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Paramagnetic Hydride Complexes

Formation and Structure of a Sterically Protected Molybdenum Hydride Complex with a 15-Electron Configuration: $[(1,2,4\text{-}C_5H_2t\text{Bu}_3)\text{Mo}(\text{PMe}_3)_2\text{H}]^{+}$**

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Hydride complexes generally feature a closed-shell configuration. They are implicated in a variety of catalytic cycles and are also intermediates of C–H oxidative-addition processes. Open-shell, paramagnetic versions have so far not demonstrated broad utility, mainly because of their instability and multitude of decomposition pathways, including deprotonation,[1] disproportionation,[2] dihydrogen reductive elimination (for complexes containing at least two hydride ligands),[3] atom transfer, and so on.[4] Yet, open-shell hydride complexes appear to play a role in enzymatic processes such as hydrogenase and nitrogenase,[5–8] and their implication in a variety of electrocatalyzed transformations may be envisaged. Therefore, they are attracting renewed interest.

One-electron oxidation of compounds containing two one-electron ligands {M(X)(Y)} may result in the reductive elimination of X–Y (oxidatively induced reductive elimination, OIRE). This has most clearly been demonstrated for dialkyl complexes $\{M(R)_2\}$ to give the organic product R–R as well as products originating from $\{M\}^+$.[9–12] When X = Y = H, the process may lead to H_2 evolution since the oxidation of a polyhydride complex $\{MH_n\}$ is expected to favor the rearrangement to a nonclassical isomer, $\{MH_{n-2}(H_2)\}^+$.[4,13,14] In fact, the oxidation of polyhydride complexes often results in dihydrogen evolution,[15] but the instability and the multitude of decomposition pathways of the intermediate oxidized polyhydride complexes often obscure the clean identification of OIRE.[4] Indeed, the oxidation of complexes $[\text{Cp*Ru(PPh}_3)\text{H}_3]$[13] ($\text{Cp*} = C_5\text{Me}_5$) and $[\text{Os(P}i\text{Pr}_3)_2\text{H}_6]$[16] leads to hydrogen evolution, but this was shown to take place following proton transfer from the unstable oxidized complex to residual starting material, rather than from direct reductive elimination.

We have recently reported the first unambiguous case of H_2 OIRE for the complex $[\text{Cp*Mo(dppe)H}_3]$ ($\text{dppe} = \text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) by characterization of the solvent-stabilized product $[\text{Cp*Mo(dppe)(solv)H}]^+$ by EPR spectroscopy (solv = thf, CH_2Cl_2)[3] and electrochemistry (solv = MeCN),[17] although the structure of the product could not be confirmed crystallographically. The oxidized trihydride complex $[\text{Cp*Mo(dppe)H}_3]^+$ also decomposes simultaneously by deprotonation and disproportionation. All three pathways occur via the nonclassical intermediate $[\text{Cp*Mo(dppe)H(H}_2)]^+$, although theoretical calculations and circumstantial evidence indicates that the oxidized complex adopts a classical structure.[17] We have argued that both stronger electron donation and greater steric protection by the ligands stabilize paramagnetic hydride complexes by disfavoring, through different mechanisms, the various decomposition pathways.[4] We have therefore turned our attention to a new Mo system, using the more strongly donating PMe_3 ligand in place of dppe and the more sterically protecting $1,2,4\text{-}C_5H_2t\text{Bu}_3$ ($\text{Cp}^{t\text{Bu}}$) ligand in place of Cp*. This has allowed us to isolate and structurally characterize, for the first time, the starting and end products of the H_2 OIRE, $[\text{Cp}^{t\text{Bu}}\text{Mo(PMe}_3)_2\text{H}_3]^+$ and $[\text{Cp}^{t\text{Bu}}\text{Mo(PMe}_3)_2\text{H}]^+$.

