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Crystal structures of *trans*-acetyldicarbonyl-(η^5 -cyclopentadienyl)(1,3,5-triaza-7-phosphaadamantane)molybdenum(II) and *trans*-acetyldicarbonyl(η^5 -cyclopentadienyl)(3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane)molybdenum(II)

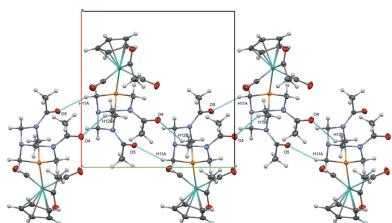
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The title compounds, $[\text{Mo}(\text{C}_5\text{H}_5)(\text{COCH}_3)(\text{C}_6\text{H}_{12}\text{N}_3\text{P})(\text{CO})_2]$, (1), and $[\text{Mo}(\text{C}_5\text{H}_5)(\text{COCH}_3)(\text{C}_9\text{H}_{16}\text{N}_3\text{O}_2\text{P})(\text{C}_6\text{H}_5)_2](\text{CO})_2$, (2), have been prepared by phosphine-induced migratory insertion from $[\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3(\text{CH}_3)]$. The molecular structures of these complexes are quite similar, exhibiting a four-legged piano-stool geometry with *trans*-disposed carbonyl ligands. The extended structures of complexes (1) and (2) differ substantially. For complex (1), the molybdenum acetyl unit plays a dominant role in the organization of the extended structure, joining the molecules into centrosymmetrical dimers through C—H \cdots O interactions with a cyclopentadienyl ligand of a neighboring molecule, and these dimers are linked into layers parallel to (100) by C—H \cdots O interactions between the molybdenum acetyl and the cyclopentadienyl ligand of another neighbor. The extended structure of (2) is dominated by C—H \cdots O interactions involving the carbonyl groups of the acetamide groups of the DAPTA ligand, which join the molecules into centrosymmetrical dimers and link them into chains along [010]. Additional C—H \cdots O interactions between the molybdenum acetyl oxygen atom and an acetamide methyl group join the chains into layers parallel to (101).

1. Chemical context

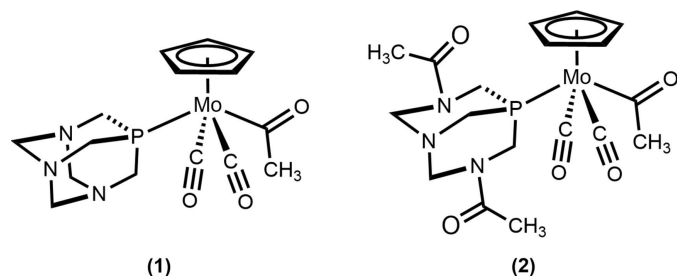
Cyclopentadienylmolybdenum polycarbonyl complexes $[\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_n]$ exhibiting 'four-legged piano-stool' geometries have been studied extensively for their electronic structure and organometallic reactivity (Kubacek *et al.*, 1982). Specifically, alkyl complexes of the form $\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_3(\text{R})$ have been shown to undergo carbonyl migratory insertion, affording acyl complexes upon exposure to L-type ligands, especially phosphines (Barnett & Treichel, 1967; Butler *et al.*, 1967). The steric bulk of the phosphine ligand strongly influences the stability of the resulting complexes, with bulkier groups exhibiting enhanced deinsertion rates (Barnett, 1969; Barnett & Pollmann, 1974).

We have previously described the solid-state structures of a number of four-legged piano-stool molybdenum acetyl complexes of the type $\text{Mo}(\text{PR}_3)(\text{C}_5\text{H}_5)(\text{CO})_2(\text{COCH}_3)$ derived from reaction of the molybdenum methyl precursor with various phosphines (Whited & Hofmeister, 2014). We have shown that the steric bulk of the phosphine substituents



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impacts the molecular structure of the insertion product in predictable ways, primarily evidenced through the Mo—P bond lengths and P—Mo—C bond angles (Whited *et al.*, 2012, 2014), consistent with earlier findings on reactivity. We have also shown that the use of tri(2-furyl)phosphine, which features heteroatoms as potential hydrogen-bond acceptors, leads to an unusual structure where the acetyl is oriented away from the Cp ring rather than toward it as in other cases (Whited *et al.*, 2013).



Here we report the structures of piano-stool molybdenum acetyl complexes with 1,3,5-triaza-7-phosphaadamantane (PTA) and 3,7-diacetyl-1,3,7-triaza-5-phospha-bicyclo[3.3.1]nonane (DAPTA) ligands featuring potential hydrogen-bond-accepting amines and carbonyl groups. The diacetylated ligand (DAPTA) shows little difference from PTA in local structure, but the introduction of acetamide groups dramatically impacts the supramolecular organization.

2. Structural commentary

The molecular structures of (1) and (2) are illustrated in Figs. 1 and 2. Both (1) and (2) exhibit a *trans* disposition of the carbonyl ligands, as seen for other compounds of this type. It was envisioned that incorporation of hydrogen-bond acceptors (amines and amides) might allow access to an alternate orientation of the acetyl group, as observed for a related structure featuring a tri(2-furyl)phosphine ligand, but instead the oxygen of the acetyl group points toward the Cp ring, consistent with other structures of related complexes.

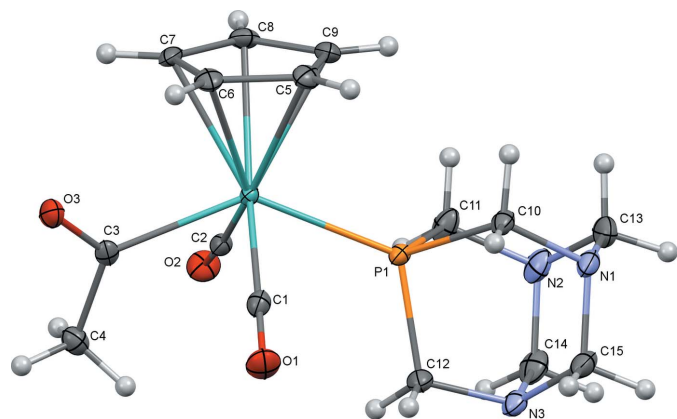


Figure 1
Molecular structure of (1) with ellipsoids at 50% probability.

Table 1
Selected geometric parameters (Å, °) for (1).

| | | | |
|-----------|-------------|-----------|-------------|
| Mo1—P1 | 2.4321 (5) | Mo1—C2 | 1.9746 (17) |
| Mo1—C1 | 1.9714 (17) | Mo1—C3 | 2.2398 (16) |
| C1—Mo1—P1 | 79.89 (5) | C2—Mo1—P1 | 78.80 (5) |
| C1—Mo1—C2 | 106.05 (7) | C2—Mo1—C3 | 78.51 (6) |
| C1—Mo1—C3 | 71.80 (6) | C3—Mo1—P1 | 136.77 (4) |

Table 2
Selected geometric parameters (Å, °) for (2).

| | | | |
|-----------|-------------|-----------|------------|
| Mo1—P1 | 2.4258 (6) | Mo1—C2 | 1.971 (2) |
| Mo1—C1 | 1.964 (2) | Mo1—C3 | 2.243 (2) |
| C1—Mo1—P1 | 77.10 (7) | C2—Mo1—P1 | 81.75 (7) |
| C1—Mo1—C2 | 108.47 (10) | C2—Mo1—C3 | 76.10 (9) |
| C1—Mo1—C3 | 72.63 (9) | C3—Mo1—P1 | 133.99 (6) |

Selected geometric parameters for (1) and (2) are presented in Tables 1 and 2. The Mo1—P1 bond lengths for PTA derivative (1) [2.4321 (5) Å] and DAPTA derivative (2) [2.4258 (6) Å] are similar to one another and slightly shorter than for the related complexes we have reported. This finding is consistent with the lower steric profile of the polycyclic PTA and DAPTA ligands relative to, for example, PPh₃, PMePh₂, and PMe₂Ph. The most significant molecular difference between (1) and (2) is seen in the C3—Mo1—P1 bond angle, which is larger for (1) [136.77 (4)°] than for (2) [133.99 (6)°].

3. Supramolecular features

Although the molecular structures of (1) and (2) are quite similar, the diacetylation of the phosphine ligand (transforming PTA to DAPTA) leads to significant differences in the extended structure. As was the case for several previously reported complexes of this sort with different phosphine ligands, the extended structure of (1) is dominated by interactions of atom O3 from the molybdenum acetyl. Short, non-classical C—H···O interactions between O3 and H8 of a

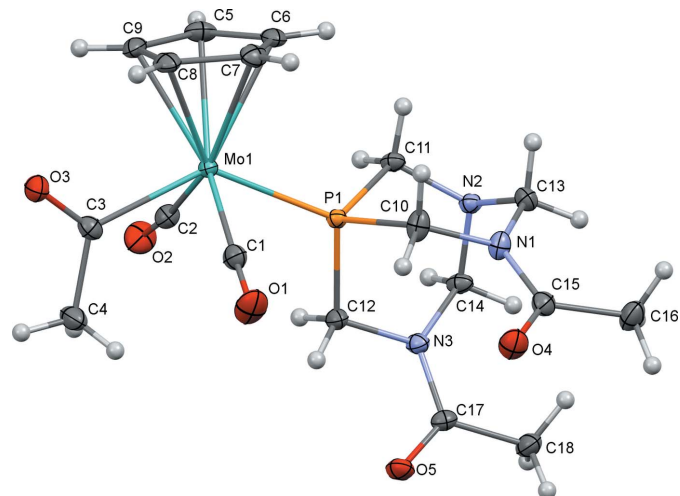


Figure 2
Molecular structure of (2) with ellipsoids at 50% probability.

