Dalton Transactions

Supplementary Material

X-Ray Crystallography

Adduct 1. A solution of **1** in dichloromethane and pentane (2:1) was concentrated by slow evaporation. Colorless blocks with well-defined faces were collected and data obtained as outlined in Table **S1**. Sixty data frames were taken at widths of 1.0°. These reflections were used in the auto-indexing procedure to determine the unit cell. A suitable cell was found and refined by nonlinear least squares and Bravais lattice procedures. The unit cell was verified by examination of the h k l overlays on several frames of data. No super-cell or erroneous reflections were observed. After careful examination of the unit cell, an extended data collection procedure (4 sets) was initiated using omega scans.

Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX2.[S1] The integration method employed a three dimensional profiling algorithm and all data were corrected for Lorentz and polarization factors, and for crystal decay effects. Finally, the data was merged and scaled to produce a suitable data set. The absorption correction program SADABS[S2] was employed to correct the data for absorption effects.

Systematic reflection conditions and statistical tests of the data suggested the space group $P2_1/n$. A solution was obtained readily using XT/XS in APEX2.[S1,S3] Hydrogen atoms were placed in idealized positions and were set riding on the respective parent atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. Unusual thermal ellipsoids on O2 and O3 indicated a possible disorder, and was modeled successfully between two positions with an occupancy ratio of 0.75:0.25. Appropriate restraints were used to keep the bond distances and the thermal ellipsoids meaningful.

Absence of additional symmetry and voids were confirmed using PLATON (ADDSYM).[S4] The structure was refined (weighted least squares refinement on F2) to convergence.[S3,S5] Olex2 was employed for the final data presentation and structure plots.[S5]

Adduct 2. A solution of **2** in dichloromethane was concentrated by slow evaporation. Colorless blocks with well-defined faces were collected, data were obtained and the structure was solved as described for **1** (20732 reflections).

Adduct 3. Assembly **3** was crystallized as **2**. Data were obtained and the structure was solved as described for **1** (68772 reflections). After careful examination of the unit cell, an extended data collection procedure (7 sets) was initiated using omega and phi scans. Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX3.[S6] The H_2O_2 molecule was found disordered between two sites and was modeled successfully with an occupancy ratio of 0.54:0.46. In the thermal ellipsoid plot only the molecule occupying 54% is shown

Adduct 4. Adduct **4** was crystallized as **1**. Data were obtained as outlined in Table **S2** and the structure was solved as described for **1** (28153 reflections). Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX3.[S6] The compound crystallizes in $C2/c$ with Z = 4, Z' = 0.5.

Adduct 5. Adduct **5** was crystallized as **2**. Data were obtained as outlined in Table **S2** and the structure was solved as described for **1** (34408 reflections). After careful examination of the unit cell, an extended data collection procedure (7 sets) was initiated using omega and phi scans. Atom C7 is found disordered (attached to C2 and C19) and was modeled successfully with an occupancy ratio of 0.76:0.24. The H_2O_2 molecule was found disordered between two sites and was modeled successfully with an occupancy ratio of 0.92:0.08. In the thermal ellipsoid plot disordered atoms are not shown, only the model with higher occupancy.

Adduct 6. A solution of **6** in toluene was concentrated by slow evaporation. Colorless blocks with well-defined faces were collected and data were obtained as outlined in Table **S2**. The structure was solved as described for **1** (13684 reflections). Integrated intensity information for each reflection was obtained by reduction of the data frames with the program APEX3.[S6] A molecule of water was found solvated. An unusual thermal ellipsoid suggested partial occupancy. The latter refined to a value close to 0.75 to which it was fixed for final refinement.

Table S1. Crystallographic data for **1**, **2**, and **3**.

