)
C(19)-C(14)-N(4)	119.0(4)
C(15)-C(14)-N(4)	122.8(4)
C(16)-C(15)-C(14)	120.2(5)
C(16)-C(15)-H(15)	119.9
C(14)-C(15)-H(15)	119.9
C(17)-C(16)-C(15)	121.0(5)
C(17)-C(16)-H(16)	119.5
C(15)-C(16)-H(16)	119.5
C(16)-C(17)-C(18)	119.4(5)
C(16)-C(17)-H(17)	120.3
C(18)-C(17)-H(17)	120.3
C(17)-C(18)-C(19)	120.0(5)
C(17)-C(18)-H(18)	120.0
C(19)-C(18)-H(18)	120.0
C(14)-C(19)-C(18)	121.1(4)
C(14)-C(19)-N(2)	120.4(4)
C(18)-C(19)-N(2)	118.4(4)
N(2)-C(20)-C(30)	125.8(4)
N(2)-C(20)-C(21)	117.4(4)
C(30)-C(20)-C(21)	116.8(4)
C(20)-C(21)-C(22)	111.7(4)
C(20)-C(21)-H(21A)	109.3
C(22)-C(21)-H(21A)	109.3
C(20)-C(21)-H(21B)	109.3
C(22)-C(21)-H(21B)	109.3
H(21A)-C(21)-H(21B)	107.9
N(1)-C(22)-C(36)	126.1(4)

N(1)-C(22)-C(21)	116.6(4)
C(36)-C(22)-C(21)	117.3(4)
C(11)-C(23)-H(23A)	109.5
C(11)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(11)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(25)-C(24)-C(29)	119.1(5)
C(25)-C(24)-C(13)	120.2(5)
C(29)-C(24)-C(13)	120.7(5)
C(24)-C(25)-C(26)	120.3(6)
C(24)-C(25)-H(25)	119.8
C(26)-C(25)-H(25)	119.8
C(27)-C(26)-C(25)	120.0(6)
C(27)-C(26)-H(26)	120.0
C(25)-C(26)-H(26)	120.0
C(28)-C(27)-C(26)	119.6(5)
C(28)-C(27)-H(27)	120.2
C(26)-C(27)-H(27)	120.2
C(27)-C(28)-C(29)	120.2(6)
C(27)-C(28)-H(28)	119.9
C(29)-C(28)-H(28)	119.9
C(24)-C(29)-C(28)	120.7(5)
C(24)-C(29)-H(29)	119.7
C(28)-C(29)-H(29)	119.7
C(35)-C(30)-C(31)	118.9(4)
C(35)-C(30)-C(20)	118.7(4)
C(31)-C(30)-C(20)	122.4(4)
C(32)-C(31)-C(30)	119.5(5)
C(32)-C(31)-H(31)	120.3
C(30)-C(31)-H(31)	120.3
C(31)-C(32)-C(33)	120.8(4)
C(31)-C(32)-H(32)	119.6
C(33)-C(32)-H(32)	119.6
C(32)-C(33)-C(34)	119.8(5)

C(32)-C(33)-H(33)	120.1
C(34)-C(33)-H(33)	120.1
C(35)-C(34)-C(33)	119.5(5)
C(35)-C(34)-H(34)	120.3
C(33)-C(34)-H(34)	120.3
C(34)-C(35)-C(30)	121.5(4)
C(34)-C(35)-H(35)	119.2
C(30)-C(35)-H(35)	119.2
C(22)-C(36)-H(36A)	109.5
C(22)-C(36)-H(36B)	109.5
H(36A)-C(36)-H(36B)	109.5
C(22)-C(36)-H(36C)	109.5
H(36A)-C(36)-H(36C)	109.5
H(36B)-C(36)-H(36C)	109.5
C(22)-N(1)-C(5)	117.8(4)
C(22)-N(1)-Mo(1)	124.9(3)
C(5)-N(1)-Mo(1)	117.3(3)
C(20)-N(2)-C(19)	118.2(4)
C(20)-N(2)-Mo(1)	124.4(3)
C(19)-N(2)-Mo(1)	116.9(3)
C(11)-N(3)-C(10)	122.6(4)
C(13)-N(4)-C(14)	129.0(4)
C(13)-N(4)-H(1N4)	111(10)
C(14)-N(4)-H(1N4)	120(10)
C(4)-Mo(1)-C(3)	88.6(2)
C(4)-Mo(1)-C(1)	83.4(2)
C(3)-Mo(1)-C(1)	84.0(2)
C(4)-Mo(1)-C(2)	84.1(2)
C(3)-Mo(1)-C(2)	86.61(19)
C(1)-Mo(1)-C(2)	164.6(2)
C(4)-Mo(1)-N(2)	98.09(17)
C(3)-Mo(1)-N(2)	172.79(18)
C(1)-Mo(1)-N(2)	94.04(18)
C(2)-Mo(1)-N(2)	96.72(16)
C(4)-Mo(1)-N(1)	176.89(16)
C(3)-Mo(1)-N(1)	94.52(18)

