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Short Intramolecular N–H···C(carbonyl) Interactions in Mixed-Ligand Molybdenum Hexacarbonyl Derivatives

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Abstract: The syntheses and single-crystal structures of $Mo(CO)_3(phen)(dipy)$ (**1**), $Mo(CO)_3(biquin)(dipy)$ (**2**) and $Mo(CO)_3(dpme)(dipy)$ (**3**), (phen = 1,10-phenanthroline, $C_{12}H_8N_2$; dipy = 2,2′-dipyridylamine, $C_{10}H_9N_3$; biquin = 2,2′-biquinoline, $C_{18}H_{12}N_2$; dpme = 2,2′-dipyridylmethane, $C_{11}H_{10}N_2$) are described. In each case, distorted *fac*-MoC_3N_3 octahedral coordination geometries arise for the metal atoms. Short intramolecular N–H···C interactions from the dipy N–H group to a carbonyl carbon atom occur in each structure. Crystal data: **1** ($C_{25}H_{17}MoN_5O_3$), $M_r = 531.38$, monoclinic, $P2_1/n$ (No. 14), $Z = 4$, $a = 11.0965$ (5) Å, $b = 13.0586$ (6) Å, $c = 16.6138$ (8) Å, $\beta = 108.324$ (1)°, $V = 2285.31$ (18) Å^3, $R(F) = 0.035$, $wR(F^2) = 0.070$. **2** ($C_{31}H_{21}MoN_5O_3$), $M_r = 607.47$, monoclinic, $P2_1/n$ (No. 14), $Z = 4$, $a = 11.4788$ (6) Å, $b = 19.073$ (1) Å, $c = 11.9881$ (6) Å, $\beta = 95.179$ (1)°, $V = 2613.9$ (2) Å^3, $R(F) = 0.030$, $wR(F^2) = 0.076$. **3** ($C_{24}H_{19}MoN_5O_3$), $M_r = 521.38$, monoclinic, $P2_1/n$ (No. 14), $Z = 4$, $a = 8.4222$ (3) Å, $b = 21.5966$ (9) Å, $c = 12.5011$ (5) Å, $\beta = 94.065$ (1)°, $V = 2268.12$ (15) Å^3, $R(F) = 0.025$, $wR(F^2) = 0.065$.

Keywords: metal carbonyls; molybdenum; back bonding; intramolecular interactions

1. Introduction

Transition metal carbonyls are one of the most familiar families of organometallic compounds, and inorganic chemists have studied them intensively for some 120 years, since the serendipitous discovery

of nickel carbonyl, $Ni(CO)_4$, in 1890 [1]. Substituted carbonyls, in which one or more of the CO molecules are replaced by incoming ligand(s), represent an even larger family. Crystallographic studies have played a vital role in characterizing these compounds. The main focus has understandably been on determining the stereochemistry of the product (for example, whether a bi-substituted octahedral carbonyl adopts a *cis* or *trans* $M(CO)_4L_2$ geometry [2] or whether a tri-substituted $M(CO)_3L_3$ species forms the *mer* or the *fac* isomer [3]), and in detailed consideration of the metal–ligand, metal–carbon and C–O bond lengths in terms of electronic-structure models of back bonding [4]. Despite this intensive study over many decades, it is notable that the crystal structures of some very simple substituted carbonyls, such as $Mo(CO)_4(bipy)$ (bipy = 2,2′-bipyridine, $C_{10}H_8N_2$; see Figure 1 below) [5], and $Mo(CO)_4(biquin)$ (biquin = 2,2′-biquinoline, $C_{18}H_{12}N_2$) [6] have been determined only very recently. These bidentate ligands naturally can only lead to *cis* isomers.