Table 3
Hydrogen-bond geometry (Å, °) for (1).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-----------------------|-------|-------------|-------------|---------------|
| $C8-H8\cdots O3^i$ | 0.95 | 2.49 | 3.269 (2) | 139 |
| $C9-H9\cdots O3^{ii}$ | 0.95 | 2.37 | 3.284 (2) | 162 |

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

cyclopentadienyl (Cp) ring (2.49 Å) link (1) into centrosymmetrical dimers (Fig. 3). These dimers are further connected into layers parallel to (100) by non-classical C—H \cdots O hydrogen bonds between O3 and H9 (2.37 Å) (Table 3, Fig. 4). Although the PTA ligand features three nitrogen atoms as potential hydrogen-bond acceptors, these are not observed to play an important organizing structural role.

The acetamide groups of DAPTA, which are not present in PTA, play an important role in the extended structure of (2). Short, non-classical C—H \cdots O interactions between O4 of an

Table 4
Hydrogen-bond geometry (Å, °) for (2).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---------------------------|-------|-------------|-------------|---------------|
| $C7-H7\cdots O4^i$ | 0.93 | 2.45 | 3.353 (3) | 163 |
| $C11-H11A\cdots O5^{ii}$ | 0.97 | 2.41 | 3.211 (3) | 140 |
| $C12-H12B\cdots O4^{ii}$ | 0.97 | 2.60 | 3.409 (3) | 141 |
| $C13-H13A\cdots O5^{iii}$ | 0.97 | 2.57 | 3.474 (3) | 156 |
| $C13-H13B\cdots O3^{iv}$ | 0.97 | 2.46 | 3.261 (3) | 139 |

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

acetamide and H7 of a Cp ring (2.45 Å) link (2) into centrosymmetrical dimers (Table 4, Fig. 5). A combination of non-classical hydrogen bonds involving acetamide groups link (2) in chains along [010]: O5 \cdots H11A (2.41 Å) and O4 \cdots H12B (2.60 Å) (Fig. 6). These chains are further joined into layers parallel to (101) through the molybdenum acetyl group *via* a

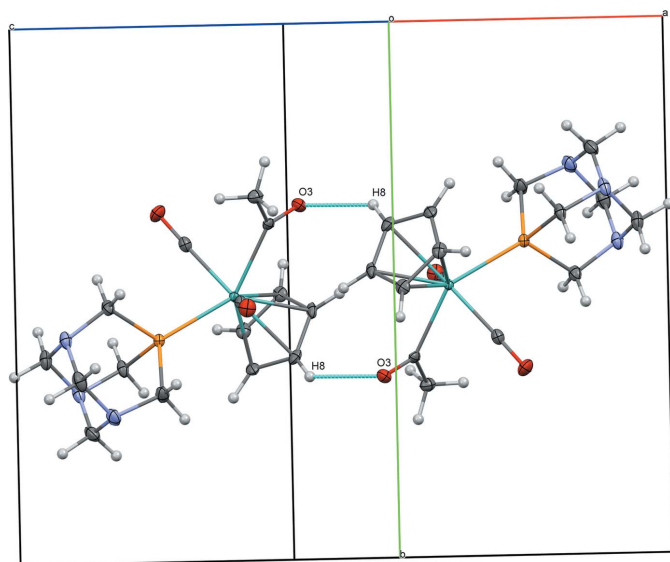


Figure 3
Centrosymmetrical dimer of (1), viewed perpendicular to (101).

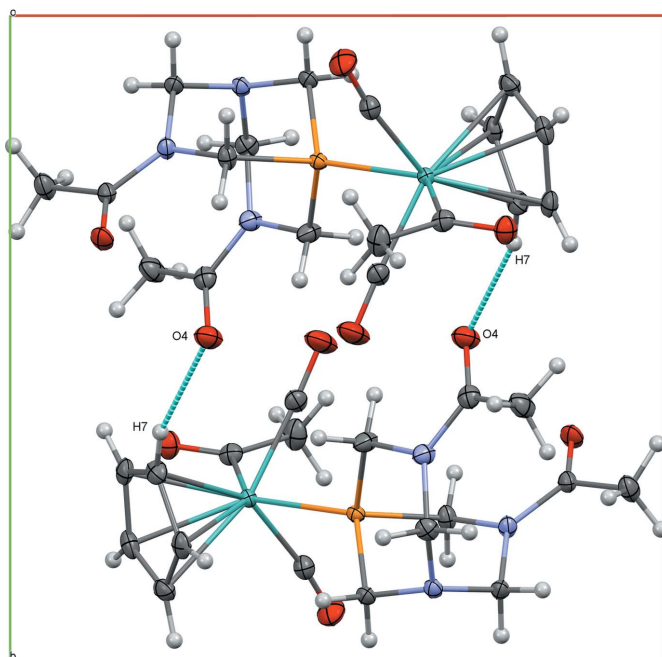


Figure 5
Centrosymmetrical dimer of (2), viewed along [001].

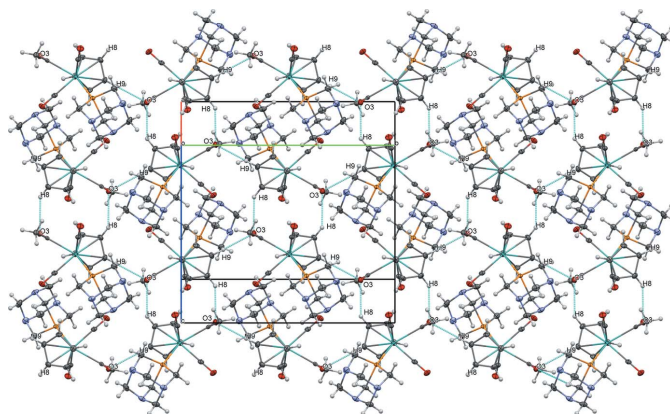


Figure 4
Layers of (1) formed by C—H \cdots O interactions, viewed perpendicular to (100).

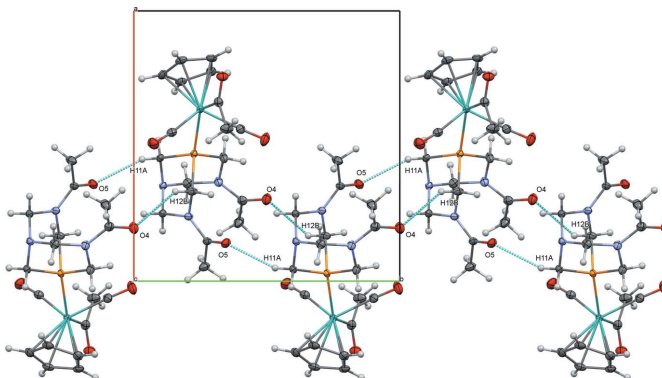


Figure 6
Chains of (2) along [010], viewed perpendicular to (010).

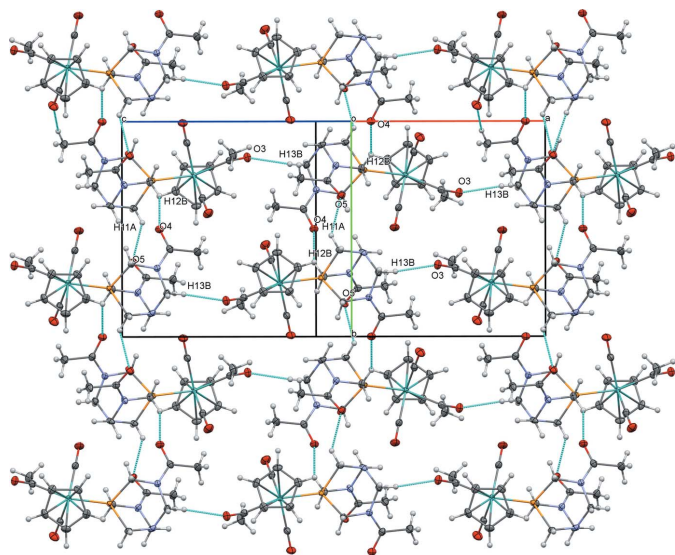


Figure 7
Layers of (2) formed by C—H...O interactions, viewed perpendicular to (101)

non-classical C—H...O interaction between O3 and H13B (2.46 Å) (Fig. 7). The extensive network of interactions involving all three acetyl groups likely contribute to the low solubility of (2) in most organic solvents.

4. Database survey

The current version of the Cambridge Structural Database (Version 5.40, updated August 2019; Groom *et al.*, 2016) has thirteen entries corresponding to molybdenum acyl complexes of the general form $\text{Mo}(\text{C}_5\text{H}_5)(\text{CO})_2(\text{PR}_3)(\text{COR})$. The *trans*-dicarbonyl structure, as observed for (1) and (2), is preferred except in cases where the phosphine and acyl ligands are covalently linked, forcing them to be *cis* (Adams *et al.*, 1991; Mercier *et al.*, 1993; Yan *et al.*, 2009).

The PTA and DAPTA ligands have not been extensively utilized on molybdenum. There are eight instances of the PTA ligand bonded to molybdenum or tungsten, five of which involve coordination of one or more of the ligand to an $\text{M}(\text{CO})_n$ center to afford an octahedral product. Most relevant to this study is the tungsten complex $\text{W}(\text{C}_5\text{H}_5)(\text{CO})_2(\text{PTA})\text{(H)}$, which is analogous to (1) and (2) but features a hydride rather than an acyl ligand (Sears *et al.*, 2015).

5. Synthesis and crystallization

$\text{CpMo}(\text{CO})_3(\text{CH}_3)$. This compound was prepared by a modification of the method used by Gladysz *et al.* (1979), as previously reported by Whited & Hofmeister (2014), with the modification that sodium triethylborohydride (1.0 M in toluene) was used as a reductant instead of lithium triethylborohydride to facilitate isolation of the product.