The starting compound $[\text{Cp}^{t\text{Bu}}\text{Mo(PMe}_3)_2\text{H}_3]$ was prepared by adapting the procedure previously employed for $[\text{Cp*Mo(dppe)H}_3]$[18] from $[\text{Cp}^{t\text{Bu}}\text{MoCl}_4]$ and LiAlH_4 in the presence of PMe_3. Its X-ray crystal structure shows a very similar geometry to that of $[\text{Cp*Mo(dppe)H}_3]$,[19] with the two PMe_3 ligands symmetrically disposed in adjacent coordination positions (P-Mo-P angle: 93.71(2)°) and far away from the $\text{Cp}^{t\text{Bu}}$ ligand (Figure 1 a).[20] When considering the $\text{Cp}^{t\text{Bu}}$ ring as occupying a single coordination position at the ring centroid, the geometry at the molybdenum center can best be described as a distorted trigonal prism.

A preliminary electrochemical investigation shows a reversible one-electron oxidation process at $E_{1/2} = -0.89$ V in THF and -0.93 V in MeCN versus the ferrocene/ferrocenium couple, thus suggesting that the oxidation product has a certain stability. The stoichiometric oxidation was accomplished by the use of $[\text{Cp}_2\text{Fe}^+]\text{PF}_6^-$ in THF and afforded a product that was sufficiently stable to be isolated and crystallized.[20] Its structure is closely related to that of the neutral precursor (Figure 1 b). The Mo–$\text{Cp}^{t\text{Bu}}$(centroid) separation is shortened upon oxidation, whereas the Mo–P bonds are lengthened. Not much significance should be attributed to the parameters involving the imprecisely determined hydride positions, but the most notable change is an apparent shortening of the H2···H3 contact (1.40 Å in the cation versus 1.63 Å in the neutral complex), thus suggesting an increased H–H attraction in the oxidized complex. The complex, however, can still be described as a classical trihydride. In THF solution, the complex exhibits a

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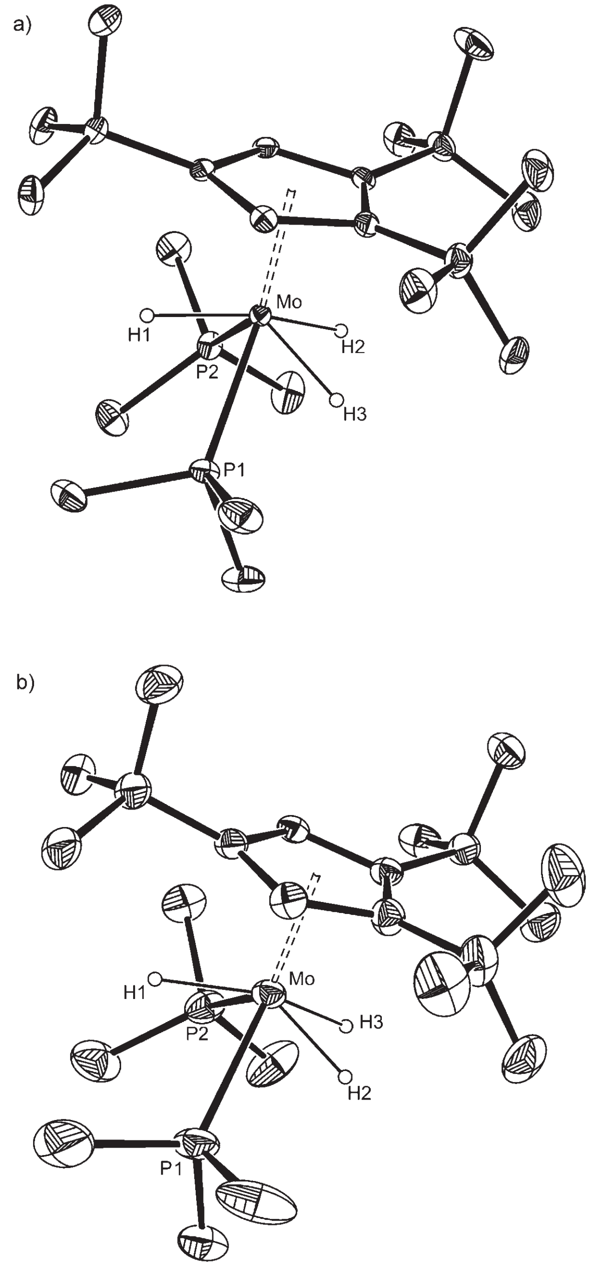

