Supporting Information
for the
Article Entitled

Carbon Monoxide-Induced N-N Bond Cleavage of Nitrous Oxide That Is Competitive with Oxygen Atom Transfer to Carbon Monoxide as Mediated by a Mo(II) / Mo(IV) Catalytic Cycle

authored by

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Details for the synthesis and isolation of **7**. Crystallographic information regarding X-ray analyses, including tables of bond lengths, angles and anisotropic displacement parameters, for **7**. NMR spectral evidence demonstrating the reactivity of **1**, **2**, **3** and **9**.

Experimental Procedures

All manipulations with air and moisture sensitive compounds were carried out under N_2 or Ar atmospheres with standard Schlenk or glovebox techniques. All solvents were dried (Na for toluene and Na/benzophenone for pentane, Et_2O and THF) and distilled under N_2 prior to use. d_6-Benzene was dried over Na/K alloy and isolated by vacuum-transfer prior to use. Celite™ was oven dried (150 °C for several days) prior to use. Cooling was performed in the internal freezer of a glovebox maintained at -30 ºC. Nitrous oxide, $^{15}N_2$-labelled nitrous oxide (98%), carbon monoxide and ^{13}C-labeled carbon monoxide (99%) were purchased from Sigma Aldrich. All purchased chemicals were used as received. Complexes **1**, **2**, **3**, **4**, **6** and **9** were prepared according to the previously reported procedures in similar yield and purity.[1,2] All ^1H NMR and ^{13}C NMR spectra were recorded at 400 MHz or 500 MHz and 125.6 MHz respectively. Light mediated reactions were performed using a Rayonet® Photochemical Reactor containing a carousel of ultraviolet lamps (catalogue number: RPR-3500A) with an output of 300-400 nm. Elemental analyses were carried out by Midwest Microlab LLC.

Synthesis of Cp*Mo[N(^{i}Pr)C(Me)N(^{i}Pr)](κ-*N*-NO)(κ-*N*-NCO) (7) using N_2O.

A solution of **1** (40 mg, 93 μmol) in 4 mL of d_6-benzene was transferred to four Pyrex J young NMR tubes. The headspaces of the tubes were evacuated and charged with nitrous oxide (10 psi) at room temperature. The tubes were exposed to UV irradiation for 10 h and left to stand at room temperature overnight to produce a brown solution. The solutions were combined in air and left under air overnight. The solutions were filtered and reduced to dryness. The crude yellow product was purified by crystallization from a toluene/pentane solution at -30 °C, to produce pale yellow crystals of **7** (8.1 mg, yield = 20%). ^1H NMR (400 MHz, d_6-benzene): 1.10 (3H, d, J = 6.6 Hz, CH(CH_3)$_2$), 1.14 (3H, d, J = 6.6 Hz, CH(CH_3)$_2$), 1.15 (3H, d, J = 6.6 Hz, CH(CH_3)$_2$), 1.18 (3H, d, J = 6.6 Hz, CH(CH_3)$_2$), 1.45 (3H, s, NC(CH_3)N), 1.58 (15H, s, C$_5$(CH_3)$_5$), 3.17 (1H, sp, J = 6.6 Hz, CH(CH$_3$)$_2$), 3.58 (1H, sp, J = 6.4 Hz, CH(CH$_3$)$_2$). IR (KBr) $\nu_{N=O}$ =2224 cm^{-1}; $\nu_{N=C=O}$ = 1603 cm^{-1}. ^{13}C-^{15}N-Labeled -**7** was prepared by this method using ^{13}C- labeled **1** and ^{15}N-labeled nitrous oxide.

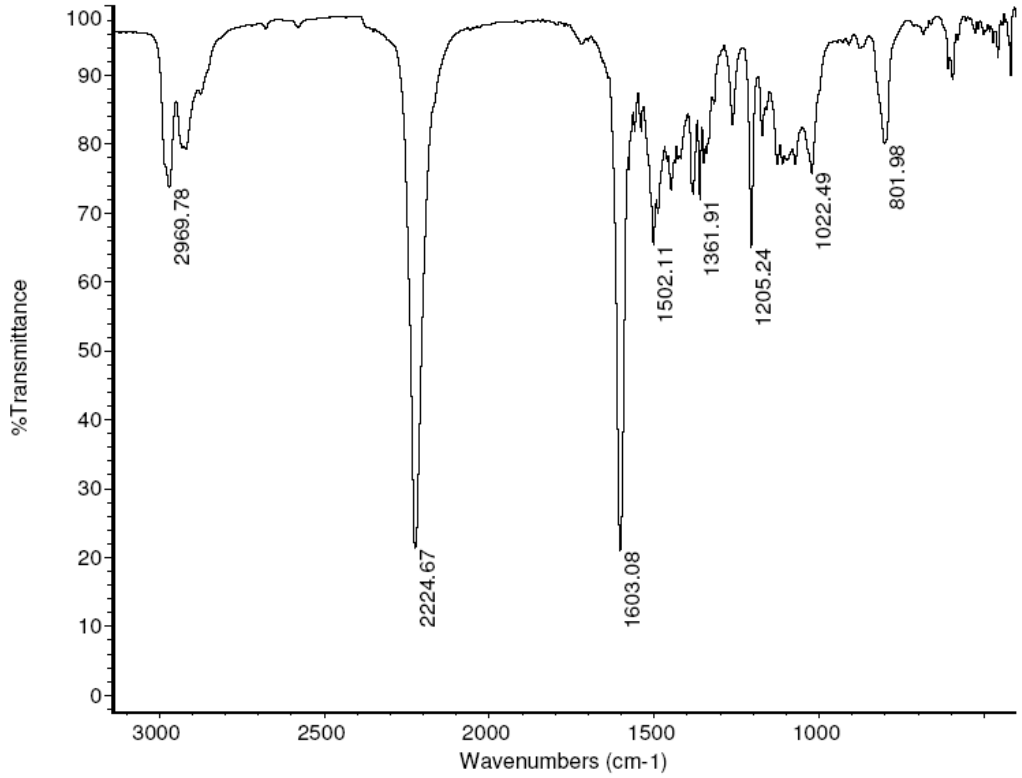

Figure 1. Solid state IR spectrum of complex **7** in KBr.

Synthesis of Cp*Mo[N(^{i}Pr)C(Me)N(^{i}Pr)](κ-*N*-NO)(κ-*N*-N^{13}CO) (^{13}C-7)

A solution of **1** (27.0 mg, 63.1 μmol) in 4 mL of d_6-benzene was transferred to three Pyrex J young NMR tubes. The headspaces of the tubes were evacuated and charged with an equimolar mixture of nitrous oxide and ^{13}C-labeled carbon monoxide (10 psi) at room temperature. The tubes were exposed to UV irradiation for 12 h. The orange solutions were combined in air and left under air overnight. The resultant yellow solutions were filtered and reduced to dryness. The crude yellow product was purified by crystallization from a toluene/pentane solution at -30 °C, to produce yellow crystals of **^{13}C-7** (15.6 mg, yield = 56%).

Synthesis of Cp*Mo[N(^{i}Pr)C(Me)N(^{i}Pr)](κ-*N*-^{15}NO)(κ-*N*-^{15}N^{13}CO) (^{15}N,^{15}N, ^{13}C-7). Indentical procedure as used for ^{13}C-**7** except that ^{15}N^{15}NO was used.

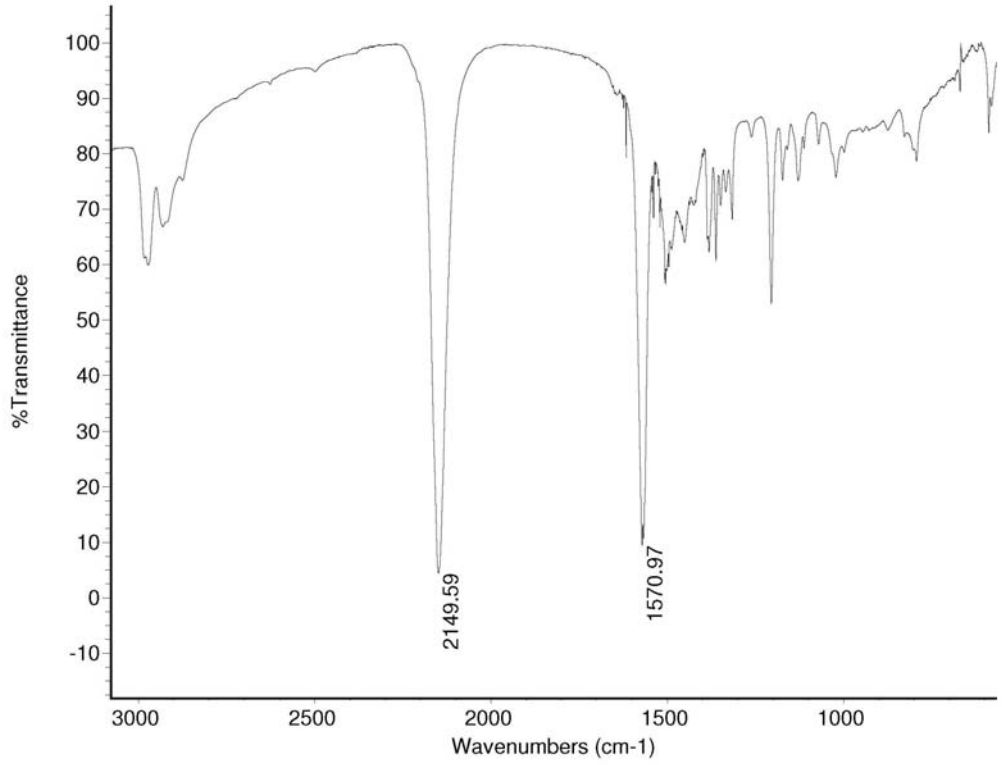

Figure 2. Solid state IR spectrum of **(^{15}N,^{15}N, ^{13}C-7)** in KBr.