$\text{CpMo}(\text{CO})_2(\text{PTA})(\text{COCH}_3)$ (1). In an inert-atmosphere glove box, $\text{CpMo}(\text{CO})_3(\text{CH}_3)$ (325 mg, 1.25 mmol, 1.18 equivalents) was dissolved in acetonitrile (10 ml). In a separ-

ate vial, 1,3,5-triaza-7-phosphaadamantane (PTA, 167 mg, 1.06 mmol, 1 equivalent) was massed. The homogeneous solution of the molybdenum complex was transferred to the vial containing PTA and the mixture was stirred at room temperature. After three days, the solution had generated a red solid that clung to the walls of the scintillation vial while the solution itself retained a red–orange color. Solvent was removed *in vacuo*, leaving a red–orange solid that was washed with hexanes (10 ml) and diethyl ether (10 ml) before a final extraction using tetrahydrofuran (THF, 10 ml). The solid obtained from the THF fraction was the pale-yellow pure form of the final product (350 mg, 79%). Crystalline material was obtained as yellow–orange blocks by a THF/toluene vapor cross diffusion, which was used to concentrate the solution in a controlled manner without exposure to the glove-box atmosphere. The procedure is as follows: 50 mg of the product were dissolved in 1 ml of THF to form a concentrated solution. This solution was transferred into a small cylindrical 5 ml vial that was placed into a 20 ml vial. The remaining volume inside the 20 ml vial was filled with 10 ml of toluene. The vial was capped and left for two days before crystals were observed and harvested. ^1H NMR (400 MHz, CDCl_3): δ 5.16 (*d*, $J = 1.2$ Hz, 5H, C_5H_5), 4.55 (*m*, 6H, P– CH_2 –N), 4.07 (*s*, 6H, N– CH_2 –N), 2.52 [*s*, 3H, C(O) CH_3]. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ –21.7 (*s*).

$\text{CpMo}(\text{CO})_2(\text{DAPTA})(\text{COCH}_3)$ (2). In an inert-atmosphere glove box, $\text{CpMo}(\text{CO})_3(\text{CH}_3)$ (310 mg, 1.19 mmol, 1.05 equivalents) was dissolved in *N,N*-dimethylformamide (10 ml). In a separate vial, 3,7-diacetyl-1,3,5-triaza-5-phosphabicyclo[3.3.1]nonane (DAPTA, 260 mg, 1.13 mmol, 1 equivalent) was massed. The homogeneous solution of the molybdenum complex was transferred to the vial containing DAPTA. The solution was not fully homogeneous, so vigorous stirring was employed. The solution had generated a pale-yellow solid after the first day while the supernatant solution was a red–orange color. The reaction mixture was filtered to obtain the pale-yellow solid, which was washed with two 2 ml portions of fresh *N,N*-dimethylformamide. The solid was dried *in vacuo* and recrystallized from a vapor diffusion of diethyl ether into a concentrated solution of the product in *N,N*-dimethylformamide, affording (2) as a pale-yellow crystalline material (80 mg, 15%). ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 5.57 (*d*, $J = 14$ Hz, 1H), 5.36 (*s*, 5H, C_5H_5), 5.27 (*dd*, $J_{\text{PH}} = 6.8$ Hz, $J_{\text{HH}} = 15.2$ Hz, 1H), 4.98 (*d*, $J_{\text{HH}} = 14.0$ Hz, 1H), 4.72 (*d*, $J_{\text{HH}} = 14.0$ Hz, 1H), 4.40 (*dd*, $J_{\text{PH}} = 7.6$ Hz, $J_{\text{HH}} = 15.6$ Hz, 1H), 4.20 (*d*, $J_{\text{HH}} = 14$ Hz, 1H), 4.05–3.98 (*m*, 1H), 3.75 (*s*, 2H), 3.46–3.39 (*m*, 1H), 2.42 (*s*, 3H, MoC(O) CH_3), 1.98 (*s*, 3H, NC(O) CH_3), 1.97 [*s*, 3H, NC(O) CH_3]. $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, $\text{DMSO}-d_6$): δ 8.06 (*s*).

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. H atoms were placed in calculated positions and refined in the riding-model approximation with distances of C—H = 0.93, 0.96, and 0.97 Å for the cyclopentadienyl, methyl, and methylene groups, respectively, and

Table 5
Experimental details.

| | (1) | (2) |
|--|--|---|
| Crystal data | | |
| Chemical formula | [Mo(C ₅ H ₅)(C ₂ H ₂ O)(C ₆ H ₁₂ N ₃ P)(CO) ₂] | [Mo(C ₅ H ₅)(C ₂ H ₃ O)(C ₉ H ₁₆ N ₃ O ₂ P)(CO) ₂] |
| M_r | 417.25 | 489.31 |
| Crystal system, space group | Monoclinic, $P2_1/c$ | Monoclinic, $P2_1/n$ |
| Temperature (K) | 100 | 100 |
| a, b, c (Å) | 9.7919 (14), 14.5757 (13), 12.1140 (12) | 12.8674 (4), 11.6366 (3), 14.4655 (5) |
| β (°) | 107.694 (6) | 113.224 (4) |
| V (Å ³) | 1647.2 (3) | 1990.45 (12) |
| Z | 4 | 4 |
| Radiation type | Mo $K\alpha$ | Mo $K\alpha$ |
| μ (mm ⁻¹) | 0.91 | 0.77 |
| Crystal size (mm) | 0.2 × 0.19 × 0.15 | 0.17 × 0.1 × 0.02 |
| Data collection | | |
| Diffractometer | Bruker D8QUEST | Rigaku XtaLAB Synergy, Single source at offset/far, Pilatus 200K |
| Absorption correction | Multi-scan (<i>SADABS</i> ; Bruker, 2016) | Multi-scan (<i>CrysAlis PRO</i> ; Rigaku, 2019) |
| T_{\min} , T_{\max} | 0.709, 0.746 | 0.868, 1.000 |
| No. of measured, independent and observed [$I > 2\sigma(I)$] reflections | 32227, 3785, 3379 | 38060, 4726, 4075 |
| R_{int} | 0.040 | 0.044 |
| $(\sin \theta/\lambda)_{\text{max}}$ (Å ⁻¹) | 0.651 | 0.658 |
| Refinement | | |
| $R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S | 0.020, 0.043, 1.07 | 0.028, 0.061, 1.09 |
| No. of reflections | 3785 | 4726 |
| No. of parameters | 210 | 256 |
| H-atom treatment | H-atom parameters constrained | H-atom parameters constrained |
| $\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³) | 0.45, -0.35 | 0.57, -0.37 |

Computer programs: *SAINT* (Bruker, 2018), *CrysAlis PRO* (Rigaku, 2019), *SHELXT2014/5* (Sheldrick, 2015a), *SHELXL2018/3* (Sheldrick, 2015b), *Mercury* (Macrae *et al.*, 2020) and *publCIF* (Westrip, 2010).

with $U_{\text{iso}}(\text{H}) = k \times U_{\text{eq}}(\text{C})$, $k = 1.2$ for cyclopentadienyl and methylene groups and 1.5 for methyl groups. Methyl group H atoms were allowed to rotate in order to find the best rotameric conformation.

A small number of intense low-angle reflections [one for (1); five for (2)] are missing from these high-quality data sets due to the arrangement of the instrument with a conservatively sized beam stop. The large number of reflections in the data sets (and the Fourier-transform relationship of intensities to atoms) ensures that no particular bias has been introduced.

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References

- Adams, H., Bailey, N. A., Day, A. N., Morris, M. J. & Harrison, M. M. (1991). *J. Organomet. Chem.* **407**, 247–258.
 Barnett, K. W. (1969). *Inorg. Chem.* **8**, 2009–2011.
 Barnett, K. W. & Pollmann, T. G. (1974). *J. Organomet. Chem.* **69**, 413–421.
 Barnett, K. W. & Treichel, P. M. (1967). *Inorg. Chem.* **6**, 294–299.
 Bruker (2016). *SADABS*. Bruker Nano, Inc., Madison, Wisconsin, USA.

- Bruker (2018). *SAINT*. Bruker Nano, Inc., Madison, Wisconsin, USA.
 Butler, I. S., Basolo, F. & Pearson, R. G. (1967). *Inorg. Chem.* **6**, 2074–2079.
 Gladysz, J. A., Williams, G. M., Tam, W., Johnson, D. L., Parker, D. W. & Selover, J. C. (1979). *Inorg. Chem.* **18**, 553–558.
 Groom, C. R., Bruno, I. J., Lightfoot, M. P. & Ward, S. C. (2016). *Acta Cryst.* **B72**, 171–179.
 Kubacek, P., Hoffmann, R. & Havlas, Z. (1982). *Organometallics*, **1**, 180–188.
 Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.
 Mercier, F., Ricard, L. & Mathey, F. (1993). *Organometallics*, **12**, 98–103.
 Rigaku (2019). *CrysAlis PRO*. Rigaku Corporation, Tokyo, Japan.
 Sears, J. M., Lee, W.-C. & Frost, B. J. (2015). *Inorg. Chim. Acta*, **431**, 248–257.
 Sheldrick, G. M. (2015a). *Acta Cryst.* **A71**, 3–8.
 Sheldrick, G. M. (2015b). *Acta Cryst.* **C71**, 3–8.
 Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
 Whited, M. T., Bakker-Arkema, J. G., Greenwald, J. E., Morrill, L. A. & Janzen, D. E. (2013). *Acta Cryst.* **E69**, m475–m476.
 Whited, M. T., Boerma, J. W., McClellan, M. J., Padilla, C. E. & Janzen, D. E. (2012). *Acta Cryst.* **E68**, m1158–m1159.
 Whited, M. T. & Hofmeister, G. E. (2014). *J. Chem. Educ.* **91**, 1050–1053.
 Whited, M. T., Hofmeister, G. E., Hodges, C. J., Jensen, L. J., Keyes, S. H., Ngamthiporn, A. & Janzen, D. E. (2014). *Acta Cryst.* **E70**, 216–220.
 Yan, X., Yu, B., Wang, L., Tang, N. & Xi, C. (2009). *Organometallics*, **28**, 6827–6830.