C(1)-Mo(1)-N(1)	96.8(2)
C(2)-Mo(1)-N(1)	96.14(17)
N(2)-Mo(1)-N(1)	78.79(13)
Cl(1)-C(1S)-Cl(2)	98.1(7)
Cl(1)-C(1S)-H(1S1)	112.1
Cl(2)-C(1S)-H(1S1)	112.1
Cl(1)-C(1S)-H(1S2)	112.1
Cl(2)-C(1S)-H(1S2)	112.1
H(1S1)-C(1S)-H(1S2)	109.8

Table S1. Torsion angles [°] for **1**.

C(10)-C(5)-C(6)-C(7)	-0.3(9)
N(1)-C(5)-C(6)-C(7)	179.1(5)
C(5)-C(6)-C(7)-C(8)	-1.8(9)
C(6)-C(7)-C(8)-C(9)	1.1(10)
C(7)-C(8)-C(9)-C(10)	1.8(10)
C(6)-C(5)-C(10)-C(9)	2.9(9)
N(1)-C(5)-C(10)-C(9)	-176.4(5)
C(6)-C(5)-C(10)-N(3)	176.2(5)
N(1)-C(5)-C(10)-N(3)	-3.1(8)
C(8)-C(9)-C(10)-C(5)	-3.7(9)
C(8)-C(9)-C(10)-N(3)	-176.5(6)
N(3)-C(11)-C(12)-C(13)	8.9(10)
C(23)-C(11)-C(12)-C(13)	-167.7(6)
C(11)-C(12)-C(13)-N(4)	-0.2(10)
C(11)-C(12)-C(13)-C(24)	175.3(6)
C(19)-C(14)-C(15)-C(16)	3.1(7)
N(4)-C(14)-C(15)-C(16)	-177.8(5)
C(14)-C(15)-C(16)-C(17)	-3.8(8)
C(15)-C(16)-C(17)-C(18)	0.8(8)
C(16)-C(17)-C(18)-C(19)	2.7(8)
C(15)-C(14)-C(19)-C(18)	0.4(7)
N(4)-C(14)-C(19)-C(18)	-178.7(4)
C(15)-C(14)-C(19)-N(2)	179.6(4)
N(4)-C(14)-C(19)-N(2)	0.5(7)
C(17)-C(18)-C(19)-C(14)	-3.3(7)
C(17)-C(18)-C(19)-N(2)	177.5(4)
N(2)-C(20)-C(21)-C(22)	63.5(6)
C(30)-C(20)-C(21)-C(22)	-114.5(5)
C(20)-C(21)-C(22)-N(1)	-60.8(5)
C(20)-C(21)-C(22)-C(36)	118.8(5)
N(4)-C(13)-C(24)-C(25)	-120.8(6)
C(12)-C(13)-C(24)-C(25)	63.6(8)
N(4)-C(13)-C(24)-C(29)	60.7(8)
C(12)-C(13)-C(24)-C(29)	-114.9(6)