NMR experiment demonstrating the formation of complexes 3 and 7 from complex 1 under an atmosphere of nitrous oxide.

A sample of 4 mg of **1** was dissolved in 0.6 mL of d_6-benzene and transferred into a Pyrex J Young NMR tube. The headspace of the J Young tube was evacuated and charged with nitrous oxide (10 psi) at room temperature. The tube was exposed to UV irradiation and ^{1}H NMR spectra recorded periodically.

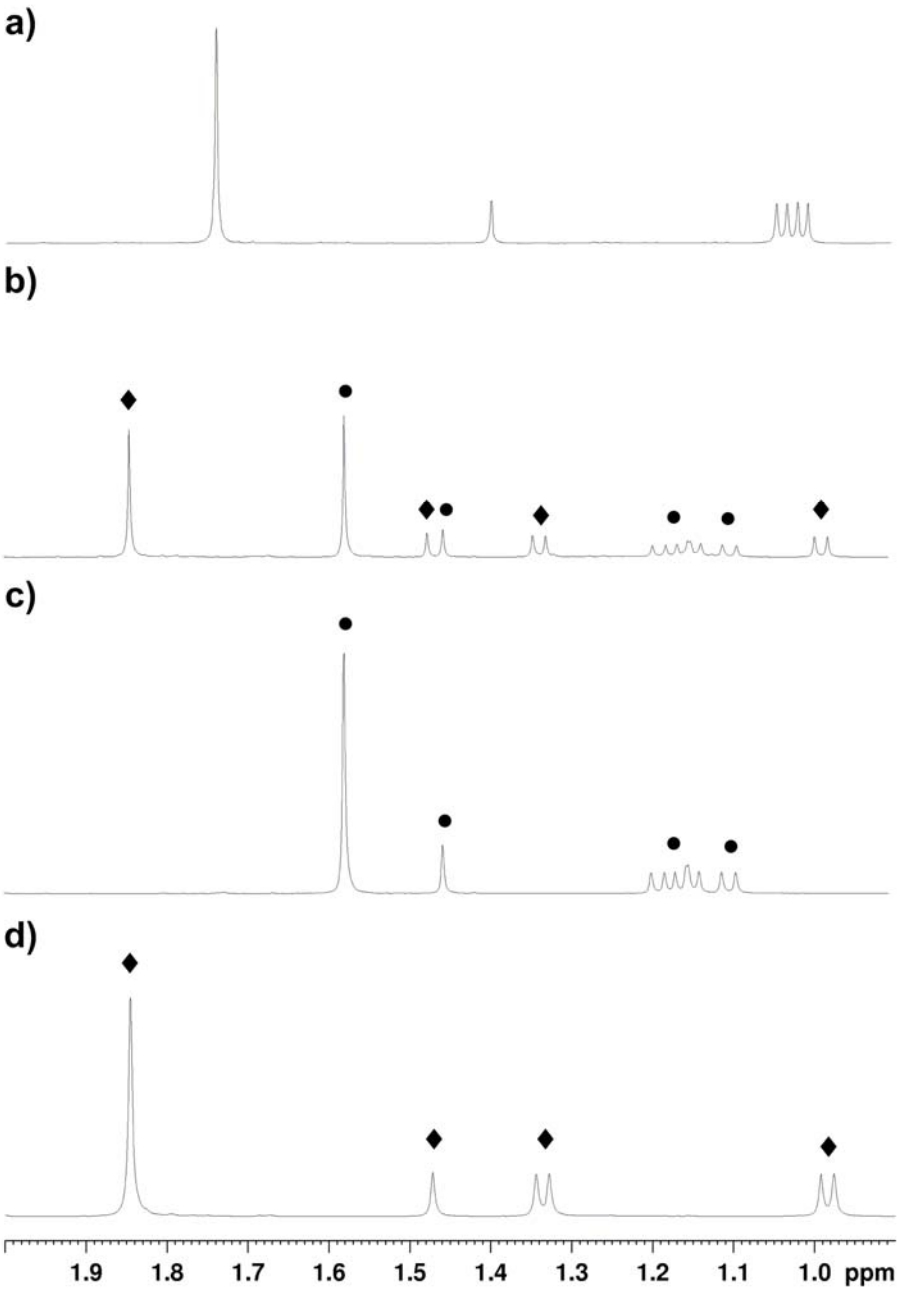

Figure 3. Partial ^{1}H-NMR spectra of **1** in the presence of nitrous oxide after irradiation by UV for a) 0 hours and b) 2 hours, c) complex **7** (●) and d) complex **3** (♦).

NMR experiment demonstrating the formation of complexes 4 from complex 2 under an atmosphere of nitrous oxide.

A sample of 4 mg of **2** was dissolved in 0.6 mL of d_6-benzene and transferred into a Pyrex J Young NMR tube. The headspace of the J Young tube was

evacuated and charged with nitrous oxide (10 psi) at room temperature. The tube was exposed to UV irradiation and ^{1}H NMR spectra recorded periodically.

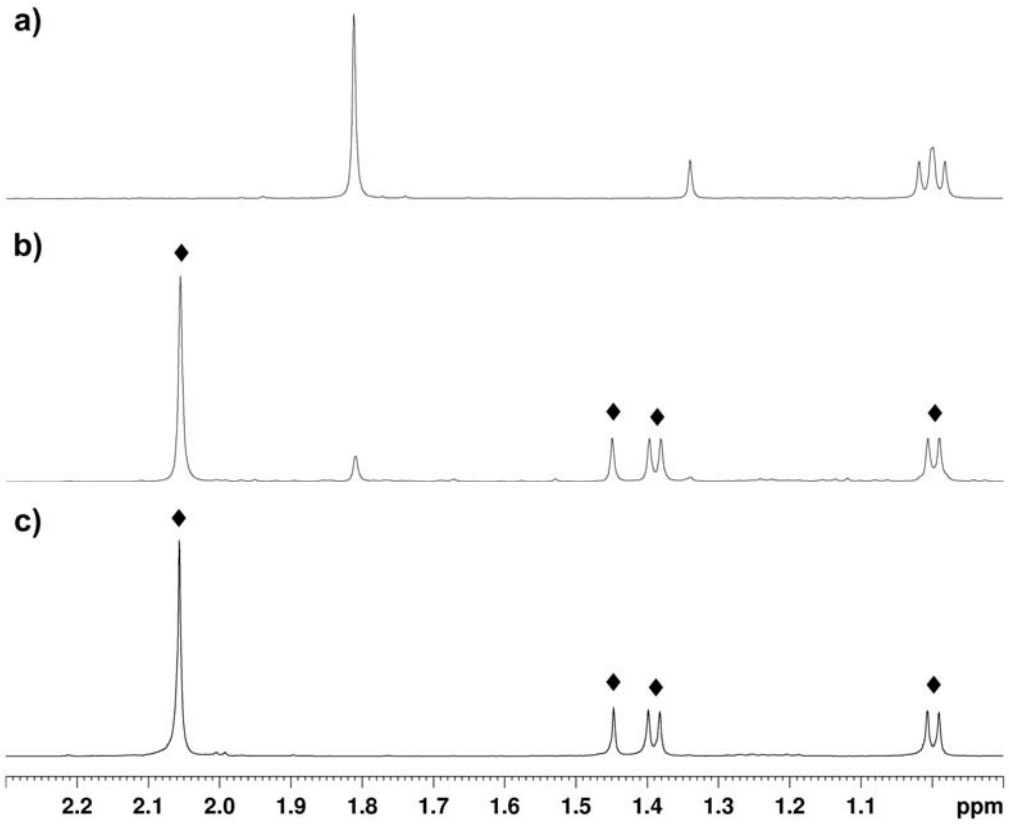

Figure 4. Partial ^{1}H-NMR spectra of **2** in the presence of nitrous oxide after irradiation by UV for a) 0 hours and b) 3 hours and c) complex **4** (♦).

NMR experiment demonstrating the formation of complex 7 and ^{13}C-labeled carbon dioxide from complex 1 under an atmosphere of nitrous oxide and ^{13}C-labeled carbon monoxide.

A stock solution of durene (11.1 mg, 83.7 μmol) in 5 mL of d_6-benzene was prepared in a volumetric flask. Complex **1** (4.1 mg, 9.6 μmol) was weighed out and dissolved in 0.6 mL of the durene stock solution. The solution was transferred to a Pyrex J Young NMR tube. The head space of the tube was evacuated and charged with an equimolar mixture of nitrous oxide and ^{13}C-

labeled carbon monoxide (10 psi). The tube was exposed to UV irradiation and ^{1}H and ^{13}C NMR spectra recorded periodically.