Further substitution of the carbonyl ligands is possible and $Mo(CO)_2(bipy)_2$ [4] and $Mo(CO)_2(phen)_2$ (phen = 1,10-phenanthroline, $C_{12}H_8N_2$) [7] both show a *cis* disposition of the two remaining carbonyl ligands. An interesting ligand in this area of chemistry is dipy (2,2′-dipyridylamine, $C_{10}H_9N_3$): due to its flexible –NH– linking group between the pyridyl rings, it can bond as a bidentate ligand in a similar fashion to bipy as seen in $Mo(CO)_4(dipy)$ [8] or possibly facilitate the formation of polymeric species in which each of the aromatic N atoms bonds to a different metal atom [9].

In this paper, we describe the syntheses and structures of three substituted molybdenum carbonyls, namely, $Mo(CO)_3(phen)(dipy)$ (**1**), $Mo(CO)_3(biquin)(dipy)$ (**2**) and $Mo(CO)_3(dpme)(dipy)$ (**3**), (dpme = 2,2′-dipyridylmethane, $C_{11}H_{10}N_2$) in which three CO ligands have been replaced by three aromatic-N atoms from the various ligands just mentioned. We also describe an unusual intramolecular N–H⋯C interaction in each compound and compare them with related compounds.

Figure 1. N-heterocyclic ligands used in this study.

bipy   phen   dipy

biquin   dpme
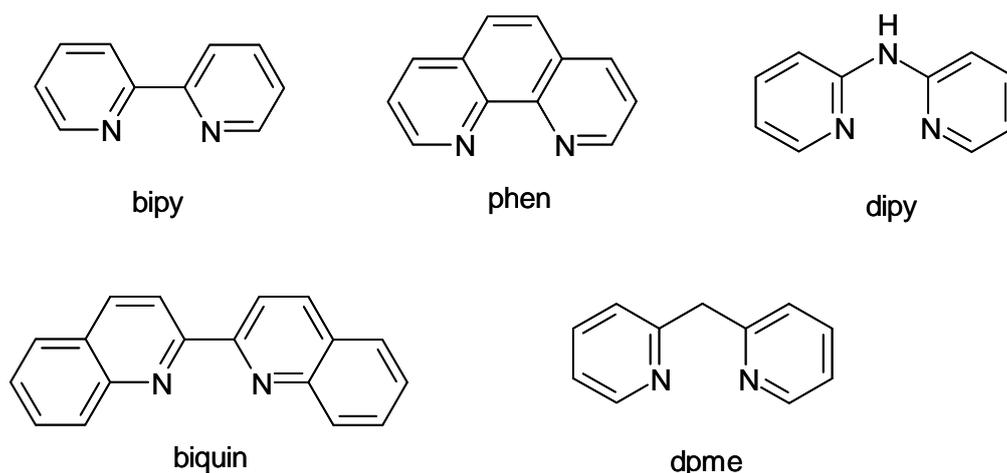
2. Results and Discussion

The data collections, structure solutions and refinements were straightforward (see experimental section): all three compounds crystallize in the monoclinic space group $P2_1/n$ (No. 14) with $Z = 4$. Their crystal structures indicate that three CO molecules in the $Mo(CO)_6$ starting material have been replaced in each case.

2.1. Structure of Mo(CO)₃(phen)(dipy)

Compound **1** (Figure 2, Table 1) shows a distorted *fac*-MoC₃N₃ geometry about the metal atom, as also seen for related compounds [10]. The N–Mo–N bite angle of the phen ligand is 73.07 (6)°, compared to a value of 73.62 (7)° in Mo(CO)₄(phen) [11].