C(29)-C(24)-C(25)-C(26)	1.9(11)
C(13)-C(24)-C(25)-C(26)	-176.6(7)
C(24)-C(25)-C(26)-C(27)	0.5(13)
C(25)-C(26)-C(27)-C(28)	-1.5(13)
C(26)-C(27)-C(28)-C(29)	0.3(11)
C(25)-C(24)-C(29)-C(28)	-3.2(10)
C(13)-C(24)-C(29)-C(28)	175.3(6)
C(27)-C(28)-C(29)-C(24)	2.1(10)
N(2)-C(20)-C(30)-C(35)	-130.6(5)
C(21)-C(20)-C(30)-C(35)	47.3(6)
N(2)-C(20)-C(30)-C(31)	51.2(7)
C(21)-C(20)-C(30)-C(31)	-130.9(5)
C(35)-C(30)-C(31)-C(32)	1.2(7)
C(20)-C(30)-C(31)-C(32)	179.4(5)
C(30)-C(31)-C(32)-C(33)	-0.2(8)
C(31)-C(32)-C(33)-C(34)	-0.7(8)
C(32)-C(33)-C(34)-C(35)	0.4(8)
C(33)-C(34)-C(35)-C(30)	0.7(8)
C(31)-C(30)-C(35)-C(34)	-1.5(8)
C(20)-C(30)-C(35)-C(34)	-179.8(5)
C(36)-C(22)-N(1)-C(5)	-1.4(7)
C(21)-C(22)-N(1)-C(5)	178.1(4)
C(36)-C(22)-N(1)-Mo(1)	-179.9(4)
C(21)-C(22)-N(1)-Mo(1)	-0.4(6)
C(6)-C(5)-N(1)-C(22)	97.9(6)
C(10)-C(5)-N(1)-C(22)	-82.8(6)
C(6)-C(5)-N(1)-Mo(1)	-83.5(5)
C(10)-C(5)-N(1)-Mo(1)	95.9(5)
C(30)-C(20)-N(2)-C(19)	1.7(7)
C(21)-C(20)-N(2)-C(19)	-176.2(4)
C(30)-C(20)-N(2)-Mo(1)	174.1(3)
C(21)-C(20)-N(2)-Mo(1)	-3.7(6)
C(14)-C(19)-N(2)-C(20)	79.6(5)
C(18)-C(19)-N(2)-C(20)	-101.2(5)
C(14)-C(19)-N(2)-Mo(1)	-93.4(4)
C(18)-C(19)-N(2)-Mo(1)	85.8(4)

C(12)-C(11)-N(3)-C(10)	176.6(5)
C(23)-C(11)-N(3)-C(10)	-7.2(9)
C(5)-C(10)-N(3)-C(11)	136.9(6)
C(9)-C(10)-N(3)-C(11)	-50.4(9)
C(12)-C(13)-N(4)-C(14)	178.2(5)
C(24)-C(13)-N(4)-C(14)	2.9(8)
C(19)-C(14)-N(4)-C(13)	-144.4(5)
C(15)-C(14)-N(4)-C(13)	36.6(8)

Table S2. Comparison of important bond lengths of X-ray structure and geometry optimization

Bond/Interaction	Experimental (Å)	Theoretical (Å)
Mo1—N1	2.265(4)	2.335
Mo1—N2	2.258(4)	2.341
Mo1—C1	2.032(6)	2.066
Mo1—C3	1.962(4)	1.990
Mo1—C2	2.040(5)	2.056
Mo1—C4	1.949(5)	1.989
C21···C2	3.288(7)	3.281
H21A···C2	2.54	2.376
C29···C_g	3.524(6)	3.760
H29···*Cg*	2.605	2.717

Table S3. Optimized Cartesian coordinates of **1**.