supporting information

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Crystal structures of *trans*-acetyldicarbonyl(η^5 -cyclopentadienyl)(1,3,5-triaza-7-phosphaadamantane)molybdenum(II) and *trans*-acetyldicarbonyl(η^5 -cyclopentadienyl)(3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo-[3.3.1]nonane)molybdenum(II)

Mitchell R. Anstey, John L. Bost, Anna S. Grumman, Nicholas D. Kennedy and Matthew T. Whited

Computing details

Data collection: *SAINT* (Bruker, 2018) for (1); *CrysAlis PRO* (Rigaku, 2019) for (2). Cell refinement: *SAINT* (Bruker, 2018) for (1); *CrysAlis PRO* (Rigaku, 2019) for (2). Data reduction: *SAINT* (Bruker, 2018) for (1); *CrysAlis PRO* (Rigaku, 2019) for (2). For both structures, program(s) used to solve structure: *SHELXT2014/5* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL2018/3* (Sheldrick, 2015b); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *publCIF* (Westrip, 2010).

trans-Acetyldicarbonyl(η^5 -cyclopentadienyl)(1,3,5-triaza-7-phosphaadamantane)molybdenum(II) (1)

Crystal data

[Mo(C₅H₅)(C₂H₂O)(C₆H₁₂N₃P)(CO)₂]
 $M_r = 417.25$
 Monoclinic, $P2_1/c$
 $a = 9.7919$ (14) Å
 $b = 14.5757$ (13) Å
 $c = 12.1140$ (12) Å
 $\beta = 107.694$ (6)°
 $V = 1647.2$ (3) Å³
 $Z = 4$

$F(000) = 848$
 $D_x = 1.683$ Mg m⁻³
 Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
 Cell parameters from 9370 reflections
 $\theta = 3.3$ – 27.5°
 $\mu = 0.91$ mm⁻¹
 $T = 100$ K
 Block, orange
 $0.2 \times 0.19 \times 0.15$ mm

Data collection

Bruker D8QUEST
 diffractometer
 ω and ϕ scans
 Absorption correction: multi-scan
 (SADABS; Bruker, 2016)
 $T_{\min} = 0.709$, $T_{\max} = 0.746$
 32227 measured reflections

3785 independent reflections
 3379 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.040$
 $\theta_{\max} = 27.6^\circ$, $\theta_{\min} = 3.3^\circ$
 $h = -12 \rightarrow 12$
 $k = -18 \rightarrow 18$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.020$
 $wR(F^2) = 0.043$

$S = 1.07$
 3785 reflections
 210 parameters
 0 restraints

Primary atom site location: dual
 Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0124P)^2 + 1.3596P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 0.45 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.35 \text{ e } \text{\AA}^{-3}$
 Extinction correction: SHELXL2018/3
 (Sheldrick 2015b),
 $F_c^* = kFc[1 + 0.001x\lambda^3/\sin(2\theta)]^{-1/4}$
 Extinction coefficient: 0.0040 (2)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | x | y | z | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|--------------|--------------|----------------------------------|
| Mo1 | 0.59777 (2) | 0.49328 (2) | 0.28768 (2) | 0.00886 (5) |
| P1 | 0.76523 (4) | 0.41400 (3) | 0.20808 (4) | 0.01095 (9) |
| O1 | 0.65998 (14) | 0.65083 (9) | 0.13519 (11) | 0.0225 (3) |
| O2 | 0.85977 (13) | 0.47150 (9) | 0.51067 (11) | 0.0203 (3) |
| O3 | 0.47562 (13) | 0.66109 (8) | 0.37491 (10) | 0.0174 (3) |
| N1 | 0.81148 (15) | 0.31674 (11) | 0.02647 (13) | 0.0187 (3) |
| N2 | 0.95915 (17) | 0.27288 (11) | 0.22389 (14) | 0.0216 (3) |
| N3 | 1.00813 (15) | 0.41777 (10) | 0.13718 (13) | 0.0172 (3) |
| C1 | 0.64170 (17) | 0.59232 (12) | 0.19293 (14) | 0.0145 (3) |
| C2 | 0.76722 (17) | 0.48263 (11) | 0.42615 (14) | 0.0131 (3) |
| C3 | 0.59049 (18) | 0.62704 (11) | 0.37674 (13) | 0.0126 (3) |
| C4 | 0.72533 (19) | 0.67895 (11) | 0.44048 (15) | 0.0172 (3) |
| H4A | 0.768353 | 0.651212 | 0.516872 | 0.026* |
| H4B | 0.701269 | 0.743146 | 0.449920 | 0.026* |
| H4C | 0.793647 | 0.676106 | 0.395903 | 0.026* |
| C5 | 0.39034 (18) | 0.42909 (12) | 0.16033 (15) | 0.0165 (3) |
| H5 | 0.372255 | 0.432040 | 0.078793 | 0.020* |
| C6 | 0.35024 (17) | 0.49564 (12) | 0.22997 (14) | 0.0155 (3) |
| H6 | 0.300765 | 0.551374 | 0.203612 | 0.019* |
| C7 | 0.39757 (17) | 0.46382 (12) | 0.34674 (15) | 0.0155 (3) |
| H7 | 0.385727 | 0.495068 | 0.412043 | 0.019* |
| C8 | 0.46496 (18) | 0.37807 (12) | 0.34879 (15) | 0.0164 (3) |
| H8 | 0.504922 | 0.340967 | 0.415265 | 0.020* |
| C9 | 0.46240 (18) | 0.35724 (11) | 0.23437 (15) | 0.0164 (3) |
| H9 | 0.502247 | 0.304029 | 0.210865 | 0.020* |
| C10 | 0.69704 (17) | 0.36231 (12) | 0.06169 (14) | 0.0155 (3) |
| H10A | 0.621580 | 0.316952 | 0.061143 | 0.019* |
| H10B | 0.653123 | 0.410872 | 0.004845 | 0.019* |
| C11 | 0.86374 (19) | 0.31312 (12) | 0.28477 (16) | 0.0196 (4) |
| H11A | 0.921558 | 0.331544 | 0.363817 | 0.023* |
| H11B | 0.794116 | 0.266087 | 0.292213 | 0.023* |
| C12 | 0.91942 (17) | 0.47689 (12) | 0.18647 (15) | 0.0163 (3) |

| | | | | |
|------|--------------|--------------|--------------|------------|
| H12A | 0.883561 | 0.529431 | 0.133844 | 0.020* |
| H12B | 0.979281 | 0.501540 | 0.261788 | 0.020* |
| C13 | 0.8764 (2) | 0.24240 (13) | 0.10693 (17) | 0.0232 (4) |
| H13A | 0.940468 | 0.206656 | 0.073719 | 0.028* |
| H13B | 0.799353 | 0.200736 | 0.113403 | 0.028* |
| C14 | 1.06640 (18) | 0.34022 (13) | 0.21383 (16) | 0.0220 (4) |
| H14A | 1.116912 | 0.364261 | 0.292037 | 0.026* |
| H14B | 1.138175 | 0.308452 | 0.184965 | 0.026* |
| C15 | 0.92521 (19) | 0.38166 (13) | 0.02367 (15) | 0.0202 (4) |
| H15A | 0.991757 | 0.350678 | -0.011587 | 0.024* |
| H15B | 0.881223 | 0.433817 | -0.027049 | 0.024* |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|--------------|-------------|--------------|--------------|--------------|---------------|
| Mo1 | 0.00893 (7) | 0.00963 (7) | 0.00871 (7) | -0.00047 (5) | 0.00374 (5) | 0.00005 (5) |
| P1 | 0.01048 (19) | 0.0127 (2) | 0.01055 (19) | 0.00010 (15) | 0.00453 (15) | -0.00002 (15) |
| O1 | 0.0294 (7) | 0.0204 (7) | 0.0202 (7) | -0.0010 (5) | 0.0112 (6) | 0.0064 (5) |
| O2 | 0.0154 (6) | 0.0258 (7) | 0.0171 (6) | 0.0012 (5) | 0.0009 (5) | 0.0017 (5) |
| O3 | 0.0188 (6) | 0.0139 (6) | 0.0211 (6) | 0.0019 (5) | 0.0087 (5) | -0.0011 (5) |
| N1 | 0.0138 (7) | 0.0263 (8) | 0.0182 (7) | -0.0026 (6) | 0.0081 (6) | -0.0083 (6) |
| N2 | 0.0202 (7) | 0.0230 (8) | 0.0251 (8) | 0.0084 (6) | 0.0119 (7) | 0.0022 (6) |
| N3 | 0.0120 (7) | 0.0238 (8) | 0.0176 (7) | -0.0007 (6) | 0.0069 (6) | -0.0027 (6) |
| C1 | 0.0131 (8) | 0.0179 (8) | 0.0128 (8) | 0.0013 (6) | 0.0044 (6) | -0.0018 (6) |
| C2 | 0.0141 (8) | 0.0124 (8) | 0.0153 (8) | -0.0004 (6) | 0.0082 (7) | -0.0005 (6) |
| C3 | 0.0193 (8) | 0.0100 (7) | 0.0094 (7) | 0.0006 (6) | 0.0057 (6) | 0.0025 (6) |
| C4 | 0.0207 (9) | 0.0139 (8) | 0.0161 (8) | -0.0017 (7) | 0.0042 (7) | 0.0000 (6) |
| C5 | 0.0139 (8) | 0.0212 (9) | 0.0136 (8) | -0.0057 (7) | 0.0027 (7) | -0.0039 (7) |
| C6 | 0.0083 (7) | 0.0182 (8) | 0.0188 (8) | -0.0017 (6) | 0.0023 (6) | -0.0021 (7) |
| C7 | 0.0124 (8) | 0.0205 (8) | 0.0169 (8) | -0.0058 (6) | 0.0094 (7) | -0.0049 (7) |
| C8 | 0.0164 (8) | 0.0168 (8) | 0.0170 (8) | -0.0062 (6) | 0.0066 (7) | 0.0021 (6) |
| C9 | 0.0167 (8) | 0.0128 (8) | 0.0226 (9) | -0.0057 (6) | 0.0101 (7) | -0.0042 (7) |
| C10 | 0.0105 (7) | 0.0222 (9) | 0.0146 (8) | -0.0018 (6) | 0.0051 (6) | -0.0047 (7) |
| C11 | 0.0217 (9) | 0.0209 (9) | 0.0190 (9) | 0.0089 (7) | 0.0105 (7) | 0.0058 (7) |
| C12 | 0.0127 (8) | 0.0181 (8) | 0.0197 (8) | -0.0029 (6) | 0.0071 (7) | -0.0043 (6) |
| C13 | 0.0218 (9) | 0.0191 (9) | 0.0328 (10) | 0.0005 (7) | 0.0143 (8) | -0.0081 (8) |
| C14 | 0.0126 (8) | 0.0319 (10) | 0.0212 (9) | 0.0048 (7) | 0.0047 (7) | -0.0025 (8) |
| C15 | 0.0154 (8) | 0.0306 (10) | 0.0173 (9) | -0.0029 (7) | 0.0090 (7) | -0.0036 (7) |