The mean Mo–C bond distance of 1.932 (3) Å in **1** is significantly less that the corresponding value of 2.057 (2) Å for Mo(CO)₆ [12]: according to the classical back-bonding model for metal carbonyls, this can be rationalized in terms of a substantial transfer of electrons from the Mo 4*d* orbitals to the CO antibonding π* orbitals [13], which enhances the double-bond character of the Mo–C bond and therefore shortens it. But because electrons are being "fed" into the CO antibonding orbitals, this effect should *lengthen* the C–O bond at the same time; the mean value of 1.165 (3) Å in **1** compares to 1.128 (4) Å in Mo(CO)₆ [12], *i.e.* the metal electrons are being "shared out" amongst fewer C–O antibonding orbitals in **1** than in Mo(CO)₆, therefore they are lengthened to a greater extent. The fact that Mo1–C1 and Mo1–C2 (both *trans* to phen-N atoms) are slightly longer than Mo1–C3 (*trans* to the bonded dipy N atom) might correlate with the different (weak) π-acceptor characters of the pyridine rings *trans* to the C atoms in question [4], although packing effects cannot be ruled out for the small differences seen here.

The phen ligand in **1** is close to planar (r.m.s. deviation = 0.022 Å for the 14 non-hydrogen atoms) and the metal atom deviates by −0.1905 (18) Å from its mean plane. The N3/C16–C20 ring of the dipy ligand makes a dihedral angle of 79.56 (9)° with the phen ring and the Mo atom is displaced by −0.280 (3) Å from the N3/C16–C20 mean plane. The dihedral angle between the two rings of the dipy ligand is 31.79 (10)°. The intramolecular C–H···N interactions in **1** are discussed below.

In the crystal of **1**, three weak C–H···O interactions (Table 1) link the molecules (in which O3 accepts all three bonds) and an aromatic π–π stacking interaction occurs between inversion-symmetry related C7–C10/C15/C14 rings with a centroid–centroid separation of 3.6509 (15) Å and a slippage [11] of 0.358 Å. The next-shortest π–π centroid separation is greater than 4.0 Å.

Figure 2. The molecular structure of **1** showing 50% displacement ellipsoids for the non-hydrogen atoms. The short intramolecular C–H···N and N–H···C interactions are shown as double-dashed lines.
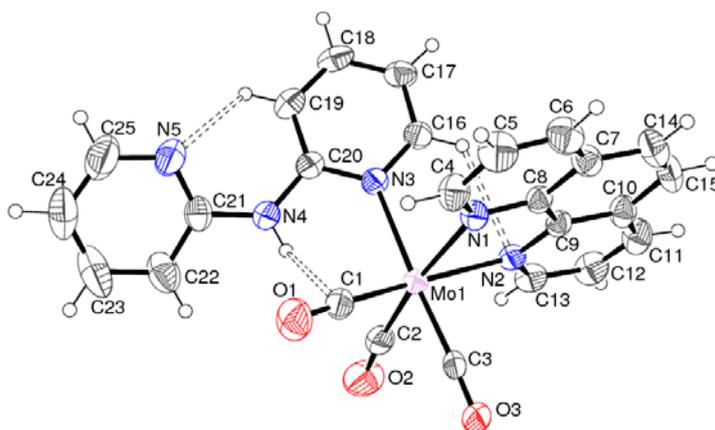
Table 1. Selected geometrical data (Å, °) for **1**.

Mo1–C3	1.922 (2)	Mo1–C1	1.936 (2)
Mo1–C2	1.937 (3)	Mo1–N1	2.2440 (17)
Mo1–N2	2.2564 (17)	Mo1–N3	2.3620 (18)
C1–O1	1.173 (3)	C2–O2	1.168 (3)
C3–O3	1.155 (3)		

C3–Mo1–C1	84.98 (10)	C3–Mo1–C2	81.32 (10)
C1–Mo1–C2	90.15 (10)	C3–Mo1–N1	94.72 (8)
C1–Mo1–N1	96.99 (8)	C2–Mo1–N1	171.54 (9)
C3–Mo1–N2	89.50 (8)	C1–Mo1–N2	168.22 (8)
C2–Mo1–N2	99.31 (8)	N1–Mo1–N2	73.07 (6)
C3–Mo1–N3	176.97 (7)	C1–Mo1–N3	97.69 (8)
C2–Mo1–N3	100.05 (8)	N1–Mo1–N3	83.56 (6)
N2–Mo1–N3	87.62 (6)		