C	1.84511500	-0.04620300	-1.97811200
C	3.16446600	-2.48497400	1.05027100
C	4.26583400	-0.79154500	-0.82169400
C	2.39416700	-2.75270000	-1.58594700
C	2.64284800	1.85718200	0.67514000
C	4.01509500	2.09028800	0.77624900
H	4.64014200	1.33714400	1.24518600
C	4.57656400	3.25593200	0.25670600
H	5.64622800	3.42343500	0.33851400
C	3.75984300	4.17858700	-0.39892700

H	4.19034800	5.07011500	-0.84663000
C	2.38887100	3.95468000	-0.49776200
H	1.77168200	4.65473300	-1.04943600
C	1.78581100	2.81011700	0.06327800
C	-0.55839300	3.35013900	0.00611700
C	-1.90566600	2.91452300	-0.26404900
H	-2.68746500	3.65355300	-0.13578800
C	-2.32343700	1.64376400	-0.62304300
C	-1.56796400	-0.67429200	-1.25279100
C	-2.38591200	-0.93983800	-2.36160000
H	-2.95425000	-0.13047300	-2.80365400
C	-2.45721000	-2.21913900	-2.90604800
H	-3.09848200	-2.39843100	-3.76413200
C	-1.68429100	-3.25356800	-2.37472800
H	-1.71919500	-4.24851800	-2.80785800
C	-0.83741100	-2.99662800	-1.29904400
H	-0.19740900	-3.77654900	-0.89949400
C	-0.78570500	-1.72590500	-0.72098400
C	-0.25450900	-1.24864400	1.54697600
C	0.78967200	-0.79853900	2.56023200
H	1.58541000	-1.55750700	2.56426700
H	0.35290700	-0.75949100	3.55926500
C	1.41779700	0.53592700	2.20033200
C	-0.42114200	4.81615900	0.39268400
H	-1.29460000	5.12971400	0.97349800
H	-0.37857000	5.45992200	-0.49488800
H	0.48091400	5.00082700	0.98069900
C	-3.78005000	1.41181400	-0.83850300
C	-4.51932600	2.29853200	-1.63758800
H	-4.00607600	3.11328800	-2.13966000
C	-5.89369000	2.12637300	-1.80634400
H	-6.44914800	2.81616300	-2.43596300
C	-6.55009800	1.06944000	-1.17339500
H	-7.62041100	0.93455000	-1.30387700
C	-5.82271300	0.18397100	-0.37381500
H	-6.32607500	-0.63857800	0.12696500

C	-4.44866000	0.34833300	-0.20987000
H	-3.89352900	-0.34196200	0.41496300
C	-1.64393100	-1.43376200	2.05493200
C	-2.37435000	-2.60262800	1.77726600
H	-1.94272100	-3.37080000	1.14697800
C	-3.64269100	-2.79228300	2.32562700
H	-4.18581200	-3.70833900	2.11116300
C	-4.20916300	-1.81731600	3.14966200
H	-5.19774500	-1.96775400	3.57441000
C	-3.49453800	-0.65071100	3.43131600
H	-3.92750100	0.11577700	4.06776000
C	-2.21936600	-0.46751500	2.89981200
H	-1.67524700	0.44436100	3.12670300
C	1.16781800	1.68762200	3.13989500
H	1.83601200	2.52667600	2.94013100
H	1.29916000	1.36137900	4.17816600
H	0.13439100	2.04336500	3.03645700
N	2.11274400	0.60095300	1.11901300
N	0.15259500	-1.45989400	0.33524300
N	0.43086900	2.49254600	-0.05090000
N	-1.43345300	0.60953500	-0.68481100
O	1.64144500	0.53506400	-2.95646200
O	3.70013600	-3.25593400	1.73331300
O	5.37343000	-0.54770200	-1.08305700
O	2.39128900	-3.67260400	-2.30038700
Mo	2.37635800	-1.19751100	-0.34633800
H	-0.48181100	0.91311000	-0.42809100

Table S4. G03/B3LYP calculated one-electron energy and percentage composition of selected frontier MOs of **1** in terms of component fragments

MO	Orbital	Energy (eV)	$Mo(CO)_4$	$Me_2Ph_2H_2TAA$
244	LUMO + 3	-0.60	3.3	96.7
243	LUMO + 2	-0.83	10.3	89.7
242	LUMO + 1	-1.57	1.2	98.8
241	**LUMO**	**-1.87**	**9.8**	**90.2**
240	**HOMO**	**-5.01**	**85.6**	**14.4**
239	HOMO – 1	-5.30	93.4	6.6
238	HOMO – 2	-5.35	91.5	8.5
237	HOMO – 3	-5.58	7.2	92.8