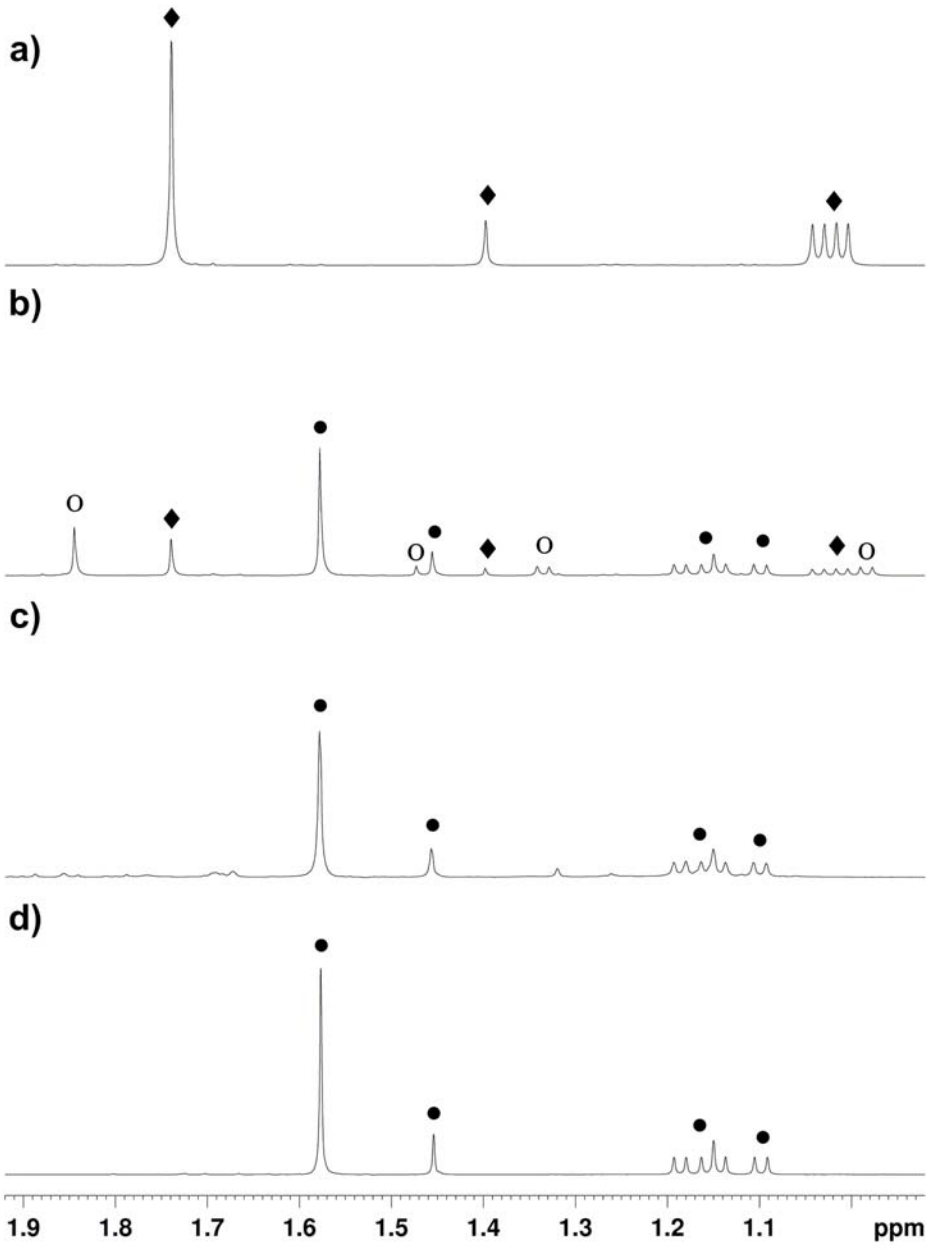

Figure 5. Partial ^{1}H-NMR spectra of **1** in the presence of an equimolar mixture of nitrous oxide and ^{13}C-labeled carbon monoxide after irradiation with UV for a) 0 hours, b) 1 hour and c) 16 hours and d) complex **7**. Labeled resonances are **1** (♦), **3** (o) and **7** (●).

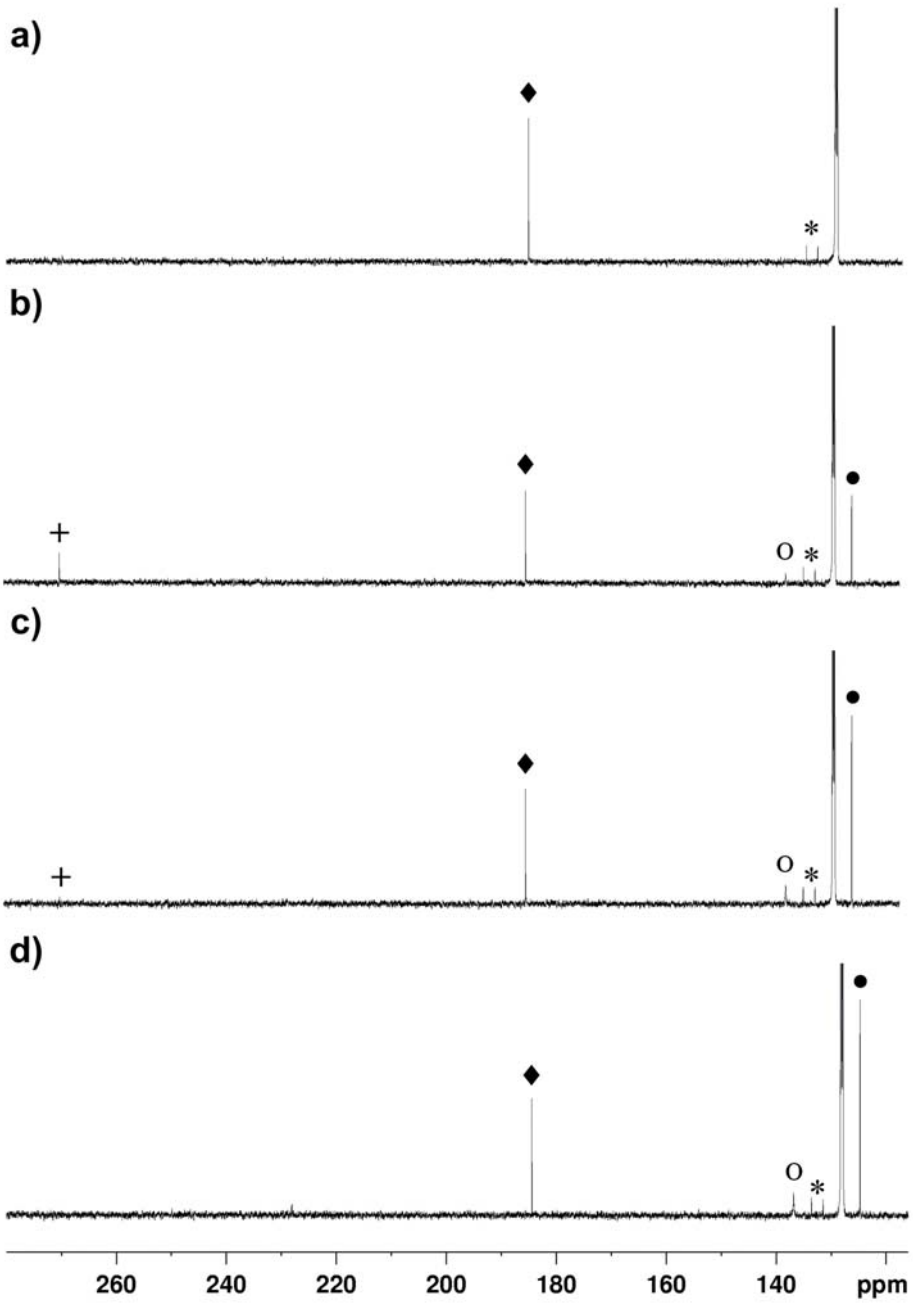

Figure 6. Partial ^{13}C-NMR spectra of **1** in the presence of an equimolar mixture of nitrous oxide and ^{13}C-labeled carbon monoxide after a) 0 hours, b) 1 hour, c) 4 hours and d) 16 hours. Labeled resonances are: ^{13}CO (♦), durene internal standard (∗), ^{13}C-labelled-**1** (**+**), ^{13}C-labelled-**7** (**o**) and $^{13}CO_2$ (●).

NMR experiment demonstrating the formation ^{13}C-labeled carbon dioxide by complex 2 under an atmosphere of nitrous oxide and ^{13}C-labeled carbon monoxide.

A stock solution of durene (11.1 mg, 83.7 μmol) in 5 mL of d_6-benzene was prepared in a volumetric flask. Complex **2** (4.9 mg, 9.6 μmol) was weighed out and dissolved in 0.6 mL of the durene stock solution. The solution was transferred to a Pyrex J Young NMR tube. The head space of the tube was evacuated and charged with an equimolar mixture of nitrous oxide and ^{13}C-labeled carbon monoxide (10 psi). The tube was exposed to UV irradiation and ^{13}C NMR spectra recorded periodically.