N4–H4⋯C1	0.82 (2)	2.36 (2)	2.956 (3)	131 (2)
C16–H16⋯N2	0.93	2.52	3.171 (3)	127
C19–H19⋯N5	0.93	2.41	2.937 (3)	116
C11–H11⋯O3[i]	0.93	2.53	3.125 (3)	122
C14–H14⋯O3[ii]	0.93	2.58	3.231 (4)	128
C18–H18⋯O3[iii]	0.93	2.36	3.258 (4)	163

Symmetry codes: (i) $1-x$, $-y$, $1-z$; (ii) $\frac{1}{2}+x$, $\frac{1}{2}-y$, $\frac{1}{2}+z$; (iii) $x-\frac{1}{2}$, $\frac{1}{2}-y$, $\frac{1}{2}+z$.

2.2. Structure of Mo(CO)₃(biquin)(dipy)

The structure of **2** has many similarities to that of **1** but also some important differences: again, a distorted *fac*-MoC$_3$N$_3$ octahedral coordination geometry arises for the metal atom (Figure 3, Table 2). The bite angle for the N atoms of the biquin ligand in **2** is 71.80 (8)° compared to 72.31 (6)° for the equivalent atoms in Mo(CO)$_4$(biquin) [6].

The bond lengths about the Mo atom in **2** show similar trends to the equivalent data for **1**: the mean Mo–C distance of 1.942 (3) Å is slightly longer than that in **1**, whereas the mean C–O separation of 1.169 (3) Å in **2** is statistically indistinguishable from the equivalent value for **1**. There is no obvious correlation between the Mo–C bond lengths in **2** and the identity of the ligand lying *trans* to the bond in question.

With respect to the biquin ligand in **2**, the Mo atom is substantially displaced from the N4/C14–C22 (r.m.s. deviation = 0.036 Å) and N5/C23–C31 (r.m.s. deviation = 0.059 Å) mean planes by 0.837 (3) Å and 0.633 (3) Å, respectively. The dihedral angle between the quinoline residues is 11.47 (11)°. An alternative geometric analysis, just considering the N4/C14/C19–C22 and N5/C23–C26/C31 pyridine rings, indicates that Mo is displaced from them by 0.812 (4) and 0.476 (4) Å, respectively. The bridging C22–C23 bond length is 1.485 (4) Å, which indicates little or no conjugation effects between the quinoline rings: a similar bond length of 1.474 (3) Å occurs in Mo(CO)$_4$(biquin) [6].

The dihedral angle between the N1- and N3-rings of the dipy ligand in **2** is 2.38 (10)°, indicating their near co-planarity, which is quite different to the situation in **1**, where the same ligand is substantially twisted. Mo1 deviates from the N1-ring by 0.168 (4) Å. These large metal-atom–ring deviations in **2** are perhaps a reflection of significant steric crowding of the ligands. The intramolecular C–H···N interactions in **1** are discussed below.

Figure 3. The molecular structure of **2** showing 50% displacement ellipsoids. The short intramolecular C–H···N interactions and N–H···C are shown as double-dashed lines. For clarity, H atoms not involved in these interactions are omitted.

Table 2. Selected geometrical data (Å, °) for **2**.

Mo1–C3	1.934 (3)	Mo1–C1	1.938 (3)
Mo1–C2	1.953 (3)	Mo1–N5	2.270 (2)
Mo1–N4	2.298 (2)	Mo1–N1	2.370 (2)
C1–O1	1.173 (3)	C2–O2	1.158 (3)
C3–O3	1.175 (3)		

C3–Mo1–C1	83.22 (11)	C3–Mo1–C2	81.12 (11)
C1–Mo1–C2	87.17 (11)	C3–Mo1–N5	103.62 (10)
C1–Mo1–N5	96.25 (10)	C2–Mo1–N5	174.43 (9)
C3–Mo1–N4	174.15 (10)	C1–Mo1–N4	100.73 (9)
C2–Mo1–N4	103.27 (10)	N5–Mo1–N4	71.80 (8)
C3–Mo1–N1	96.26 (9)	C1–Mo1–N1	176.67 (9)
C2–Mo1–N1	89.50 (9)	N5–Mo1–N1	87.07 (7)
N4–Mo1–N1	80.04 (7)		