Geometric parameters (Å, °)

| | | | |
|--------|-------------|--------|-----------|
| Mo1—P1 | 2.4321 (5) | C4—H4A | 0.9800 |
| Mo1—C1 | 1.9714 (17) | C4—H4B | 0.9800 |
| Mo1—C2 | 1.9746 (17) | C4—H4C | 0.9800 |
| Mo1—C3 | 2.2398 (16) | C5—H5 | 0.9500 |
| Mo1—C5 | 2.3401 (16) | C5—C6 | 1.417 (2) |
| Mo1—C6 | 2.3097 (16) | C5—C9 | 1.419 (2) |
| Mo1—C7 | 2.3221 (16) | C6—H6 | 0.9500 |

| | | | |
|-----------|-------------|-------------|-------------|
| Mo1—C8 | 2.3759 (16) | C6—C7 | 1.426 (2) |
| Mo1—C9 | 2.3634 (16) | C7—H7 | 0.9500 |
| P1—C10 | 1.8543 (17) | C7—C8 | 1.410 (2) |
| P1—C11 | 1.8468 (17) | C8—H8 | 0.9500 |
| P1—C12 | 1.8517 (17) | C8—C9 | 1.412 (2) |
| O1—C1 | 1.151 (2) | C9—H9 | 0.9500 |
| O2—C2 | 1.154 (2) | C10—H10A | 0.9900 |
| O3—C3 | 1.223 (2) | C10—H10B | 0.9900 |
| N1—C10 | 1.473 (2) | C11—H11A | 0.9900 |
| N1—C13 | 1.467 (2) | C11—H11B | 0.9900 |
| N1—C15 | 1.470 (2) | C12—H12A | 0.9900 |
| N2—C11 | 1.476 (2) | C12—H12B | 0.9900 |
| N2—C13 | 1.471 (2) | C13—H13A | 0.9900 |
| N2—C14 | 1.469 (2) | C13—H13B | 0.9900 |
| N3—C12 | 1.473 (2) | C14—H14A | 0.9900 |
| N3—C14 | 1.464 (2) | C14—H14B | 0.9900 |
| N3—C15 | 1.466 (2) | C15—H15A | 0.9900 |
| C3—C4 | 1.514 (2) | C15—H15B | 0.9900 |
| | | | |
| C1—Mo1—P1 | 79.89 (5) | C6—C5—H5 | 126.2 |
| C1—Mo1—C2 | 106.05 (7) | C6—C5—C9 | 107.66 (15) |
| C1—Mo1—C3 | 71.80 (6) | C9—C5—Mo1 | 73.34 (9) |
| C1—Mo1—C5 | 102.02 (6) | C9—C5—H5 | 126.2 |
| C1—Mo1—C6 | 101.98 (6) | Mo1—C6—H6 | 119.7 |
| C1—Mo1—C7 | 131.98 (6) | C5—C6—Mo1 | 73.43 (9) |
| C1—Mo1—C8 | 159.38 (6) | C5—C6—H6 | 126.2 |
| C1—Mo1—C9 | 131.21 (6) | C5—C6—C7 | 107.62 (15) |
| C2—Mo1—P1 | 78.80 (5) | C7—C6—Mo1 | 72.55 (9) |
| C2—Mo1—C3 | 78.51 (6) | C7—C6—H6 | 126.2 |
| C2—Mo1—C5 | 149.93 (6) | Mo1—C7—H7 | 119.7 |
| C2—Mo1—C6 | 142.35 (6) | C6—C7—Mo1 | 71.60 (9) |
| C2—Mo1—C7 | 107.08 (6) | C6—C7—H7 | 125.8 |
| C2—Mo1—C8 | 94.47 (6) | C8—C7—Mo1 | 74.63 (9) |
| C2—Mo1—C9 | 115.01 (6) | C8—C7—C6 | 108.37 (15) |
| C3—Mo1—P1 | 136.77 (4) | C8—C7—H7 | 125.8 |
| C3—Mo1—C5 | 121.15 (6) | Mo1—C8—H8 | 122.9 |
| C3—Mo1—C6 | 87.06 (6) | C7—C8—Mo1 | 70.46 (9) |
| C3—Mo1—C7 | 81.90 (6) | C7—C8—H8 | 126.1 |
| C3—Mo1—C8 | 111.38 (6) | C7—C8—C9 | 107.74 (15) |
| C3—Mo1—C9 | 139.87 (6) | C9—C8—Mo1 | 72.19 (9) |
| C5—Mo1—P1 | 95.93 (4) | C9—C8—H8 | 126.1 |
| C5—Mo1—C8 | 58.34 (6) | Mo1—C9—H9 | 121.3 |
| C5—Mo1—C9 | 35.12 (6) | C5—C9—Mo1 | 71.54 (9) |
| C6—Mo1—P1 | 131.22 (4) | C5—C9—H9 | 125.7 |
| C6—Mo1—C5 | 35.48 (6) | C8—C9—Mo1 | 73.15 (9) |
| C6—Mo1—C7 | 35.85 (6) | C8—C9—C5 | 108.60 (15) |
| C6—Mo1—C8 | 58.76 (6) | C8—C9—H9 | 125.7 |
| C6—Mo1—C9 | 58.66 (6) | P1—C10—H10A | 109.2 |

| | | | |
|---------------|--------------|---------------|-------------|
| C7—Mo1—P1 | 140.20 (4) | P1—C10—H10B | 109.2 |
| C7—Mo1—C5 | 58.95 (6) | N1—C10—P1 | 112.07 (11) |
| C7—Mo1—C8 | 34.91 (6) | N1—C10—H10A | 109.2 |
| C7—Mo1—C9 | 58.20 (6) | N1—C10—H10B | 109.2 |
| C8—Mo1—P1 | 106.65 (4) | H10A—C10—H10B | 107.9 |
| C9—Mo1—P1 | 83.27 (4) | P1—C11—H11A | 109.2 |
| C9—Mo1—C8 | 34.66 (6) | P1—C11—H11B | 109.2 |
| C10—P1—Mo1 | 118.82 (5) | N2—C11—P1 | 112.21 (12) |
| C11—P1—Mo1 | 119.40 (6) | N2—C11—H11A | 109.2 |
| C11—P1—C10 | 97.98 (8) | N2—C11—H11B | 109.2 |
| C11—P1—C12 | 98.14 (8) | H11A—C11—H11B | 107.9 |
| C12—P1—Mo1 | 119.85 (6) | P1—C12—H12A | 109.2 |
| C12—P1—C10 | 97.93 (8) | P1—C12—H12B | 109.2 |
| C13—N1—C10 | 110.79 (14) | N3—C12—P1 | 111.98 (11) |
| C13—N1—C15 | 108.21 (14) | N3—C12—H12A | 109.2 |
| C15—N1—C10 | 111.40 (14) | N3—C12—H12B | 109.2 |
| C13—N2—C11 | 110.75 (14) | H12A—C12—H12B | 107.9 |
| C14—N2—C11 | 110.66 (14) | N1—C13—N2 | 114.68 (15) |
| C14—N2—C13 | 108.68 (14) | N1—C13—H13A | 108.6 |
| C14—N3—C12 | 111.03 (14) | N1—C13—H13B | 108.6 |
| C14—N3—C15 | 108.41 (14) | N2—C13—H13A | 108.6 |
| C15—N3—C12 | 111.33 (13) | N2—C13—H13B | 108.6 |
| O1—C1—Mo1 | 176.52 (15) | H13A—C13—H13B | 107.6 |
| O2—C2—Mo1 | 174.40 (14) | N2—C14—H14A | 108.6 |
| O3—C3—Mo1 | 120.54 (12) | N2—C14—H14B | 108.6 |
| O3—C3—C4 | 117.45 (15) | N3—C14—N2 | 114.69 (14) |
| C4—C3—Mo1 | 122.01 (11) | N3—C14—H14A | 108.6 |
| C3—C4—H4A | 109.5 | N3—C14—H14B | 108.6 |
| C3—C4—H4B | 109.5 | H14A—C14—H14B | 107.6 |
| C3—C4—H4C | 109.5 | N1—C15—H15A | 108.6 |
| H4A—C4—H4B | 109.5 | N1—C15—H15B | 108.6 |
| H4A—C4—H4C | 109.5 | N3—C15—N1 | 114.65 (14) |
| H4B—C4—H4C | 109.5 | N3—C15—H15A | 108.6 |
| Mo1—C5—H5 | 121.2 | N3—C15—H15B | 108.6 |
| C6—C5—Mo1 | 71.09 (9) | H15A—C15—H15B | 107.6 |
| Mo1—P1—C10—N1 | -179.79 (10) | C10—N1—C15—N3 | 66.86 (19) |
| Mo1—P1—C11—N2 | 179.31 (10) | C11—P1—C10—N1 | -49.79 (14) |
| Mo1—P1—C12—N3 | -179.75 (9) | C11—P1—C12—N3 | 49.41 (13) |
| Mo1—C5—C6—C7 | -64.99 (11) | C11—N2—C13—N1 | 67.75 (19) |
| Mo1—C5—C9—C8 | 64.24 (12) | C11—N2—C14—N3 | -67.81 (19) |
| Mo1—C6—C7—C8 | -66.13 (11) | C12—P1—C10—N1 | 49.65 (14) |
| Mo1—C7—C8—C9 | -62.98 (11) | C12—P1—C11—N2 | -49.56 (14) |
| Mo1—C8—C9—C5 | -63.20 (11) | C12—N3—C14—N2 | 68.04 (18) |
| C5—C6—C7—Mo1 | 65.58 (11) | C12—N3—C15—N1 | -67.16 (19) |
| C5—C6—C7—C8 | -0.55 (18) | C13—N1—C10—P1 | 60.54 (16) |
| C6—C5—C9—Mo1 | -63.24 (11) | C13—N1—C15—N3 | -55.17 (19) |
| C6—C5—C9—C8 | 1.00 (18) | C13—N2—C11—P1 | -60.33 (18) |