Figure 1. ORTEP views of a) $[Cp^{tBu}Mo(PMe_3)_2H_3]$ and b) the cation in $[Cp^{tBu}Mo(PMe_3)_2H_3]PF_6$. Ellipsoids are drawn at the 30% probability level. All hydrogen atoms except the hydrides are omitted for clarity. Relevant parameters are listed in the order (a)/(b) (the parameters for the cation are averaged over two independent molecules in the asymmetric unit). Selected bond lengths [Å] and angles [°]: Mo-CNT 2.0150(2)/2.002(2), Mo-P1 2.3832(6)/2.473(2), Mo-P2 2.3801(6)/2.473(2), Mo-H1 1.58(3)/1.62(4), Mo-H2 1.57(3)/1.54(4), Mo-H3, 1.58(3)/1.57(4) H2⋯H3 1.63/1.40; CNT-Mo-P1 130.62(2)/127.0(8), CNT-Mo-P2 132.14(2)/127.4(3), P1-Mo-P2 93.71(2)/100.3(1), CNT-Mo-H1 106(1)/104(2), CNT-Mo-H2 107(1)/108(2), CNT-Mo-H3 114(1)/108(2). CNT = centroid of the Cp^{tBu} ring.

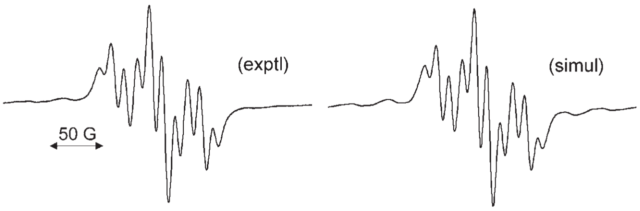

Figure 2. Experimental and simulated EPR spectra of compound $[Cp^{tBu}Mo(PMe_3)_2H_3]PF_6$ in THF ($T = 193$ K).

rather broad EPR spectrum at ambient temperature, but sharpening occurs at lower temperatures, thus allowing the identification of the expected quartet-of-triplet feature, which results from coupling to three equivalent hydride ligands and to the P nuclei of two equivalent phosphine ligands, additionally flanked by ^{95}Mo and ^{97}Mo isotope satellites. Satisfactory simulation (Figure 2) provides the hyperfine coupling constants $a_P = 36.2$ G, $a_H = 11.4$ G, and $a_{Mo} = 30.8$ G, which compare with those of the analogous but less thermally stable $[Cp^*Mo(dppe)H_3]^+$ complex ($a_P = 29.8$ G, $a_H = 11.8$ G).

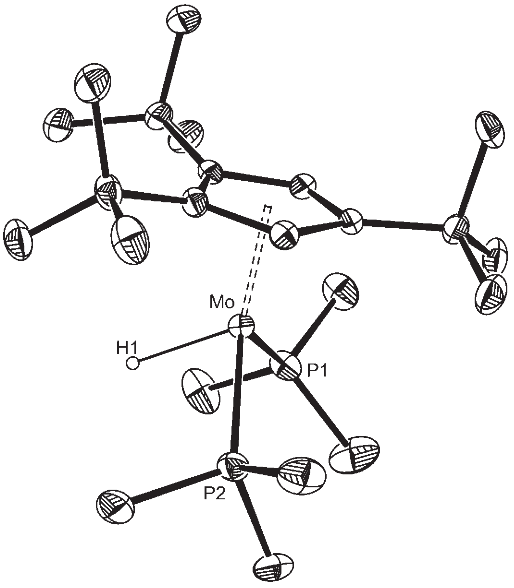

Figure 3. ORTEP view of the cation in $[Cp^{tBu}Mo(PMe_3)_2H]PF_6$. Ellipsoids are drawn at the 30% probability level. All hydrogen atoms except the hydride are omitted for clarity. Selected bond lengths [Å] and angles [°]: Mo-CNT 2.0096(3), Mo-P1 2.4801(8), Mo-P2 2.4685(9), Mo-H1 1.83(3); CNT-Mo-P1 122.02(2), CNT-Mo-P2 121.57(2), P1-Mo-P2 109.55(3), CNT-Mo-H1 125.2(9). CNT is the Cp^{tBu} ring centroid.