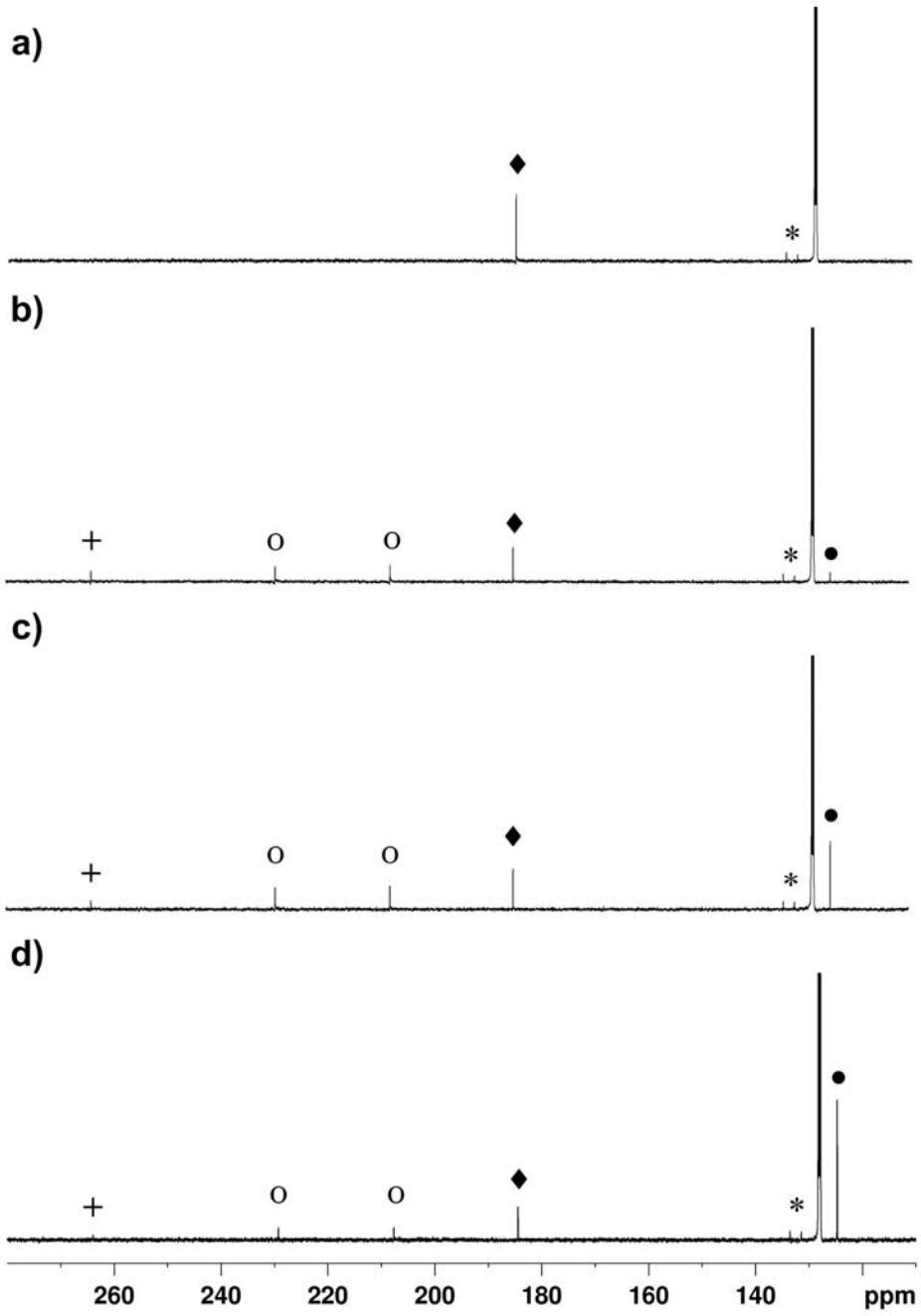

Figure 7. Partial ^{13}C-NMR spectra of **2** in the presence of an equimolar mixture of nitrous oxide and ^{13}C-labeled carbon monoxide after a) 0 hours, b) 1 hour, c) 4 hours and d) 16 hours. Labeled resonances are: ^{13}CO (♦), durene internal standard (∗), ^{13}C-labelled-**2** (**+**), ^{13}C-labelled-**6** (**o**) and $^{13}CO_2$ (●).

NMR experiment demonstrating the formation of complex 7 from complex 9 under an atmosphere of nitrous oxide and ^{13}C-labeled carbon monoxide.

A sample of 4 mg of **9** was dissolved in 0.6 mL d_6-benzene and transferred into a Pyrex J Young NMR tube. The headspace of the J Young tube was evacuated and charged with an equimolar mixture of nitrous oxide and ^{13}C-labeled carbon monoxide (10 psi). The tube was left in the dark at room temperature and ^{1}H and ^{13}C NMR spectra recorded periodically.

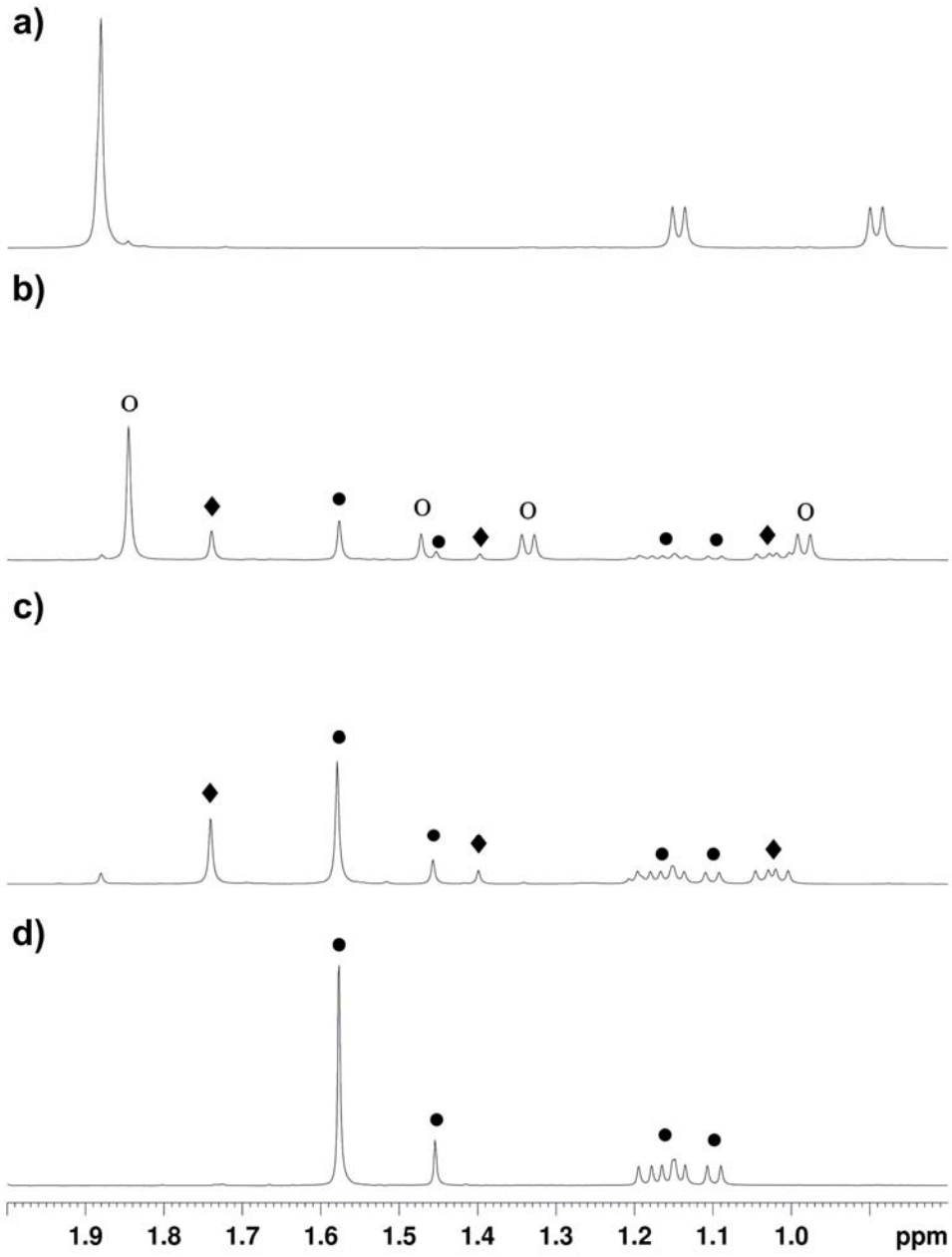

Figure 8. Partial ^{1}H-NMR spectra of **9** in the presence of an equimolar mixture of nitrous oxide and ^{13}C-labeled carbon monoxide after a) 0 hours, b) 3 hours and c) 4 days and d) complex **7**. Labeled resonances are 1 (♦), 3 (**o**) and 7 (●).

NMR experiment demonstrating the formation of complex 7 from complex 3 under an atmosphere of nitrous oxide and ^{13}C-labeled carbon monoxide.

A sample of 4 mg of **3** was dissolved in 0.6 mL d^{6}-benzene and transferred into a J Young tube. The headspace of the J Young tube was evacuated and charged with an equimolar mixture of nitrous oxide and ^{13}C-labeled carbon monoxide (10 psi). The tube was left in the dark at room temperature and ^{1}H and ^{13}C NMR spectra recorded periodically.