| | | | |
|---------------|-------------|---------------|-------------|
| C6—C7—C8—Mo1 | 64.14 (11) | C13—N2—C14—N3 | 54.00 (19) |
| C6—C7—C8—C9 | 1.17 (18) | C14—N2—C11—P1 | 60.25 (17) |
| C7—C8—C9—Mo1 | 61.86 (11) | C14—N2—C13—N1 | -54.01 (19) |
| C7—C8—C9—C5 | -1.34 (18) | C14—N3—C12—P1 | -60.30 (16) |
| C9—C5—C6—Mo1 | 64.71 (11) | C14—N3—C15—N1 | 55.25 (19) |
| C9—C5—C6—C7 | -0.28 (18) | C15—N1—C10—P1 | -59.98 (17) |
| C10—P1—C11—N2 | 49.70 (14) | C15—N1—C13—N2 | 54.43 (19) |
| C10—P1—C12—N3 | -49.88 (13) | C15—N3—C12—P1 | 60.59 (17) |
| C10—N1—C13—N2 | -67.97 (19) | C15—N3—C14—N2 | -54.55 (19) |

Hydrogen-bond geometry (Å, °)

| <i>D</i> —H... <i>A</i> | <i>D</i> —H | H... <i>A</i> | <i>D</i> ... <i>A</i> | <i>D</i> —H... <i>A</i> |
|--------------------------|-------------|---------------|-----------------------|-------------------------|
| C8—H8...O3 ⁱ | 0.95 | 2.49 | 3.269 (2) | 139 |
| C9—H9...O3 ⁱⁱ | 0.95 | 2.37 | 3.284 (2) | 162 |

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1, y-1/2, -z+1/2$.***trans*-Acetyldicarbonyl(η^5 -cyclopentadienyl)(3,7-diacetyl-1,3,7-triaza-5-phosphabicyclo[3.3.1]nonane)molybdenum(II) (2)***Crystal data*[Mo(C₅H₅)(C₂H₃O)(C₉H₁₆N₃O₂P)(CO)₂] $M_r = 489.31$ Monoclinic, $P2_1/n$ $a = 12.8674$ (4) Å $b = 11.6366$ (3) Å $c = 14.4655$ (5) Å $\beta = 113.224$ (4)° $V = 1990.45$ (12) Å³ $Z = 4$ $F(000) = 1000$ $D_x = 1.633$ Mg m⁻³Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 13952 reflections

 $\theta = 2.5$ – 31.0 ° $\mu = 0.77$ mm⁻¹ $T = 100$ K

Plate, clear colorless

 $0.17 \times 0.1 \times 0.02$ mm*Data collection*

Rigaku XtaLAB Synergy, Single source at offset/far, Pilatus 200K diffractometer

Radiation source: micro-focus sealed X-ray tube, PhotonJet (Mo) X-ray Source

Mirror monochromator

Detector resolution: 5.8140 pixels mm⁻¹ ω scans

Absorption correction: multi-scan (CrysAlisPro; Rigaku, 2019)

 $T_{\min} = 0.868$, $T_{\max} = 1.000$

38060 measured reflections

4726 independent reflections

4075 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.044$ $\theta_{\text{max}} = 27.9$ °, $\theta_{\text{min}} = 2.3$ ° $h = -16$ → 16 $k = -15$ → 15 $l = -19$ → 19 *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.028$ $wR(F^2) = 0.061$ $S = 1.09$

4726 reflections

256 parameters

0 restraints

Primary atom site location: dual

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0017P)^2 + 3.9699P]$ where $P = (F_o^2 + 2F_c^2)/3$

$$(\Delta/\sigma)_{\max} = 0.002$$

$$\Delta\rho_{\max} = 0.57 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.37 \text{ e } \text{\AA}^{-3}$$

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|------|--------------|--------------|--------------|----------------------------------|
| Mo1 | 0.63575 (2) | 0.25030 (2) | 0.30169 (2) | 0.01028 (5) |
| P1 | 0.47121 (4) | 0.22642 (5) | 0.34228 (4) | 0.01101 (11) |
| O1 | 0.52463 (17) | 0.49328 (16) | 0.25544 (15) | 0.0312 (4) |
| O2 | 0.50920 (15) | 0.07353 (16) | 0.13206 (13) | 0.0270 (4) |
| O3 | 0.75732 (14) | 0.33298 (15) | 0.17091 (12) | 0.0209 (4) |
| O4 | 0.30320 (15) | 0.49974 (15) | 0.41980 (13) | 0.0242 (4) |
| O5 | 0.14095 (13) | 0.34628 (14) | 0.16401 (12) | 0.0195 (3) |
| N1 | 0.36745 (16) | 0.31852 (17) | 0.46343 (14) | 0.0165 (4) |
| N2 | 0.35305 (15) | 0.11049 (16) | 0.43014 (13) | 0.0135 (4) |
| N3 | 0.23918 (15) | 0.20618 (16) | 0.27035 (14) | 0.0147 (4) |
| C1 | 0.5628 (2) | 0.4017 (2) | 0.26999 (18) | 0.0185 (5) |
| C2 | 0.55033 (19) | 0.1431 (2) | 0.19267 (17) | 0.0173 (5) |
| C3 | 0.66223 (19) | 0.3187 (2) | 0.16760 (16) | 0.0163 (4) |
| C4 | 0.5638 (2) | 0.3496 (2) | 0.06996 (18) | 0.0239 (5) |
| H4A | 0.519961 | 0.281951 | 0.041945 | 0.036* |
| H4B | 0.592380 | 0.380455 | 0.023061 | 0.036* |
| H4C | 0.516914 | 0.405872 | 0.083315 | 0.036* |
| C5 | 0.76382 (19) | 0.1081 (2) | 0.39905 (17) | 0.0197 (5) |
| H5 | 0.748692 | 0.030017 | 0.387962 | 0.024* |
| C6 | 0.73813 (19) | 0.1777 (2) | 0.46709 (16) | 0.0179 (5) |
| H6 | 0.702176 | 0.153239 | 0.508153 | 0.022* |
| C7 | 0.77602 (19) | 0.2908 (2) | 0.46259 (17) | 0.0184 (5) |
| H7 | 0.770231 | 0.353153 | 0.500496 | 0.022* |
| C8 | 0.82445 (18) | 0.2920 (2) | 0.38987 (17) | 0.0188 (5) |
| H8 | 0.855613 | 0.355473 | 0.371134 | 0.023* |
| C9 | 0.81675 (19) | 0.1787 (2) | 0.35077 (17) | 0.0192 (5) |
| H9 | 0.842145 | 0.155039 | 0.301873 | 0.023* |
| C10 | 0.4569 (2) | 0.3377 (2) | 0.42664 (18) | 0.0184 (5) |
| H10A | 0.528327 | 0.344180 | 0.484207 | 0.022* |
| H10B | 0.442864 | 0.410721 | 0.391445 | 0.022* |
| C11 | 0.45578 (18) | 0.09925 (19) | 0.41018 (16) | 0.0135 (4) |
| H11A | 0.450942 | 0.030898 | 0.370298 | 0.016* |
| H11B | 0.521186 | 0.091764 | 0.473140 | 0.016* |
| C12 | 0.33213 (18) | 0.2198 (2) | 0.23700 (17) | 0.0168 (5) |
| H12A | 0.320423 | 0.289683 | 0.197633 | 0.020* |
| H12B | 0.331263 | 0.155760 | 0.193769 | 0.020* |