Although compound $[Cp^{tBu}Mo(PMe_3)_2H_3]PF_6$ is quite stable as a crystallized solid and in THF solution at low temperatures, it slowly decomposes above 0 °C, as indicated by a color change from orange to green. Well-formed green crystals were obtained by slow crystallization from THF/pentane at −20 °C. The X-ray diffraction analysis revealed the identity of the compound as the H_2-elimination product $[Cp^{tBu}Mo(PMe_3)_2H]^+PF_6^-$ (Figure 3).[20] Its formation from $[Cp^{tBu}Mo(PMe_3)_2H_3]^+$ can be viewed as the collapse of the H2 and H3 atoms (Figure 1b) to yield a putative $[Cp^{tBu}Mo(PMe_3)_2H(H_2)]^+PF_6^-$ nonclassical intermediate, followed by H_2 dissociation. Although, once again, structural parameters involving the hydride position may be imprecise, the quality of the data set allowed the identification of a single hydride ligand with a high level of confidence. Therefore, the product is a 15-electron complex of Mo^{III}. When protected from air, the compound is stable over several months in the solid state and at least for several hours in THF solution at room temperature. This stability can be attributed to steric protection, since no additional electron density is available on the ligands for a π-stabilization mechanism.

Although the 15-electron configuration is quite common in the coordination chemistry of Mo^{III} (associated without fail to a spin quartet state), it is extremely rare for organometallic compounds because of the lower electron-pairing energy in the presence of softer organic ligands.[21,22] Two examples that also enjoy high steric protection and adopt a spin quartet ground state are $[(C_5Ph_5)_2Mo]^+$[23] and $[Mo(SC_6H_3Mes_2)_3]$ (Mes = 2,4,6-$Me_3C_6H_2$).[24] Open-shell hydride complexes are also extremely rare. An example with a 15-electron configuration is $[(Tp^{tBu,Me})CoH]$ ($Tp^{tBu,Me}$ = hydridotris(3-*tert*-butyl-5-methylpyrazolyl)borate).[25]

The spin configuration for the complex $[Cp^{tBu}Mo(PMe_3)_2H]^+$ could not be determined by magnetic methods because of our inability to prepare a pure bulk sample (the compound crystallized together with other decomposition products, for example, $[Cp^{tBu}Mo(PMe_3)_2H_4]^+$ obtained by proton-transfer processes).[26] However, we were able to confirm the spin quartet ground state by EPR spectroscopy. Unlike the spin doublet configuration, a spin quartet ground state is notoriously difficult to observe by EPR spectroscopy for second- and third-row transition metals with large zero-field splitting. According to theory, a slightly rhombically distorted tetragonal tensor should have g_x and g_y values close to four and a g_z value close to two for the spin-allowed $\pm \frac{1}{2}$ transition.[27] Moreover, a spin-forbidden $\pm \frac{3}{2}$ transition may also be accessible, yielding a weak feature at $g \approx 6$ for the *z* component. A rare example for Mo^{III} is given by $[Mo(acac)_3]$, for which a relatively broad spectrum can be observed between liquid-nitrogen and liquid-helium temperatures.[28] Solutions of $[Cp^{tBu}Mo(PMe_3)_2H]PF_6$ in THF were EPR-silent at room temperature and showed only a small resonance at liquid-nitrogen temperature, which is characteristic of residual $[Cp^{tBu}Mo(PMe_3)_2H_3]PF_6$. The solid sample, however, exhibited the features shown in Figure 4 at liquid-helium temperature. The *x* and *y* components of the *g* tensor (± 1/2 transition) are indeed visible at $g = 3.74$ and $g \approx 3.45$, as well as a weak feature attributed to the $\pm \frac{3}{2}$ transition (*z* component) at $g = 5.33$. The $g = 3.74$ peak appears to display a fine structure, possibly a result of coupling to the two equivalent P nuclei. The g_z component of the $\pm \frac{1}{2}$ transition is not visible because it is overshadowed by stronger resonances of residual 17-electron trihydride at $g = 2.009$.