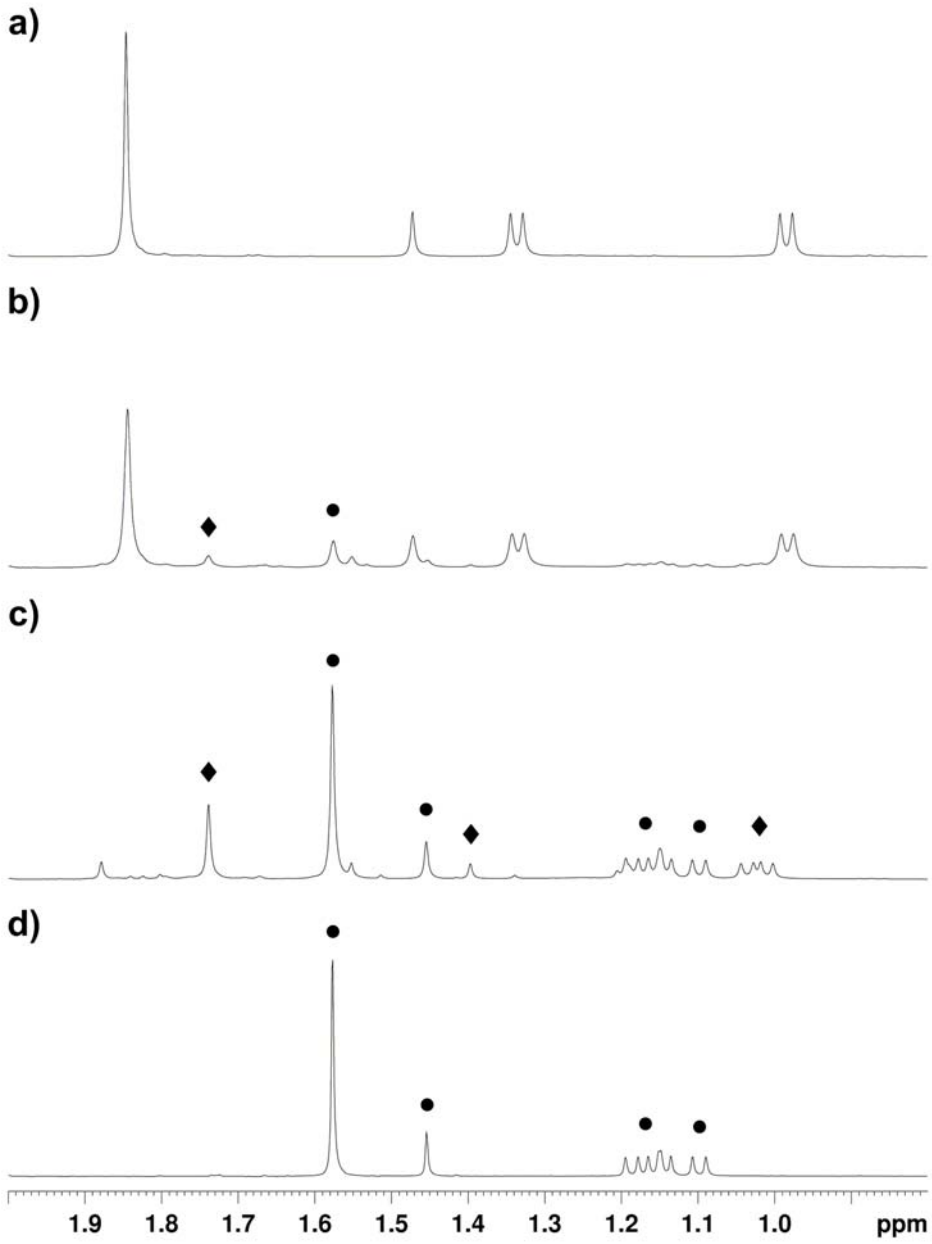

Figure 9. Partial ^{1}H-NMR spectra of **3** in the presence of an equimolar mixture of nitrous oxide and ^{13}C-labeled carbon monoxide after a) 0 hours, b) 3 hours and c) 4 days and d) complex **7**. Labeled resonances are **1** (♦) and **7** (●).

References

1. Fontaine, P. P.; Yonke, B. L.; Zavalij, P. Y.; Sita, L. R. *J. Am. Chem. Soc.* **2010**, *132*, 12273-12285.
2. Yonke, B. L.; Reeds, J. P.; Zavalij, P. Y.; Sita, L. R. *Angew. Chem. Int. Ed.* **2011**, *50*, in press.

Crystallographic Information

Cp*Mo[N(^{i}Pr)C(Me)N(^{i}Pr)](κ-*N*-NO)(κ-*N*-NCO) (7)

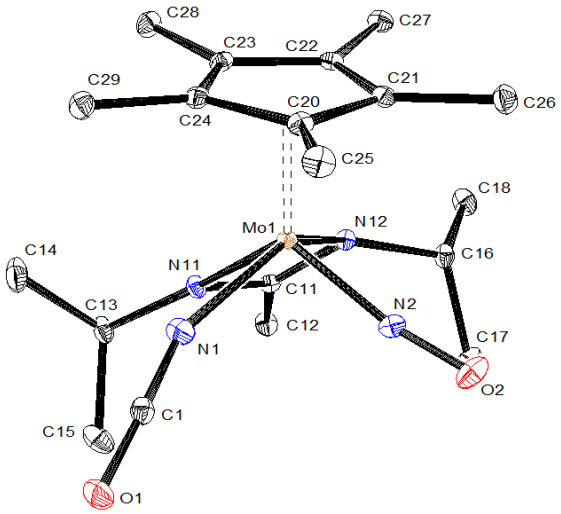

Figure 9. Crystal structure of **7** with hydrogen atoms omitted for clarity, ellipsoids for the non-hydrogen atoms are shown at the 30% probability level.

A clear yellow-orange plate-like specimen of $C_{19}H_{32}MoN_4O_2$, approximate dimensions 0.08 mm × 0.27 mm × 0.31 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker Smart Apex2, CCD system equipped with a graphite monochromator and a MoKα fine focus sealed tube (λ = 0.71073 Å). Data collection temperature was 100 K.

The total exposure time was 19.24 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm. The integration of the data using a monoclinic unit cell yielded a total of 15955 reflections to a maximum θ angle of 29.99° (0.71 Å resolution), of which 5959 were independent (average redundancy 2.677, completeness = 99.9%, R_{int} = 1.53%, R_{sig} = 1.65%) and 5912 (99.21%) were greater than $2\sigma(F^2)$. The final cell constants of a = 9.1178(4) Å, b = 13.4299(6) Å, c = 17.0872(8) Å, β = 90.5680(10)°, V = 2092.24(16) Å^3, are based upon the refinement of the XYZ-centroids of 9965 reflections above 20 σ(I) with 4.766° < 2θ < 62.23°. Data were corrected for absorption effects using the multi-scan method (SADABS). The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.8247 and 0.9531.

The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group Cc, with Z = 4 for the formula unit, $C_{19}H_{32}MoN_4O_2$. The final anisotropic full-matrix least-squares refinement on F^2 with 256 variables converged at R_1 = 1.57%, for the observed data and wR_2 = 3.75% for all data. The goodness-of-fit was 1.000. The largest peak in the final difference electron density synthesis was 0.891 $e^-/Å^3$ and the largest hole was -0.375 $e^-/Å^3$ with an RMS deviation of 0.045 $e^-/Å^3$. On the basis of the final model, the calculated density was 1.411 g/cm^3 and F(000), 928 e^-

APEX2 Version 2010.11-3 (Bruker AXS Inc.)

SAINT Version 7.68A (Bruker AXS Inc., 2009)

SADABS Version 2008/1 (G. M. Sheldrick, Bruker AXS Inc.)

XPREP Version 2008/2 (G. M. Sheldrick, Bruker AXS Inc.)

XS Version 2008/1 (G. M. Sheldrick, *Acta Cryst.* (2008). A**64**, 112-122)

XL Version 2008/4 (G. M. Sheldrick, *Acta Cryst.* (2008). A**64**, 112-122)

Platon (A. L. Spek, *Acta Cryst.* (1990). A**46**, C-34)

Table 1. Sample and crystal data for **7**.

Identification code	2161
Chemical formula	$C_{19}H_{32}MoN_4O_2$
Formula weight	444.43
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal size	0.08 × 0.27 × 0.31 mm
Crystal habit	clear yellow-orange plate
Crystal system	monoclinic
Space group	Cc
Unit cell dimensions	a = 9.1178(4) Å α = 90°
	b = 13.4299(6) Å β = 90.5680(10)°
	c = 17.0872(8) Å γ = 90°
Volume	2092.24(16) $Å^3$
Z	4
Density (calculated)	1.411 Mg/cm^3
Absorption coefficient	0.647 mm^{-1}
F(000)	928

Table 2. Data collection and structure refinement for **7**.

Diffractometer	Bruker Smart Apex2, CCD
Radiation source	fine focus sealed tube, MoKα
Theta range for data collection	2.38 to 29.99°

Index ranges	$-12 \le h \le 12$, $-18 \le k \le 18$, $-24 \le l \le 23$
Reflections collected	15955
Independent reflections	5959 [R(int) = 0.0153]
Coverage of independent reflections	99.9%
Absorption correction	multi-scan
Max. and min. transmission	0.9531 and 0.8247
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick, 2008)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-97 (Sheldrick, 2008)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	5959 / 2 / 256
Goodness-of-fit on F^2	1.000
Final R indices	5912 data; I>2σ(I) $R_1 = 0.0157$, $wR_2 = 0.0374$
	all data $R_1 = 0.0159$, $wR_2 = 0.0375$
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0100P)^2+2.3850P]$, $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	-0.0(0)
Largest diff. peak and hole	0.891 and -0.375 eÅ^{-3}
R.M.S. deviation from mean	0.045 eÅ^{-3}

$R_{int} = \Sigma|F_o^2 - F_o^2(\text{mean})| / \Sigma[F_o^2]$ $\quad R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$

$\text{GOOF} = S = \{\Sigma[w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$ $\quad wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$

Table 3. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2) for **7**.