| | | | | |
|------|--------------|--------------|--------------|------------|
| C13 | 0.3622 (2) | 0.2021 (2) | 0.50113 (17) | 0.0170 (5) |
| H13A | 0.429693 | 0.189409 | 0.561541 | 0.020* |
| H13B | 0.297707 | 0.197899 | 0.519767 | 0.020* |
| C14 | 0.25059 (18) | 0.10856 (19) | 0.33896 (17) | 0.0151 (4) |
| H14A | 0.185886 | 0.108202 | 0.357482 | 0.018* |
| H14B | 0.248845 | 0.037642 | 0.303134 | 0.018* |
| C15 | 0.29827 (19) | 0.4079 (2) | 0.46058 (17) | 0.0176 (5) |
| C16 | 0.2176 (2) | 0.3947 (2) | 0.5127 (2) | 0.0250 (5) |
| H16A | 0.259315 | 0.397149 | 0.584258 | 0.037* |
| H16B | 0.178938 | 0.322462 | 0.494274 | 0.037* |
| H16C | 0.163490 | 0.456177 | 0.492731 | 0.037* |
| C17 | 0.14790 (18) | 0.27602 (19) | 0.22978 (16) | 0.0152 (4) |
| C18 | 0.05350 (19) | 0.2655 (2) | 0.26638 (18) | 0.0216 (5) |
| H18A | 0.010423 | 0.335387 | 0.252252 | 0.032* |
| H18B | 0.084905 | 0.251691 | 0.337578 | 0.032* |
| H18C | 0.005112 | 0.202610 | 0.232574 | 0.032* |

Atomic displacement parameters (Å²)

| | U^{11} | U^{22} | U^{33} | U^{12} | U^{13} | U^{23} |
|-----|-------------|-------------|-------------|--------------|-------------|--------------|
| Mo1 | 0.00936 (8) | 0.01073 (9) | 0.01029 (8) | 0.00077 (7) | 0.00339 (6) | 0.00039 (7) |
| P1 | 0.0108 (2) | 0.0103 (3) | 0.0115 (2) | 0.00093 (19) | 0.0039 (2) | 0.00144 (19) |
| O1 | 0.0374 (11) | 0.0174 (9) | 0.0469 (12) | 0.0094 (8) | 0.0253 (10) | 0.0102 (8) |
| O2 | 0.0255 (9) | 0.0273 (10) | 0.0249 (9) | -0.0042 (8) | 0.0063 (8) | -0.0112 (8) |
| O3 | 0.0181 (8) | 0.0268 (9) | 0.0193 (8) | -0.0005 (7) | 0.0088 (7) | 0.0017 (7) |
| O4 | 0.0283 (9) | 0.0172 (9) | 0.0308 (10) | 0.0027 (7) | 0.0158 (8) | 0.0035 (7) |
| O5 | 0.0175 (8) | 0.0192 (9) | 0.0203 (8) | 0.0031 (7) | 0.0059 (7) | 0.0087 (7) |
| N1 | 0.0185 (9) | 0.0144 (10) | 0.0204 (10) | -0.0016 (7) | 0.0117 (8) | -0.0020 (7) |
| N2 | 0.0118 (9) | 0.0135 (9) | 0.0143 (9) | 0.0015 (7) | 0.0042 (7) | 0.0042 (7) |
| N3 | 0.0113 (8) | 0.0164 (9) | 0.0155 (9) | 0.0001 (7) | 0.0041 (7) | 0.0037 (7) |
| C1 | 0.0183 (11) | 0.0194 (12) | 0.0197 (11) | -0.0009 (9) | 0.0096 (9) | 0.0032 (9) |
| C2 | 0.0144 (10) | 0.0199 (12) | 0.0179 (11) | 0.0017 (9) | 0.0066 (9) | 0.0013 (9) |
| C3 | 0.0192 (11) | 0.0156 (11) | 0.0136 (10) | -0.0007 (9) | 0.0060 (9) | -0.0003 (8) |
| C4 | 0.0195 (12) | 0.0338 (14) | 0.0164 (11) | -0.0006 (10) | 0.0048 (10) | 0.0068 (10) |
| C5 | 0.0172 (11) | 0.0161 (12) | 0.0193 (11) | 0.0047 (9) | 0.0002 (9) | 0.0023 (9) |
| C6 | 0.0122 (10) | 0.0251 (12) | 0.0126 (10) | 0.0029 (9) | 0.0008 (8) | 0.0057 (9) |
| C7 | 0.0170 (11) | 0.0209 (12) | 0.0132 (10) | 0.0007 (9) | 0.0016 (9) | -0.0031 (9) |
| C8 | 0.0101 (10) | 0.0258 (12) | 0.0164 (11) | -0.0005 (9) | 0.0008 (9) | 0.0027 (9) |
| C9 | 0.0120 (10) | 0.0280 (13) | 0.0154 (11) | 0.0058 (9) | 0.0031 (9) | -0.0007 (9) |
| C10 | 0.0219 (12) | 0.0134 (11) | 0.0248 (12) | -0.0041 (9) | 0.0144 (10) | -0.0041 (9) |
| C11 | 0.0122 (10) | 0.0121 (10) | 0.0146 (10) | 0.0015 (8) | 0.0037 (8) | 0.0032 (8) |
| C12 | 0.0127 (10) | 0.0217 (12) | 0.0152 (10) | 0.0020 (8) | 0.0048 (8) | 0.0041 (8) |
| C13 | 0.0183 (11) | 0.0187 (11) | 0.0154 (11) | 0.0013 (9) | 0.0081 (9) | 0.0032 (9) |
| C14 | 0.0120 (10) | 0.0131 (11) | 0.0179 (11) | -0.0006 (8) | 0.0034 (9) | 0.0038 (8) |
| C15 | 0.0177 (11) | 0.0194 (12) | 0.0147 (10) | -0.0006 (9) | 0.0054 (9) | -0.0025 (9) |
| C16 | 0.0245 (13) | 0.0229 (13) | 0.0336 (14) | 0.0066 (10) | 0.0180 (11) | 0.0043 (10) |
| C17 | 0.0122 (10) | 0.0151 (11) | 0.0150 (10) | 0.0003 (8) | 0.0019 (8) | -0.0007 (8) |
| C18 | 0.0156 (10) | 0.0251 (13) | 0.0252 (12) | 0.0051 (10) | 0.0091 (9) | 0.0079 (10) |

Geometric parameters (Å, °)

| | | | |
|-----------|-------------|-----------|------------|
| Mo1—P1 | 2.4258 (6) | C4—H4C | 0.9600 |
| Mo1—C1 | 1.964 (2) | C5—H5 | 0.9300 |
| Mo1—C2 | 1.971 (2) | C5—C6 | 1.411 (3) |
| Mo1—C3 | 2.243 (2) | C5—C9 | 1.415 (3) |
| Mo1—C5 | 2.368 (2) | C6—H6 | 0.9300 |
| Mo1—C6 | 2.385 (2) | C6—C7 | 1.413 (3) |
| Mo1—C7 | 2.363 (2) | C7—H7 | 0.9300 |
| Mo1—C8 | 2.306 (2) | C7—C8 | 1.419 (3) |
| Mo1—C9 | 2.306 (2) | C8—H8 | 0.9300 |
| P1—C10 | 1.838 (2) | C8—C9 | 1.423 (3) |
| P1—C11 | 1.830 (2) | C9—H9 | 0.9300 |
| P1—C12 | 1.838 (2) | C10—H10A | 0.9700 |
| O1—C1 | 1.157 (3) | C10—H10B | 0.9700 |
| O2—C2 | 1.157 (3) | C11—H11A | 0.9700 |
| O3—C3 | 1.217 (3) | C11—H11B | 0.9700 |
| O4—C15 | 1.234 (3) | C12—H12A | 0.9700 |
| O5—C17 | 1.231 (3) | C12—H12B | 0.9700 |
| N1—C10 | 1.463 (3) | C13—H13A | 0.9700 |
| N1—C13 | 1.471 (3) | C13—H13B | 0.9700 |
| N1—C15 | 1.359 (3) | C14—H14A | 0.9700 |
| N2—C11 | 1.466 (3) | C14—H14B | 0.9700 |
| N2—C13 | 1.453 (3) | C15—C16 | 1.512 (3) |
| N2—C14 | 1.451 (3) | C16—H16A | 0.9600 |
| N3—C12 | 1.464 (3) | C16—H16B | 0.9600 |
| N3—C14 | 1.477 (3) | C16—H16C | 0.9600 |
| N3—C17 | 1.357 (3) | C17—C18 | 1.509 (3) |
| C3—C4 | 1.522 (3) | C18—H18A | 0.9600 |
| C4—H4A | 0.9600 | C18—H18B | 0.9600 |
| C4—H4B | 0.9600 | C18—H18C | 0.9600 |
| | | | |
| C1—Mo1—P1 | 77.10 (7) | C5—C6—H6 | 125.6 |
| C1—Mo1—C2 | 108.47 (10) | C5—C6—C7 | 108.8 (2) |
| C1—Mo1—C3 | 72.63 (9) | C7—C6—Mo1 | 71.84 (13) |
| C1—Mo1—C5 | 157.27 (9) | C7—C6—H6 | 125.6 |
| C1—Mo1—C6 | 125.17 (9) | Mo1—C7—H7 | 121.9 |
| C1—Mo1—C7 | 99.22 (9) | C6—C7—Mo1 | 73.52 (13) |
| C1—Mo1—C8 | 104.03 (9) | C6—C7—H7 | 126.2 |
| C1—Mo1—C9 | 136.72 (9) | C6—C7—C8 | 107.7 (2) |
| C2—Mo1—P1 | 81.75 (7) | C8—C7—Mo1 | 70.12 (12) |
| C2—Mo1—C3 | 76.10 (9) | C8—C7—H7 | 126.2 |
| C2—Mo1—C5 | 94.08 (9) | Mo1—C8—H8 | 119.1 |
| C2—Mo1—C6 | 119.45 (9) | C7—C8—Mo1 | 74.54 (13) |
| C2—Mo1—C7 | 151.96 (9) | C7—C8—H8 | 126.2 |
| C2—Mo1—C8 | 135.18 (9) | C7—C8—C9 | 107.6 (2) |
| C2—Mo1—C9 | 101.20 (9) | C9—C8—Mo1 | 72.05 (13) |
| C3—Mo1—P1 | 133.99 (6) | C9—C8—H8 | 126.2 |