N2–H2···C3	0.73 (3)	2.60 (3)	3.246 (3)	149 (3)
C7–H7···N3	0.93	2.29	2.894 (4)	122
C13–H13···O2^i	0.93	2.57	3.365 (4)	144
C28–H28···O2^{ii}	0.93	2.59	3.384 (4)	143

Symmetry codes: (i) 1–*x*, 1–*y*, 1–*z*; (ii) *x*–½, ½–*y*, *z*+½

In the crystal of **2**, two C–H···O interactions to the same acceptor O atom occur (Table 2) and a weak aromatic π–π stacking interaction between the N4/C14/C19–C22 and the C14–C19 rings occurs [centroid–centroid separation = 3.7570 (17) Å] is seen.

2.3. Structure of Mo(CO)$_3$(dpme)(dipy)

The structure of **3** (Figure 4, Table 3) again reveals a distorted *fac*-MoC$_3$N$_3$ octahedral geometry for the metal atom. The bite angle for the dpme ligand is 81.18 (6)° and the Mo atom deviates from the N1-ring by −0.058 (3) Å and from the N2-ring by −0.072 (4) Å. The dihedral angle between the pyridine rings in the dpme ligand is 51.58 (9)° and the bridging methylene-group C atom deviates from the N1- and N2-rings by −0.074 (4) and −0.004 (4) Å, respectively.

The bond lengths about the Mo atom in **3** show similar trends to the equivalent data for **1** and **2**: the mean Mo–C distance of 1.936 (3) Å in **3** is indistinguishable from that in **1**, and very slightly shorter than that in **2**. The mean C–O separation of 1.171 (3) Å in **3** is statistically indistinguishable from the equivalent values for **1** and **2**. However, it is perhaps notable that all three C–O bond lengths in **3** are essentially identically, which does seem to correlate with the fact that the three *trans* ligands are all (electronically) isolated pyridine rings.

Figure 4. The molecular structure of **3** showing 50% displacement ellipsoids. The short intramolecular C–H···N and N–H···C interactions are shown as double-dashed lines. For clarity, H atoms not involved in these interactions are omitted.
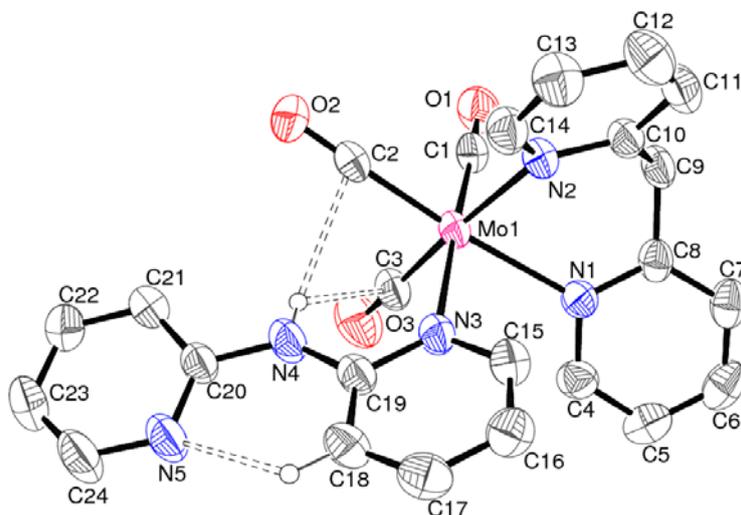
The dihedral angle between the rings of the dipy ligand is 13.69 (13)°, indicating a conformation intermediate between those in **1** and **2**. The molybdenum atom deviates from the N3-ring mean plane by 0.127 (4) Å. These data suggest that there is significantly less steric hindrance in **3** than in **2**, which is hardly unexpected. The intramolecular interactions in **3** are discussed below.