	1	**2**	**3**
empirical formula	$C_{21}H_{23}O_3P$	$C_{21}H_{23}O_3P$	$C_{20}H_{21}O_3P$
formula weight	354.36	354.36	340.34
temperature [K]	110	110	100
diffractometer	Bruker APEX 2	Bruker APEX 2	Bruker Quest
wavelength [Å]	0.71073	0.71073	0.71073
crystal system	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
unit cell dimensions:			
a [Å]	10.937(3)	9.133(2)	8.9873(5)
b [Å]	17.920(4)	15.855(4)	15.7070(7)
c [Å]	10.968(3)	12.790(3)	12.4419(6)
α [°]	90	90	90
β [°]	117.255(2)	101.117(3)	100.431(2)
γ [°]	90	90	90
V [Å^3]	1911.1(8)	1817.4(7)	1727.32(15)
Z	4	4	4
ρ_{calc} [Mg/m^3]	1.232	1.295	1.309
μ [mm^{-1}]	0.160	0.168	0.174
F(000)	752	752	720
crystal size [mm^3]	0.565 × 0.482 × 0.212	0.772 × 0.582 × 0.396	0.233 × 0.142 × 0.133
Θ limit [°]	2.178 to 27.636	2.070 to 27.655	2.110 to 27.628
index range (h, k, l)	−14, 14; −21, 23; −14, 14	−11, 11; −20, 20; −16, 16	−11, 11; −20, 20; −16, 16
reflections collected	19083	20732	68772
independent reflections	4416	4199	4000
R(int)	0.0487	0.0373	0.0626
completeness to Θ	100.0 %	99.9 %	100 %
max. and min. transmission	0.7456 and 0.6095	0.7456 and 0.6787	0.7411 and 0.6956
data/restraints/parameters	4416 / 43 / 248	4199 / 0 / 229	4000 / 42 / 239
goodness-of-fit on F^2	1.034	1.026	1.100
R indices (final) [$I > 2\sigma(I)$]			
R_1	0.0465	0.0438	0.0550
wR_2	0.1202	0.1056	0.1221
R indices (all data)			
R_1	0.0628	0.0571	0.0754
wR_2	0.1316	0.1138	0.1325
largest diff. peak and hole [eÅ^{-3}]	0.833 and -0.274	0.481 and -0.387	0.494 and -0.444

Table S2. Crystallographic data for **4**, **5**, and **6**.

	4	**5**	**6**
empirical formula	$C_{42}H_{44}O_4P_2$	$C_{19}H_{18}O_2P$	$C_{20}H_{20.5}O_{1.75}P$
formula weight	674.71	309.30	319.83
temperature [K]	110.0	110.0	110.0
diffractometer	Bruker Quest	Bruker APEX 2	Bruker Quest
wavelength [Å]	0.71073	0.71073	0.71073
crystal system	monoclinic	triclinic	monoclinic
space group	*C*2/*c*	*P*-1	$P2_1/c$
unit cell dimensions:			
a [Å]	15.5361(11)	8.606(3)	8.7455(6)
b [Å]	12.2423(9)	10.259(3)	15.6756(10)
c [Å]	19.5371(14)	18.844(6)	12.2448(9)
α [°]	90	94.697(5)	90
β [°]	104.688(2)	90.536(5)	98.131(2)
γ [°]	90	102.113(5)	90
V [Å^3]	3594.5(4)	1620.7(9)	1661.8(2)
Z	4	4	4
ρ_{calc} [Mg/m^3]	1.247	1.268	1.278
μ [mm^{-1}]	0.163	0.174	0.171
F(000)	1432	652	678
crystal size [mm^3]	0.432 × 0.415 × 0.372	0.526 × 0.481 × 0.226	0.438 × 0.216 × 0.198
Θ limit [°]	2.146 to 24.998	1.085 to 27.613	2.688 to 24.998
index range (*h*, *k*, *l*)	−18, 18; −14, 14; −23, 23	−11, 11; −13, 13; −24, 24	−7, 10; −18, 18; −14, 14
reflections collected	28153	34408	13684
independent reflections	3170	7421	2925
R(int)	0.0944	0.0286	0.0464
completeness to Θ	100.0 %	99.7 %	99.7 %
max. and min. transmission	0.7456 and 0.4820	0.7456 and 0.6707	0.7456 and 0.6127
data/restraints/parameters	3170 / 0 / 220	7421 / 91 / 421	2925 / 0 / 213
goodness-of-fit on F^2	1.084	1.214	1.167
R indices (final) [$I > 2\sigma(I)$]			
R_1	0.0595	0.0632	0.0489
wR_2	0.1406	0.1214	0.0997
R indices (all data)			
R_1	0.0744	0.0735	0.0650
wR_2	0.1501	0.1259	0.1151
largest diff. peak and hole [eÅ^{-3}]	0.569 and -0.511	0.656 and -0.428	0.378 and -0.396

References

[S1] Bruker (2012). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
[S2] Bruker (2001). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
[S3] Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112-122. Sheldrick, G. M. (2015), *Acta Cryst*. A**71**, 3-8. XT, XS, BRUKER AXS Inc., 5465 East Cheryl Parkway, Madison, WI 53711-5373 USA.
[S4] Spek, A. L. (2009). *Acta Cryst*. D**65**, 148-155.
[S5] Dolomanov, O. V; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. J. (2009) *Appl. Cryst*., **42**, 339-341.
[S6] Bruker (2013). *APEX3*. Bruker AXS Inc., Madison, Wisconsin, USA.