| | | | |
|------------|-------------|---------------|-------------|
| C3—Mo1—C5 | 117.05 (8) | Mo1—C9—H9 | 119.2 |
| C3—Mo1—C6 | 141.34 (8) | C5—C9—Mo1 | 74.77 (13) |
| C3—Mo1—C7 | 117.61 (8) | C5—C9—C8 | 108.3 (2) |
| C3—Mo1—C8 | 85.28 (8) | C5—C9—H9 | 125.9 |
| C3—Mo1—C9 | 85.13 (8) | C8—C9—Mo1 | 72.00 (13) |
| C5—Mo1—P1 | 104.19 (6) | C8—C9—H9 | 125.9 |
| C5—Mo1—C6 | 34.54 (8) | P1—C10—H10A | 108.4 |
| C6—Mo1—P1 | 84.62 (6) | P1—C10—H10B | 108.4 |
| C7—Mo1—P1 | 100.66 (6) | N1—C10—P1 | 115.67 (16) |
| C7—Mo1—C5 | 58.09 (8) | N1—C10—H10A | 108.4 |
| C7—Mo1—C6 | 34.64 (8) | N1—C10—H10B | 108.4 |
| C8—Mo1—P1 | 136.01 (6) | H10A—C10—H10B | 107.4 |
| C8—Mo1—C5 | 58.94 (9) | P1—C11—H11A | 109.8 |
| C8—Mo1—C6 | 58.33 (8) | P1—C11—H11B | 109.8 |
| C8—Mo1—C7 | 35.35 (8) | N2—C11—P1 | 109.32 (14) |
| C8—Mo1—C9 | 35.95 (9) | N2—C11—H11A | 109.8 |
| C9—Mo1—P1 | 139.10 (6) | N2—C11—H11B | 109.8 |
| C9—Mo1—C5 | 35.20 (9) | H11A—C11—H11B | 108.3 |
| C9—Mo1—C6 | 58.12 (8) | P1—C12—H12A | 109.0 |
| C9—Mo1—C7 | 58.84 (8) | P1—C12—H12B | 109.0 |
| C10—P1—Mo1 | 113.94 (8) | N3—C12—P1 | 112.74 (15) |
| C11—P1—Mo1 | 120.83 (7) | N3—C12—H12A | 109.0 |
| C11—P1—C10 | 98.79 (11) | N3—C12—H12B | 109.0 |
| C11—P1—C12 | 97.73 (10) | H12A—C12—H12B | 107.8 |
| C12—P1—Mo1 | 117.51 (7) | N1—C13—H13A | 108.6 |
| C12—P1—C10 | 105.05 (11) | N1—C13—H13B | 108.6 |
| C10—N1—C13 | 115.65 (18) | N2—C13—N1 | 114.62 (18) |
| C15—N1—C10 | 118.14 (19) | N2—C13—H13A | 108.6 |
| C15—N1—C13 | 126.21 (19) | N2—C13—H13B | 108.6 |
| C13—N2—C11 | 112.11 (17) | H13A—C13—H13B | 107.6 |
| C14—N2—C11 | 112.71 (17) | N2—C14—N3 | 114.37 (18) |
| C14—N2—C13 | 116.44 (18) | N2—C14—H14A | 108.7 |
| C12—N3—C14 | 115.27 (17) | N2—C14—H14B | 108.7 |
| C17—N3—C12 | 118.24 (18) | N3—C14—H14A | 108.7 |
| C17—N3—C14 | 126.23 (19) | N3—C14—H14B | 108.7 |
| O1—C1—Mo1 | 176.4 (2) | H14A—C14—H14B | 107.6 |
| O2—C2—Mo1 | 173.5 (2) | O4—C15—N1 | 121.4 (2) |
| O3—C3—Mo1 | 120.51 (16) | O4—C15—C16 | 120.1 (2) |
| O3—C3—C4 | 117.4 (2) | N1—C15—C16 | 118.5 (2) |
| C4—C3—Mo1 | 122.10 (16) | C15—C16—H16A | 109.5 |
| C3—C4—H4A | 109.5 | C15—C16—H16B | 109.5 |
| C3—C4—H4B | 109.5 | C15—C16—H16C | 109.5 |
| C3—C4—H4C | 109.5 | H16A—C16—H16B | 109.5 |
| H4A—C4—H4B | 109.5 | H16A—C16—H16C | 109.5 |
| H4A—C4—H4C | 109.5 | H16B—C16—H16C | 109.5 |
| H4B—C4—H4C | 109.5 | O5—C17—N3 | 121.3 (2) |
| Mo1—C5—H5 | 122.1 | O5—C17—C18 | 120.1 (2) |
| C6—C5—Mo1 | 73.39 (13) | N3—C17—C18 | 118.6 (2) |

| | | | |
|----------------|--------------|----------------|--------------|
| C6—C5—H5 | 126.2 | C17—C18—H18A | 109.5 |
| C6—C5—C9 | 107.6 (2) | C17—C18—H18B | 109.5 |
| C9—C5—Mo1 | 70.03 (13) | C17—C18—H18C | 109.5 |
| C9—C5—H5 | 126.2 | H18A—C18—H18B | 109.5 |
| Mo1—C6—H6 | 122.2 | H18A—C18—H18C | 109.5 |
| C5—C6—Mo1 | 72.07 (13) | H18B—C18—H18C | 109.5 |
| Mo1—P1—C10—N1 | -172.38 (14) | C11—P1—C10—N1 | -42.89 (19) |
| Mo1—P1—C11—N2 | 176.42 (11) | C11—P1—C12—N3 | 49.62 (18) |
| Mo1—P1—C12—N3 | -179.56 (13) | C11—N2—C13—N1 | 67.4 (2) |
| Mo1—C5—C6—C7 | -62.85 (16) | C11—N2—C14—N3 | -64.3 (2) |
| Mo1—C5—C9—C8 | 64.72 (15) | C12—P1—C10—N1 | 57.6 (2) |
| Mo1—C6—C7—C8 | -62.18 (15) | C12—P1—C11—N2 | -54.99 (16) |
| Mo1—C7—C8—C9 | -64.94 (15) | C12—N3—C14—N2 | 57.2 (3) |
| Mo1—C8—C9—C5 | -66.55 (15) | C12—N3—C17—O5 | 2.6 (3) |
| C5—C6—C7—Mo1 | 63.00 (15) | C12—N3—C17—C18 | -177.9 (2) |
| C5—C6—C7—C8 | 0.8 (2) | C13—N1—C10—P1 | 46.5 (2) |
| C6—C5—C9—Mo1 | -64.27 (15) | C13—N1—C15—O4 | -173.8 (2) |
| C6—C5—C9—C8 | 0.5 (2) | C13—N1—C15—C16 | 8.8 (3) |
| C6—C7—C8—Mo1 | 64.41 (15) | C13—N2—C11—P1 | -67.49 (19) |
| C6—C7—C8—C9 | -0.5 (2) | C13—N2—C14—N3 | 67.3 (2) |
| C7—C8—C9—Mo1 | 66.60 (15) | C14—N2—C11—P1 | 66.2 (2) |
| C7—C8—C9—C5 | 0.0 (2) | C14—N2—C13—N1 | -64.5 (2) |
| C9—C5—C6—Mo1 | 62.07 (15) | C14—N3—C12—P1 | -53.5 (2) |
| C9—C5—C6—C7 | -0.8 (2) | C14—N3—C17—O5 | -171.1 (2) |
| C10—P1—C11—N2 | 51.64 (16) | C14—N3—C17—C18 | 8.4 (3) |
| C10—P1—C12—N3 | -51.70 (19) | C15—N1—C10—P1 | -133.89 (18) |
| C10—N1—C13—N2 | -55.1 (3) | C15—N1—C13—N2 | 125.4 (2) |
| C10—N1—C15—O4 | 6.6 (3) | C17—N3—C12—P1 | 132.06 (18) |
| C10—N1—C15—C16 | -170.7 (2) | C17—N3—C14—N2 | -128.9 (2) |

Hydrogen-bond geometry (\AA , $^\circ$)

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|-------------------------------------|-------|-------------|-------------|---------------|
| C7—H7 \cdots O4 ⁱ | 0.93 | 2.45 | 3.353 (3) | 163 |
| C11—H11A \cdots O5 ⁱⁱ | 0.97 | 2.41 | 3.211 (3) | 140 |
| C12—H12B \cdots O4 ⁱⁱ | 0.97 | 2.60 | 3.409 (3) | 141 |
| C13—H13A \cdots O5 ⁱⁱⁱ | 0.97 | 2.57 | 3.474 (3) | 156 |
| C13—H13B \cdots O3 ^{iv} | 0.97 | 2.46 | 3.261 (3) | 139 |

Symmetry codes: (i) $-x+1, -y+1, -z+1$; (ii) $-x+1/2, y-1/2, -z+1/2$; (iii) $x+1/2, -y+1/2, z+1/2$; (iv) $x-1/2, -y+1/2, z+1/2$.