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Mo1	**0.721534(9)**	**0.07772(6)**	**0.161841(8)**	**0.01091(2)**
N1	0.70036(14)	0.98519(10)	0.06269(8)	0.0189(2)
C1	0.72086(15)	0.91694(10)	0.02111(8)	0.0158(2)
O1	0.73997(14)	0.84865(9)	0.97683(7)	0.0250(2)
N2	0.77892(13)	0.97229(9)	0.21748(8)	0.0158(2)
O2	0.79400(13)	0.90160(8)	0.26053(7)	0.0248(2)
N11	0.88895(13)	0.15495(10)	0.09566(7)	0.0144(2)
N12	0.88543(12)	0.16439(8)	0.22310(6)	0.0125(2)
C11	0.96469(16)	0.18108(10)	0.15928(9)	0.0132(2)
C12	0.11909(15)	0.22106(11)	0.15749(8)	0.0182(3)
C13	0.94663(16)	0.16529(12)	0.01632(8)	0.0189(3)
C14	0.82230(19)	0.19025(16)	0.95928(9)	0.0301(4)
C15	0.02844(18)	0.07201(13)	0.99089(10)	0.0262(3)
C16	0.94861(16)	0.14691(11)	0.30211(8)	0.0161(2)
C17	0.07620(19)	0.07262(12)	0.30237(10)	0.0227(3)
C18	0.99161(17)	0.24309(12)	0.34519(9)	0.0221(3)
C20	0.47341(14)	0.05114(10)	0.17583(8)	0.0143(2)

	x/a	y/b	z/c	U(eq)
C21	0.52403(15)	0.09638(10)	0.24692(8)	0.0141(2)
C22	0.56764(15)	0.19548(11)	0.22850(9)	0.0135(3)
C23	0.54140(15)	0.21246(10)	0.14659(8)	0.0139(2)
C24	0.48138(14)	0.12478(10)	0.11433(8)	0.0141(2)
C25	0.40436(17)	0.95011(11)	0.16884(9)	0.0201(3)
C26	0.51920(17)	0.05009(12)	0.32709(9)	0.0200(3)
C27	0.61638(16)	0.27387(10)	0.28547(8)	0.0173(3)
C28	0.56217(17)	0.31023(11)	0.10572(9)	0.0196(3)
C29	0.42945(17)	0.11161(12)	0.03120(9)	0.0179(3)

Table 4. Bond lengths (Å) for **7**.

Mo1-N2	1.7812(12)	Mo1-N1	2.1084(13)
Mo1-N12	2.1570(11)	Mo1-N11	2.1723(12)
Mo1-C20	2.3051(13)	Mo1-C21	2.3390(13)
Mo1-C22	2.4081(14)	Mo1-C24	2.4121(13)
Mo1-C23	2.4560(13)	N1-C1	1.1758(19)
C1-O1	1.2028(18)	N2-O2	1.2080(16)
N11-C11	1.3292(18)	N11-C13	1.4656(18)
N12-C11	1.3331(18)	N12-C16	1.4814(17)
C11-C12	1.5073(19)	C12-H12A	0.98
C12-H12B	0.98	C12-H12C	0.98
C13-C15	1.523(2)	C13-C14	1.525(2)
C13-H13	1.0	C14-H14A	0.98
C14-H14B	0.98	C14-H14C	0.98
C15-H15A	0.98	C15-H15B	0.98
C15-H15C	0.98	C16-C17	1.532(2)
C16-C18	1.536(2)	C16-H16	1.0
C17-H17A	0.98	C17-H17B	0.98
C17-H17C	0.98	C18-H18A	0.98
C18-H18B	0.98	C18-H18C	0.98
C20-C21	1.4305(19)	C20-C24	1.4453(19)
C20-C25	1.5001(19)	C21-C22	1.4251(19)
C21-C26	1.505(2)	C22-C23	1.436(2)
C22-C27	1.498(2)	C23-C24	1.4087(19)
C23-C28	1.5000(19)	C24-C29	1.5032(19)
C25-H25A	0.98	C25-H25B	0.98
C25-H25C	0.98	C26-H26A	0.98
C26-H26B	0.98	C26-H26C	0.98
C27-H27A	0.98	C27-H27B	0.98
C27-H27C	0.98	C28-H28A	0.98
C28-H28B	0.98	C28-H28C	0.98
C29-H29A	0.98	C29-H29B	0.98
C29-H29C	0.98		

Table 5. Bond angles (°) for **7**.

N2-Mo1-N1	89.11(6)	N2-Mo1-N12	88.37(5)
N1-Mo1-N12	139.95(5)	N2-Mo1-N11	116.95(5)
N1-Mo1-N11	85.54(5)	N12-Mo1-N11	60.52(4)
N2-Mo1-C20	96.03(5)	N1-Mo1-C20	84.83(5)
N12-Mo1-C20	135.17(5)	N11-Mo1-C20	145.42(5)
N2-Mo1-C21	88.70(5)	N1-Mo1-C21	119.84(5)
N12-Mo1-C21	100.05(5)	N11-Mo1-C21	145.26(5)
C20-Mo1-C21	35.87(5)	N2-Mo1-C22	116.04(6)
N1-Mo1-C22	135.89(5)	N12-Mo1-C22	79.64(5)
N11-Mo1-C22	110.39(6)	C20-Mo1-C22	58.37(5)
C21-Mo1-C22	34.90(5)	N2-Mo1-C24	130.45(5)
N1-Mo1-C24	78.95(5)	N12-Mo1-C24	130.11(4)
N11-Mo1-C24	109.87(5)	C20-Mo1-C24	35.59(5)
C21-Mo1-C24	58.61(5)	C22-Mo1-C24	57.04(5)
N2-Mo1-C23	146.61(5)	N1-Mo1-C23	107.05(5)
N12-Mo1-C23	96.50(4)	N11-Mo1-C23	93.76(5)
C20-Mo1-C23	57.93(5)	C21-Mo1-C23	57.91(5)
C22-Mo1-C23	34.32(5)	C24-Mo1-C23	33.62(4)
C1-N1-Mo1	158.62(12)	N1-C1-O1	178.10(16)
O2-N2-Mo1	168.76(12)	C11-N11-C13	122.90(12)
C11-N11-Mo1	93.57(9)	C13-N11-Mo1	141.93(10)
C11-N12-C16	124.27(12)	C11-N12-Mo1	94.15(8)
C16-N12-Mo1	128.17(8)	N11-C11-N12	110.07(12)
N11-C11-C12	123.72(13)	N12-C11-C12	126.19(13)
C11-C12-H12A	109.5	C11-C12-H12B	109.5
H12A-C12-H12B	109.5	C11-C12-H12C	109.5
H12A-C12-H12C	109.5	H12B-C12-H12C	109.5
N11-C13-C15	111.54(13)	N11-C13-C14	109.92(12)
C15-C13-C14	111.19(14)	N11-C13-H13	108.0
C15-C13-H13	108.0	C14-C13-H13	108.0
C13-C14-H14A	109.5	C13-C14-H14B	109.5
H14A-C14-H14B	109.5	C13-C14-H14C	109.5
H14A-C14-H14C	109.5	H14B-C14-H14C	109.5
C13-C15-H15A	109.5	C13-C15-H15B	109.5
H15A-C15-H15B	109.5	C13-C15-H15C	109.5
H15A-C15-H15C	109.5	H15B-C15-H15C	109.5
N12-C16-C17	113.21(12)	N12-C16-C18	113.49(12)
C17-C16-C18	110.86(12)	N12-C16-H16	106.2
C17-C16-H16	106.2	C18-C16-H16	106.2
C16-C17-H17A	109.5	C16-C17-H17B	109.5
H17A-C17-H17B	109.5	C16-C17-H17C	109.5
H17A-C17-H17C	109.5	H17B-C17-H17C	109.5
C16-C18-H18A	109.5	C16-C18-H18B	109.5
H18A-C18-H18B	109.5	C16-C18-H18C	109.5
H18A-C18-H18C	109.5	H18B-C18-H18C	109.5
C21-C20-C24	107.98(12)	C21-C20-C25	125.69(13)

C24-C20-C25	125.81(12)	C21-C20-Mo1	73.35(7)
C24-C20-Mo1	76.24(7)	C25-C20-Mo1	122.91(10)
C22-C21-C20	107.31(12)	C22-C21-C26	126.67(13)
C20-C21-C26	125.82(13)	C22-C21-Mo1	75.20(8)
C20-C21-Mo1	70.77(7)	C26-C21-Mo1	123.44(10)
C21-C22-C23	108.63(12)	C21-C22-C27	126.47(13)
C23-C22-C27	124.55(13)	C21-C22-Mo1	69.90(8)
C23-C22-Mo1	74.66(8)	C27-C22-Mo1	126.75(9)
C24-C23-C22	108.00(12)	C24-C23-C28	126.86(12)
C22-C23-C28	124.91(12)	C24-C23-Mo1	71.48(7)
C22-C23-Mo1	71.02(7)	C28-C23-Mo1	127.37(10)
C23-C24-C20	108.03(12)	C23-C24-C29	125.85(13)
C20-C24-C29	126.08(13)	C23-C24-Mo1	74.90(8)
C20-C24-Mo1	68.16(7)	C29-C24-Mo1	124.31(9)
C20-C25-H25A	109.5	C20-C25-H25B	109.5
H25A-C25-H25B	109.5	C20-C25-H25C	109.5
H25A-C25-H25C	109.5	H25B-C25-H25C	109.5
C21-C26-H26A	109.5	C21-C26-H26B	109.5
H26A-C26-H26B	109.5	C21-C26-H26C	109.5
H26A-C26-H26C	109.5	H26B-C26-H26C	109.5
C22-C27-H27A	109.5	C22-C27-H27B	109.5
H27A-C27-H27B	109.5	C22-C27-H27C	109.5
H27A-C27-H27C	109.5	H27B-C27-H27C	109.5
C23-C28-H28A	109.5	C23-C28-H28B	109.5
H28A-C28-H28B	109.5	C23-C28-H28C	109.5
H28A-C28-H28C	109.5	H28B-C28-H28C	109.5
C24-C29-H29A	109.5	C24-C29-H29B	109.5
H29A-C29-H29B	109.5	C24-C29-H29C	109.5
H29A-C29-H29C	109.5	H29B-C29-H29C	109.5

Table 6. Torsion angles (°) for **7**.