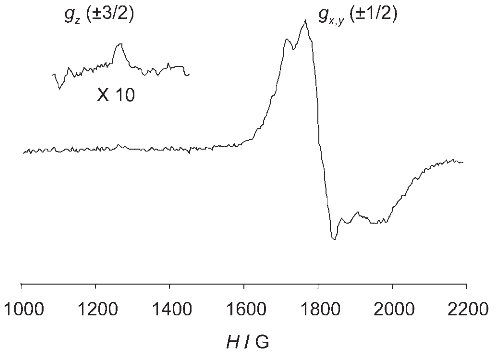

Figure 4. Liquid-helium, X-band EPR spectrum of compound $[Cp^{tBu}Mo(PMe_3)_2H]PF_6$ (polycrystalline solid sample).

In summary, we have presented the first structural characterization of the starting and end products of an H_2 oxidatively induced reductive elimination. The end product is a rare example of a 15-electron hydride complex.

Experimental Section

All operations were carried out in an argon atmosphere with Schlenk line and dry-box techniques. Solvents were dehydrated by standard methods and distilled under dinitrogen. The following instrumentation was used: EG&G 362 potentiostat for cyclic voltammetry, Bruker AC200 for ^1H and ^{31}P NMR spectroscopy, Bruker ESP300 for EPR spectroscopy, Oxford-Diffraction XCALIBUR and Stoe IPDS for X-ray diffraction. Compound $[Cp^{tBu}MoCl_4]$ was obtained from $[Cp^{tBu}Mo(CO)_3(CH_3)]$ and $PhICl_2$, the carbonyl compound being obtained in turn from $[Mo(CO)_6]$ and $NaCp^{tBu}$ by adapting the literature procedure used for the Cp* analogue.[29]

$[Cp^{tBu}Mo(PMe_3)_2H_3]$: PMe_3 (1 M in THF, 8 mL, 8 mmol) was added to $[Cp^{tBu}MoCl_4]$ (1.42 g, 3.00 mmol) in THF (20 mL). After stirring for 30 min, a suspension of $LiAlH_4$ (ca. 650 mg) in THF (40 mL) was carefully added, resulting in gas evolution. After stirring for 5 h, MeOH (ca. 6 mL) was added dropwise, thereby causing vigorous gas evolution. After an additional 1 h of stirring the suspension was dried in vacuum. The residue was then extracted with Et_2O (150 mL) and filtered through celite. The final solution was dried in vacuo, and the pale yellow solid was washed with methanol and dried in vacuo. Yield: 727 mg (50 %). Elemental analysis (%) calcd for $C_{23}H_{50}MoP_2$: C 57.01, H 10.40; found: C 56.48, H 10.88; ^1H NMR (C_6D_6): $\delta = -5.20$ (t, $J = 51.0$ Hz, 3H, MoH), 1.37 (s, 9H, *t*Bu), 1.49 (br, 18H, PMe_3), 1.58 (s, 18H, 2 × *t*Bu), 4.86 ppm (s, 2H, $C_5H_2tBu_3$); $^{31}P\{^1H\}$ NMR (C_6D_6): $\delta = 17.9$ ppm (s). A single crystal for the X-ray analysis was obtained by slow diffusion of a MeOH layer into a pentane solution at 5 °C.

$[Cp^{tBu}Mo(PMe_3)_2H_3]PF_6$: A suspension of $[Cp_2Fe]PF_6$ (32 mg, 0.10 mmol) in THF (5 mL) was added dropwise to a cold solution (193 K) of $[Cp^{tBu}Mo(PMe_3)_2H_3]$ (53 mg, 0.11 mmol) in THF (10 mL). The solution color immediately changed from pale yellow to dark blue and, within a few minutes, to orange. The reaction mixture was slowly warmed up to 253 K and then concentrated to about 1 mL. Addition of cold pentane (253 K, 10 mL) afforded a brown precipitate that was decanted and further washed with cold pentane (253 K, 3 × 10 mL) and finally dried in vacuum. Yield: 48 mg (70 %). A single crystal for the X-ray analysis was obtained by diffusion of a pentane layer into a THF solution at −80 °C. EPR (THF, 193 K): $g = 2.016$ (triplet of quartets), $a_P = 36.2$ G, $a_H = 11.4$ G, $a_{Mo} = 30.8$ G.