In the crystal of **3**, there are no intermolecular C–H···O interactions, unlike the situation in **1** and **2**. Inversion related N1/C4–C8 rings are disposed at a centroid–centroid separation of 3.6045 (14) Å (slippage = 0.793 Å) [14] and a weaker interaction between the N2/C10–C14 and N5/C20–C24 rings [centroid–centroid separation = 3.8686 (16) Å, inter-planar angle = 3.44°] also occurs.

Table 3. Selected geometrical data (Å, °) for **3**.

Mo1–C1	1.929 (3)	Mo1–C2	1.940 (2)
Mo1–C3	1.940 (3)	Mo1–N2	2.2788 (18)
Mo1–N1	2.2908 (18)	Mo1–N3	2.3719 (18)
C1–O1	1.168 (3)	C2–O2	1.171 (3)
C3–O3	1.173 (3)		

C1–Mo1–C2	83.78 (9)	C1–Mo1–C3	83.69 (10)
C2–Mo1–C3	88.41 (10)	C1–Mo1–N2	96.47 (8)
C2–Mo1–N2	94.96 (8)	C3–Mo1–N2	176.63 (8)
C1–Mo1–N1	94.22 (8)	C2–Mo1–N1	175.45 (8)
C3–Mo1–N1	95.45 (8)	N2–Mo1–N1	81.18 (7)
C1–Mo1–N3	177.83 (8)	C2–Mo1–N3	98.30 (8)
C3–Mo1–N3	96.97 (8)	N2–Mo1–N3	82.75 (6)
N1–Mo1–N3	83.66 (6)		

N4–H4···C2	0.78 (3)	2.38 (3)	3.083 (3)	151 (3)
N4–H4···C3	0.78 (3)	2.59 (3)	3.175 (3)	133 (2)
C18–H18···N5	0.93	2.37	2.959 (3)	121

2.4. Intramolecular interactions

The intramolecular interactions in **1**, **2** and **3** listed in the Tables above are worthy of special attention. Each structure features a C–H···N bond within the dipy ligand. This type of "non-classical" hydrogen bond has been accepted as a "real" interaction for 30 years [15] and a similar example within the dipy ligand also occurs in Mo(CO)$_3$(dipy)(bipy) [16], which correlates with the approximate *anti* orientation of the N atoms of the aromatic rings in that compound, as also seen for **1**, **2** and **3**. Structure **1** also features a similar interaction from a dipy C–H donor to a phen N-atom acceptor.

Each structure also shows a far less expected interaction: a remarkably short N–H···C contact, where the C atom is part of one of the carbonyl groups attached to the metal atom. In each case the position of the H atom was freely refined to achieve the best possible estimate for its geometry. The Bondi [17] contact distance for C and H is about 2.90 Å, thus the shortest such contact (in **1**) of 2.36 (2) Å is some 0.54 Å shorter than the van der Waals' separation. The situation in **3** could be regarded as a bifurcated N–H···(C,C) interaction.

A survey of the Cambridge Structural Database [18] (version 5.32 of November 2010 with two updates) was made to determine if other organometallic structures showed similar intramolecular N–H···C(carbonyl) contacts (Table 4). The search cut-offs were an H···C separation of less than 2.50 Å and an N–H···C angle of greater than 120°.

Table 4. Short intramolecular N–H⋯C(carbonyl) interactions.