N2-Mo1-N1-C1	-25.0(3)	N12-Mo1-N1-C1	61.4(4)
N11-Mo1-N1-C1	92.1(3)	C20-Mo1-N1-C1	-121.2(3)
C21-Mo1-N1-C1	-113.0(3)	C22-Mo1-N1-C1	-153.0(3)
C24-Mo1-N1-C1	-156.6(3)	C23-Mo1-N1-C1	-175.3(3)
Mo1-N1-C1-O1	-164.(5)	N1-Mo1-N2-O2	-105.0(6)
N12-Mo1-N2-O2	115.0(6)	N11-Mo1-N2-O2	170.5(6)
C20-Mo1-N2-O2	-20.3(6)	C21-Mo1-N2-O2	14.9(6)
C22-Mo1-N2-O2	37.4(6)	C24-Mo1-N2-O2	-30.3(6)
C23-Mo1-N2-O2	15.7(6)	N2-Mo1-N11-C11	-63.11(10)
N1-Mo1-N11-C11	-149.84(9)	N12-Mo1-N11-C11	7.98(8)
C20-Mo1-N11-C11	135.96(10)	C21-Mo1-N11-C11	70.39(12)
C22-Mo1-N11-C11	72.49(10)	C24-Mo1-N11-C11	133.61(9)
C23-Mo1-N11-C11	103.33(9)	N2-Mo1-N11-C13	101.13(17)
N1-Mo1-N11-C13	14.40(17)	N12-Mo1-N11-C13	172.22(19)
C20-Mo1-N11-C13	-59.8(2)	C21-Mo1-N11-C13	-125.37(16)

C22-Mo1-N11-C13	-123.28(16)	C24-Mo1-N11-C13	-62.15(18)
C23-Mo1-N11-C13	-92.43(17)	N2-Mo1-N12-C11	114.51(9)
N1-Mo1-N12-C11	27.84(12)	N11-Mo1-N12-C11	-7.96(8)
C20-Mo1-N12-C11	-148.58(8)	C21-Mo1-N12-C11	-157.10(8)
C22-Mo1-N12-C11	-128.64(9)	C24-Mo1-N12-C11	-99.94(9)
C23-Mo1-N12-C11	-98.62(9)	N2-Mo1-N12-C16	-26.31(12)
N1-Mo1-N12-C16	-112.99(12)	N11-Mo1-N12-C16	-148.79(13)
C20-Mo1-N12-C16	70.60(13)	C21-Mo1-N12-C16	62.08(12)
C22-Mo1-N12-C16	90.54(12)	C24-Mo1-N12-C16	119.24(12)
C23-Mo1-N12-C16	120.56(12)	C13-N11-C11-N12	179.49(13)
Mo1-N11-C11-N12	-12.02(12)	C13-N11-C11-C12	-2.0(2)
Mo1-N11-C11-C12	166.54(12)	C16-N12-C11-N11	155.17(13)
Mo1-N12-C11-N11	12.12(12)	C16-N12-C11-C12	-23.3(2)
Mo1-N12-C11-C12	-166.40(12)	C11-N11-C13-C15	89.93(17)
Mo1-N11-C13-C15	-71.2(2)	C11-N11-C13-C14	-146.26(15)
Mo1-N11-C13-C14	52.6(2)	C11-N12-C16-C17	-45.98(18)
Mo1-N12-C16-C17	84.34(14)	C11-N12-C16-C18	81.53(17)
Mo1-N12-C16-C18	-148.16(10)	N2-Mo1-C20-C21	79.34(9)
N1-Mo1-C20-C21	167.90(9)	N12-Mo1-C20-C21	-14.42(11)
N11-Mo1-C20-C21	-117.69(10)	C22-Mo1-C20-C21	-37.62(8)
C24-Mo1-C20-C21	-113.89(11)	C23-Mo1-C20-C21	-78.27(8)
N2-Mo1-C20-C24	-166.77(8)	N1-Mo1-C20-C24	-78.22(8)
N12-Mo1-C20-C24	99.47(9)	N11-Mo1-C20-C24	-3.80(13)
C21-Mo1-C20-C24	113.89(11)	C22-Mo1-C20-C24	76.26(8)
C23-Mo1-C20-C24	35.62(7)	N2-Mo1-C20-C25	-42.78(12)
N1-Mo1-C20-C25	45.77(12)	N12-Mo1-C20-C25	-136.54(11)
N11-Mo1-C20-C25	120.19(12)	C21-Mo1-C20-C25	-122.12(15)
C22-Mo1-C20-C25	-159.75(13)	C24-Mo1-C20-C25	123.99(15)
C23-Mo1-C20-C25	159.61(13)	C24-C20-C21-C22	-2.10(15)
C25-C20-C21-C22	-174.16(13)	Mo1-C20-C21-C22	66.92(9)
C24-C20-C21-C26	173.07(13)	C25-C20-C21-C26	1.0(2)
Mo1-C20-C21-C26	-117.90(14)	C24-C20-C21-Mo1	-69.02(9)
C25-C20-C21-Mo1	118.92(14)	N2-Mo1-C21-C22	143.13(9)
N1-Mo1-C21-C22	-128.64(8)	N12-Mo1-C21-C22	55.02(9)
N11-Mo1-C21-C22	3.43(12)	C20-Mo1-C21-C22	-114.71(12)
C24-Mo1-C21-C22	-76.14(9)	C23-Mo1-C21-C22	-36.39(8)
N2-Mo1-C21-C20	-102.16(8)	N1-Mo1-C21-C20	-13.93(10)
N12-Mo1-C21-C20	169.73(8)	N11-Mo1-C21-C20	118.14(9)
C22-Mo1-C21-C20	114.71(12)	C24-Mo1-C21-C20	38.57(8)
C23-Mo1-C21-C20	78.32(8)	N2-Mo1-C21-C26	18.67(12)
N1-Mo1-C21-C26	106.90(12)	N12-Mo1-C21-C26	-69.44(12)
N11-Mo1-C21-C26	-121.03(12)	C20-Mo1-C21-C26	120.83(15)
C22-Mo1-C21-C26	-124.46(15)	C24-Mo1-C21-C26	159.39(13)
C23-Mo1-C21-C26	-160.85(13)	C20-C21-C22-C23	1.17(15)
C26-C21-C22-C23	-173.95(13)	Mo1-C21-C22-C23	65.13(10)
C20-C21-C22-C27	174.60(13)	C26-C21-C22-C27	-0.5(2)
Mo1-C21-C22-C27	-121.45(14)	C20-C21-C22-Mo1	-63.96(9)
C26-C21-C22-Mo1	120.92(14)	N2-Mo1-C22-C21	-41.88(10)