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[20] The structures were solved by direct methods (SIR97) and refined by full-matrix least squares (SHELXL97). H atoms were treated with the riding model except for the hydride ligands, which were fully refined with isotropic thermal parameters. CCDC-619352–619354 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Crystal data for $[\mathrm{Cp}^{t\mathrm{Bu}}\mathrm{Mo}(\mathrm{PMe}_3)_2\mathrm{H}_3]$: $\mathrm{C}_{23}\mathrm{H}_{50}\mathrm{MoP}_2$, $M_r = 484.51$, monoclinic, space group $P2_1/n$, $a = 16.2915(15)$, $b = 17.4655(16)$, $c = 9.2144(8)$ Å, $\beta = 92.651(10)°$, $V = 2619.1(4)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.229\ \mathrm{g\,cm^{-3}}$, $\mu = 0.629\ \mathrm{mm^{-1}}$, $\mathrm{Mo}_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 180$ K, $2\theta_{\max} = 52.32°$, scan mode ϕ (Stoe IPDS diffractometer), 20750 measured reflections (5171 independent, $R_{\mathrm{int}} = 0.0337$), 262 refined parameters. Absorption correction (multiscan), transmission factors 0.8299/0.7768. $R = 0.0270$, $wR = 0.0657$ refined against $|F^2|$, GOF = 1.034, $[\Delta\rho]_{\max}$ 0.514, $[\Delta\rho]_{\min}$ $-0.524\ \mathrm{e\,A^{-3}}$. Crystal data for $[\mathrm{Cp}^{t\mathrm{Bu}}\mathrm{Mo}(\mathrm{PMe}_3)_2\mathrm{H}_3]\mathrm{PF}_6$: $\mathrm{C}_{23}\mathrm{H}_{50}\mathrm{F}_6\mathrm{MoP}_3$, $M_r = 629.48$, monoclinic, space group $P2_1/c$, $a = 14.0847(10)$, $b = 26.216(2)$, $c = 20.1855(15)$ Å, $\beta = 99.221(8)°$, $V = 7357.2(10)$ Å^3, $Z = 8$, $\rho_{\mathrm{calcd}} = 1.269\ \mathrm{g\,cm^{-3}}$, $\mu = 0.535\ \mathrm{mm^{-1}}$, $\mathrm{Mo}_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 180$ K, $2\theta_{\max} = 50.00°$, scan mode ϕ (Stoe IPDS diffractometer), 50093 measured reflections (12934 independent, $R_{\mathrm{int}} = 0.0853$), 763 refined parameters. Absorption correction (multiscan), transmission factors 0.8843/0.8674. $R = 0.0488$, $wR = 0.1052$ refined against $|F^2|$, GOF = 0.835, $[\Delta\rho]_{\max}$ 0.802, $[\Delta\rho]_{\min}$ $-0.441\ \mathrm{e\,A^{-3}}$. Crystal data for $[\mathrm{Cp}^{t\mathrm{Bu}}\mathrm{Mo}(\mathrm{PMe}_3)_2\mathrm{H}]\mathrm{PF}_6$: $\mathrm{C}_{23}\mathrm{H}_{48}\mathrm{F}_6\mathrm{MoP}_3$, $M_r = 627.46$, monoclinic, space group $P2_1/c$, $a = 9.6185(5)$, $b = 16.8699(10)$, $c = 18.7489(12)$ Å, $\beta = 90.441(5)°$, $V = 3042.2(3)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.370\ \mathrm{g\,cm^{-3}}$, $\mu = 0.636\ \mathrm{mm^{-1}}$, $\mathrm{Mo}_{K\alpha}$ radiation ($\lambda = 0.71073$ Å), $T = 180$ K, $2\theta_{\max} = 52.74°$, scan mode ω and ϕ (Oxford-Diffraction XCALIBUR diffractometer), 25511 measured reflections (18993 independent, $R_{\mathrm{int}} = 0.0513$), 317 refined parameters. Absorption correction (multiscan), transmission factors 0.8363/0.7206. $R = 0.0507$, $wR = 0.1428$ refined against $|F^2|$, GOF = 1.070, $[\Delta\rho]_{\max}$ 1.073, $[\Delta\rho]_{\min}$ $-0.981\ \mathrm{e\,A^{-3}}$.

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