CCDC Refcode	Metal	N–H	H⋯C	N⋯C	N–H⋯C	Ref.
ALODOU	Mo	0.86	2.32	3.152	164	[19]
DOCBEC01	Mo	0.75	2.40	2.978	135	[16]
EBISUD	Mo	0.76	2.48	3.237	171	[20]
GIJKAL	Os	1.04	2.31	3.014	123	[21]
GOBMUF	Mo	0.89	2.45	3.267	153	[22]
GOBNEQ	Mo	0.89	2.27	3.150	170	[22]
INUFUS	Ru	0.97	2.21	3.011	152	[23]
KOQBUN	W	0.92	2.30	3.154	154	[24]
OFAFOR	W	0.85	2.46	3.112	141	[25]
OHUDOK	Re	0.91	2.42	3.208	144	[26]
RUZDEV	Mo	0.86	2.49	3.087	127	[27]
TERVIW	Re	0.77	2.42	3.035	138	[28]
XAWKAI	Cr	0.93	2.31	3.148	150	[29]
XAWKEM	Mo	0.93	2.38	3.203	148	[29]
XAWKIQ	W	0.93	2.39	3.207	149	[29]
ZOMRAU	Re	0.68	2.46	3.064	148	[30]

These data indicate that short intramolecular N–H⋯C(carbonyl) contacts occur in a wide range of structures, with many different ligands (containing the N–H grouping) and metals involved. This interaction, which appears to be more than a steric contact, is puzzling and theoretical analysis of the bonding might give further insights.

3. Experimental Section

Compounds **1**, **2** and **3** were synthesized by standard techniques in organometallic chemistry [19]. Stoichiometric quantities of $Mo(CO)_6$, dipy and the appropriate second ligand were refluxed in toluene under a nitrogen atmosphere for six to seven hours and cooled to room temperature. Product recovery by vacuum filtration and rinsing with light petroleum ether gave single-crystal products in each case.

The single-crystal data for **1**, **2** and **3** were collected on a Bruker SMART CCD diffractometer (graphite monochromated Mo Kα radiation, λ = 0.71073 Å) at room temperature. Suitable crystals were selected and mounted on thin glass fibers with cyanoacrylate adhesive. After preliminary scans indicated good crystal quality and established initial unit cells, intensity data were collected with the aid of the SMART program. Data reduction with SAINT then proceeded in each case and empirical (multi-scan) absorption corrections were applied with SADABS, as summarized in the paragraphs below. The systematic absences uniquely identified the space group as $P2_1/n$ (No. 14) in each case and the structures were solved by direct methods with SHELXS and the atomic models refined against $|F|^2$ with SHELXL [20]. The "observed data" threshold for calculating the $R(F)$ residuals was set as $I > 2\sigma(I)$. All the non-hydrogen atoms were routinely located during the refinements and modeled with anisotropic displacement factors and in final difference maps most of the H atoms were visible. The carbon-bound H atoms were relocated to idealized locations (C–H = 0.93–0.97 Å) and further refined as riding atoms with the constraint $U_{iso}(H) = 1.2U_{eq}(C)$ applied. The positions of the N-bound H atoms

of the dipy ligands were freely refined from their difference-map locations and the constraint $U_{iso}(H) = 1.2U_{eq}(N)$ was applied in each case. Full details are given in the deposited cifs.

Crystal data for **1**: very dark red chunk, $0.22 \times 0.20 \times 0.13$ mm, $C_{25}H_{17}MoN_3O_5$, $M_r = 531.38$, monoclinic, $P2_1/n$ (No. 14), $a = 11.0965$ (5) Å, $b = 13.0586$ (6) Å, $c = 16.6135$ (8) Å, $\beta = 108.324$ (1)°, $V = 2285.31$ (18) Å^3, $Z = 4$, $F(000) = 1072$, $T = 293$ K, $\rho_{calc} = 1.544$ g cm^{-3}, $\mu = 0.611$ mm^{-1}, $T_{min} = 0.877$, $T_{max} = 0.925$, 19982 reflections measured ($-8 \le h \le 15$, $-18 \le k \le 18$, $-23 \le l \le 23$; 3.92° $\le 2\theta \le 60.14$°), $R_{Int} = 0.040$, 6642 merged reflections, 4201 with $I > 2\sigma(I)$, 310 parameters, $R(F) = 0.035$, $wR(F^2) = 0.070$, $w = 1/[\sigma^2(F_o^2) + 0.0280P^2]$, where $P = (F_o^2 + 2 F_c^2)/3$, min./max. $\Delta\rho = -0.65, +0.42$ e Å^{-3}. Cambridge Database deposition number: CSD-823643.