N1-Mo1-C22-C21	76.75(11)	N12-Mo1-C22-C21	-124.90(9)
N11-Mo1-C22-C21	-177.91(7)	C20-Mo1-C22-C21	38.70(8)
C24-Mo1-C22-C21	81.06(9)	C23-Mo1-C22-C21	116.94(12)
N2-Mo1-C22-C23	-158.82(8)	N1-Mo1-C22-C23	-40.19(11)
N12-Mo1-C22-C23	118.16(8)	N11-Mo1-C22-C23	65.14(9)
C20-Mo1-C22-C23	-78.25(9)	C21-Mo1-C22-C23	-116.94(12)
C24-Mo1-C22-C23	-35.88(8)	N2-Mo1-C22-C27	79.23(13)
N1-Mo1-C22-C27	-162.13(11)	N12-Mo1-C22-C27	-3.79(12)
N11-Mo1-C22-C27	-56.80(14)	C20-Mo1-C22-C27	159.81(14)
C21-Mo1-C22-C27	121.11(16)	C24-Mo1-C22-C27	-157.83(14)
C23-Mo1-C22-C27	-121.95(16)	C21-C22-C23-C24	0.23(15)
C27-C22-C23-C24	-173.35(13)	Mo1-C22-C23-C24	62.29(9)
C21-C22-C23-C28	175.08(13)	C27-C22-C23-C28	1.5(2)
Mo1-C22-C23-C28	-122.86(14)	C21-C22-C23-Mo1	-62.06(10)
C27-C22-C23-Mo1	124.36(14)	N2-Mo1-C23-C24	-81.24(12)
N1-Mo1-C23-C24	34.60(9)	N12-Mo1-C23-C24	-178.18(8)
N11-Mo1-C23-C24	121.09(8)	C20-Mo1-C23-C24	-37.74(8)
C21-Mo1-C23-C24	-80.37(9)	C22-Mo1-C23-C24	-117.38(12)
N2-Mo1-C23-C22	36.14(13)	N1-Mo1-C23-C22	151.98(8)
N12-Mo1-C23-C22	-60.80(8)	N11-Mo1-C23-C22	-121.53(9)
C20-Mo1-C23-C22	79.64(9)	C21-Mo1-C23-C22	37.01(8)
C24-Mo1-C23-C22	117.38(12)	N2-Mo1-C23-C28	156.07(12)
N1-Mo1-C23-C28	-88.10(12)	N12-Mo1-C23-C28	59.12(12)
N11-Mo1-C23-C28	-1.61(12)	C20-Mo1-C23-C28	-160.44(14)
C21-Mo1-C23-C28	156.94(14)	C22-Mo1-C23-C28	119.92(15)
C24-Mo1-C23-C28	-122.70(16)	C22-C23-C24-C20	-1.53(15)
C28-C23-C24-C20	-176.25(13)	Mo1-C23-C24-C20	60.46(9)
C22-C23-C24-C29	176.32(13)	C28-C23-C24-C29	1.6(2)
Mo1-C23-C24-C29	-121.68(14)	C22-C23-C24-Mo1	-61.99(9)
C28-C23-C24-Mo1	123.29(14)	C21-C20-C24-C23	2.27(15)
C25-C20-C24-C23	174.31(13)	Mo1-C20-C24-C23	-64.81(9)
C21-C20-C24-C29	-175.58(13)	C25-C20-C24-C29	-3.5(2)
Mo1-C20-C24-C29	117.34(13)	C21-C20-C24-Mo1	67.08(9)
C25-C20-C24-Mo1	-120.88(14)	N2-Mo1-C24-C23	134.38(9)
N1-Mo1-C24-C23	-146.42(9)	N12-Mo1-C24-C23	2.37(10)
N11-Mo1-C24-C23	-65.32(9)	C20-Mo1-C24-C23	116.97(11)
C21-Mo1-C24-C23	78.10(9)	C22-Mo1-C24-C23	36.64(8)
N2-Mo1-C24-C20	17.40(11)	N1-Mo1-C24-C20	96.61(9)
N12-Mo1-C24-C20	-114.60(8)	N11-Mo1-C24-C20	177.71(8)
C21-Mo1-C24-C20	-38.88(8)	C22-Mo1-C24-C20	-80.34(9)
C23-Mo1-C24-C20	-116.97(11)	N2-Mo1-C24-C29	-102.24(13)
N1-Mo1-C24-C29	-23.04(12)	N12-Mo1-C24-C29	125.75(11)
N11-Mo1-C24-C29	58.06(13)	C20-Mo1-C24-C29	-119.65(15)
C21-Mo1-C24-C29	-158.52(14)	C22-Mo1-C24-C29	160.02(14)
C23-Mo1-C24-C29	123.38(15)		

Table 7. Anisotropic atomic displacement parameters (Å^2) for **7**.

The anisotropic atomic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U_{11} + ... + 2 h k a^* b^* U_{12}]$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Mo1	0.00896(4)	0.01175(4)	0.01202(4)	-0.00087(5)	0.00014(3)	-0.00040(5)
N1	0.0154(6)	0.0214(6)	0.0199(6)	-0.0036(5)	-0.0005(5)	-0.0008(4)
C1	0.0139(6)	0.0191(6)	0.0145(6)	0.0022(5)	0.0004(5)	-0.0018(5)
O1	0.0339(6)	0.0211(5)	0.0199(5)	-0.0066(4)	0.0011(5)	0.0019(4)
N2	0.0135(5)	0.0139(5)	0.0201(6)	-0.0016(4)	-0.0021(5)	-0.0002(4)
O2	0.0224(5)	0.0181(5)	0.0339(6)	0.0087(4)	-0.0055(5)	-0.0012(4)
N11	0.0127(5)	0.0184(6)	0.0123(5)	-0.0002(5)	0.0011(4)	-0.0019(5)
N12	0.0108(5)	0.0131(5)	0.0135(5)	-0.0002(4)	-0.0009(4)	-0.0019(4)
C11	0.0112(5)	0.0116(6)	0.0168(6)	-0.0005(4)	0.0005(5)	0.0004(4)
C12	0.0124(6)	0.0232(7)	0.0189(7)	0.0010(5)	0.0014(5)	-0.0043(5)
C13	0.0166(6)	0.0273(7)	0.0128(6)	0.0004(5)	0.0025(5)	-0.0034(5)
C14	0.0233(8)	0.0521(11)	0.0151(7)	0.0065(7)	0.0006(6)	-0.0003(7)
C15	0.0195(8)	0.0336(9)	0.0255(8)	-0.0086(6)	0.0082(6)	-0.0041(6)
C16	0.0138(6)	0.0205(7)	0.0139(6)	0.0021(5)	-0.0015(5)	-0.0030(5)
C17	0.0192(7)	0.0222(7)	0.0267(8)	0.0064(6)	-0.0056(6)	0.0003(5)
C18	0.0207(7)	0.0281(7)	0.0176(7)	-0.0050(6)	-0.0022(5)	-0.0053(6)
C20	0.0096(5)	0.0153(6)	0.0179(6)	0.0007(5)	0.0008(5)	-0.0020(4)
C21	0.0110(6)	0.0162(6)	0.0151(6)	0.0003(5)	0.0025(5)	-0.0001(5)
C22	0.0104(6)	0.0131(6)	0.0170(6)	-0.0018(5)	0.0020(5)	0.0009(5)
C23	0.0101(6)	0.0139(6)	0.0177(6)	0.0020(5)	0.0006(5)	0.0009(5)
C24	0.0096(5)	0.0170(6)	0.0158(6)	0.0009(5)	0.0002(4)	0.0006(5)
C25	0.0178(7)	0.0171(6)	0.0255(7)	-0.0005(5)	0.0017(5)	-0.0060(5)
C26	0.0208(7)	0.0226(7)	0.0168(6)	0.0034(5)	0.0028(5)	-0.0015(5)
C27	0.0163(6)	0.0166(6)	0.0189(6)	-0.0035(5)	0.0010(5)	0.0004(5)
C28	0.0211(7)	0.0162(6)	0.0214(7)	0.0041(5)	0.0002(5)	-0.0007(5)
C29	0.0141(6)	0.0225(7)	0.0170(6)	-0.0007(5)	-0.0032(5)	-0.0011(6)

Table 8. Hydrogen atomic coordinates and isotropic atomic displacement parameters (Å^2) for **7**.

	x/a	y/b	z/c	U(eq)
H12A	1.1459	0.2470	0.2093	0.035(3)
H12B	1.1250	0.2747	0.1188	0.035(3)
H12C	1.1867	0.1675	0.1433	0.035(3)
H13	1.0175	0.2221	0.0164	0.012(4)
H14A	0.7509	0.1357	-0.0414	0.045(4)
H14B	0.8621	0.1993	-0.0933	0.045(4)
H14C	0.7740	0.2518	-0.0241	0.045(4)
H15A	1.0975	0.0519	0.0323	0.037(4)
H15B	1.0824	0.0860	-0.0572	0.037(4)
H15C	0.9580	0.0181	-0.0188	0.037(4)

	x/a	y/b	z/c	U(eq)
H16	0.8691	0.1156	0.3336	0.019
H17A	1.0475	0.0128	0.2732	0.033(3)
H17B	1.1010	0.0544	0.3564	0.033(3)
H17C	1.1617	0.1032	0.2777	0.033(3)
H18A	1.0763	0.2734	0.3195	0.034(3)
H18B	1.0170	0.2276	0.3997	0.034(3)
H18C	0.9089	0.2897	0.3438	0.034(3)
H25A	0.4453	-0.0939	0.2092	0.031(3)
H25B	0.4245	-0.0776	0.1170	0.031(3)
H25C	0.2981	-0.0441	0.1757	0.031(3)
H26A	0.5879	0.0849	0.3621	0.042(4)
H26B	0.5469	-0.0203	0.3236	0.042(4)
H26C	0.4197	0.0555	0.3478	0.042(4)
H27A	0.5344	0.3189	0.2962	0.029(3)
H27B	0.6977	0.3119	0.2631	0.029(3)
H27C	0.6490	0.2422	0.3343	0.029(3)
H28A	0.5254	0.3052	0.0518	0.036(3)
H28B	0.6667	0.3271	0.1053	0.036(3)
H28C	0.5080	0.3623	0.1334	0.036(3)
H29A	0.3481	0.1575	0.0205	0.037(4)
H29B	0.3962	0.0429	0.0234	0.037(4)
H29C	0.5102	0.1259	-0.0045	0.037(4)

Table 9. Data collection details for **7**.

Axis	dx/mm	2θ/°	ω/°	φ/°	χ/°	Width/°	Frames	Time/s
Omega	50.065	-31.50	328.50	90.00	54.71	-0.30	610	25.00
Omega	50.065	-31.50	328.50	210.00	54.71	-0.30	610	25.00
Omega	50.065	-31.50	328.50	330.00	54.71	-0.30	610	25.00
Phi	50.065	-31.50	148.50	0.00	54.71	-0.30	941	25.00