Crystal data for **2**: dark green chunk, $0.39 \times 0.26 \times 0.15$ mm, $C_{31}H_{21}MoN_3O_5$, $M_r = 607.47$, monoclinic, $P2_1/n$ (No. 14), $a = 11.4788$ (6) Å, $b = 19.073$ (1) Å, $c = 11.9881$ (6) Å, $\beta = 95.179$ (1)°, $V = 2613.9$ (2) Å^3, $Z = 4$, $F(000) = 1232$, $T = 296$ K, $\rho_{calc} = 1.544$ g cm^{-3}, $\mu = 0.546$ mm^{-1}, $T_{min} = 0.815$, $T_{max} = 0.924$, 15449 reflections measured ($-13 \le h \le 13$, $-21 \le k \le 22$, $-11 \le l \le 14$; 4.02° $\le 2\theta \le 50.08$°), $R_{Int} = 0.033$, 4620 merged reflections, 3915 with $I > 2\sigma(I)$, 364 parameters, $R(F) = 0.030$, $wR(F^2) = 0.076$, $w = 1/[\sigma^2(F_o^2) + 0.0384P^2 + 1.292P]$, where $P = (F_o^2 + 2 F_c^2)/3$, min./max. $\Delta\rho = -0.36, +0.50$ e Å^{-3}. Cambridge Database deposition number: CSD-823644.

Crystal data for **3**: dark orange block, $0.39 \times 0.19 \times 0.16$ mm, $C_{24}H_{19}MoN_3O_5$, $M_r = 521.38$, monoclinic, $P2_1/n$ (No. 14), $a = 8.4222$ (3) Å, $b = 21.5966$ (9) Å, $c = 12.5011$ (5) Å, $\beta = 94.065$ (1)°, $V = 2268.12$ (15) Å^3, $Z = 4$, $F(000) = 1056$, $T = 296$ K, $\rho_{calc} = 1.527$ g cm^{-3}, $\mu = 0.614$ mm^{-1}, $T_{min} = 0.828$, $T_{max} = 0.908$, 13657 reflections measured ($-10 \le h \le 8$, $-25 \le k \le 25$, $-14 \le l \le 14$; 3.78° $\le 2\theta \le 50.06$°), $R_{Int} = 0.024$, 3998 merged reflections, 3269 with $I > 2\sigma(I)$, 301 parameters, $R(F) = 0.025$, $wR(F^2) = 0.061$, $w = 1/[\sigma^2(F_o^2) + 0.0398P^2]$, where $P = (F_o^2 + 2 F_c^2)/3$, min./max. $\Delta\rho = -0.20, +0.25$ e Å^{-3}. Cambridge Database deposition number: CSD-823645.

4. Conclusions

We have prepared and structurally characterized Mo(CO)$_3$(phen)(dipy), Mo(CO)$_3$(biquin)(dipy) and Mo(CO)$_3$(dpme)(dipy). In each case, distorted *fac*-MoC$_3$N$_3$ octahedral coordination geometries arise for the molybdenum atoms. The Mo–C and C≡O distances are broadly understandable in terms of electronic models of back bonding. As might be expected on steric grounds, Mo(CO)$_3$(biquin)(dipy) shows the largest structural distortions. The crystal structures feature intermolecular C–H⋯O bonds and aromatic π–π stacking interactions. Short intramolecular N–H⋯C interactions from the dipy N–H group to a carbonyl carbon atom occur in each structure. A survey of the Cambridge Database indicated that these unusual interactions occur in a wide variety of organometallic compounds and they may be worthy of further theoretical analysis.

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