

Activation of B-H Bonds by an Oxo-rhenium Complex

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Single-Crystal X-ray Diffraction Studies

Single-crystals of $(\text{PPh}_3)_2(\text{O})(\text{I})\text{Re}(\text{H})\text{OBcat} \cdot 2(\text{C}_7\text{H}_8)$ (**1**) and $(\text{PPh}_3)_2(\text{O})(\text{I})\text{Re}(\text{H})\text{OBpin} \cdot 1.5(\text{C}_7\text{H}_8)$ (**2**) were manually harvested from the crystallisation vials and mounted on Hampton Research CryoLoops using FOMBLIN Y perfluoropolyether vacuum oil (LVAC 25/6 - purchased from Aldrich)¹ with the help of a Stemi 2000 stereomicroscope equipped with Carl Zeiss lenses. Data were collected on a Bruker X8 Kappa APEX II charge-coupled device (CCD) area-detector diffractometer (Mo $\text{K}\alpha$ graphite-monochromated radiation, $\lambda = 0.71073 \text{ \AA}$) controlled by the APEX2 software package,² and equipped with an Oxford Cryosystems Series 700 cryostream monitored remotely using the software interface Cryopad.³ Images were processed using the software package SAINT+,⁴ and data were corrected for absorption by the multi-scan semi-empirical method implemented in SADABS.⁵ Structures were solved using the Patterson synthesis algorithm implemented in SHELXS-97,^{6, 7} which allowed the immediate location of the heaviest atoms (namely Re and I). All remaining non-hydrogen atoms composing the $(\text{PPh}_3)_2(\text{O})(\text{I})\text{Re}(\text{H})\text{OBcat}$ and $(\text{PPh}_3)_2(\text{O})(\text{I})\text{Re}(\text{H})\text{OBpin}$ complexes were straightforwardly located in difference Fourier maps calculated from successive full-matrix least squares refinement cycles on F^2 using SHELXL-97.^{6, 8} With the exception of some carbon atoms belonging to solvent molecules (see details below) all non-hydrogen atoms were successfully refined using anisotropic displacement parameters.

The hydride atoms bound to the rhenium metallic centres were markedly visible in difference Fourier maps and were included in the final structures models with refineable isotropic displacement parameters. For **2**, the atomic positions of the hydride atom were allowed to refine freely with the final $\text{Re}(1)\text{--H}(1)$ distance converging to $1.71(7) \text{ \AA}$, a value which is in good agreement with those typically found in related materials. Indeed, a search in the Cambridge Structural Database (CSD, Version 5.28 with three updates)^{9, 10} for geometrical parameters related with $\text{Re}\text{--H}$ bonds in which the hydrogen atom is terminal, reveals that the interatomic distances range from *ca.* 1.20 to $2.36 \text{ \AA}$ with the median being $1.66 \text{ \AA}$ (from a total of 145 hits in the database). Moreover, nearly half of these structures contain $\text{Re}\text{--H}$ bonds with distances in the $1.68\text{--}1.71 \text{ \AA}$ range. In compound **1**, even though the hydride atom could also be located, full convergence could only be reached when the $\text{Re}\text{--H}$ distance was constrained to $1.70(1) \text{ \AA}$. Hydrogen atoms bound to carbon were placed at their idealised positions using appropriate *HFIX* instructions in SHELXL (*43* for the aromatic and *137* for the terminal methyl groups) and included in subsequent refinement cycles in riding-motion approximation with isotropic thermal displacements parameters (U_{iso}) fixed at 1.2 (for the aromatic hydrogen atoms) or 1.5 (for the methyl moieties) times U_{eq} of the carbon atom to which they are attached.

During crystal refinement using the original integrated and scaled data sets, it was clearly visible from difference Fourier maps that complexes $(\text{PPh}_3)_2(\text{O})(\text{I})\text{Re}(\text{H})\text{OBcat}$ and $(\text{PPh}_3)_2(\text{O})(\text{I})\text{Re}(\text{H})\text{OBpin}$ close pack in the solid state with toluene solvent molecules. For each structure, one toluene molecule was successfully located from difference Fourier maps and included in the final structural models. Even

though in **2** the carbon atoms composing this located toluene could be freely refined using anisotropic displacement parameters, in **1** the analogous chemical moiety is surrounded by a considerable smeared-out electron density and a common isotropic displacement parameter for all carbon atoms was used instead (the aromatic ring was further constrained to planarity using the appropriate AFIX instruction, and the C–C distance associated with the methyl group was heavily restrained in order to ensure a chemically reasonable geometry). For the two structures, it was clear from difference Fourier maps that some extra electron density residing in the void spaces was most likely attributed to remaining toluene molecules. Attempts to include these chemical moieties using a battery of crystallographic constraints proved to be unfruitful, particularly due to the fact that the observed electron density was located at centres of inversion in the crystal structures. The original data sets were then treated using the *SQUEEZE*¹¹ subroutines provided with the software package *PLATON*^{12, 13} in order to eliminate from the overall electron density the contribution of the highly disordered toluene molecules present in the solvent-accessible area. *PLATON* estimated that, for **1** and **2**, the respective unit cells contain *ca.* 892 and 817 Å³ of potential solvent accessible area (*ca.* 9.6 and 8.4% of the total volumes), distributed across several large (but symmetry-related) cavities containing a total of *ca.* 296 and 198 electrons. Since each toluene molecule contributes with 50 electrons, it is feasible to assume the presence of extra 1 and 0.5 molecules of toluene per rhenium(V) complex for compounds **1** and **2**, respectively. These assumptions are also in good agreement with the elemental composition data obtained for the two compounds (see section dedicated to the synthesis). Even though these extra solvent molecules are not included in the final structural models, they have been added to the empirical formula of the compounds (Table 1). The resulting solvent-free reflection files produced by *PLATON* were used in subsequent refinement cycles using full-matrix least squares on F^2 in SHELXL-97. The last difference Fourier map synthesis showed, for **1**, the highest peak (5.445 eÅ⁻³) and deepest hole (-5.076 eÅ⁻³) located at 0.75 and 0.74 Å, respectively, from Re(1); for **2**, the highest peak (5.532 eÅ⁻³) and deepest hole (-2.245 eÅ⁻³) were located at 0.79 and 0.64 Å, respectively, also from Re(1). Information concerning crystallographic data collection using SQUEEZE data sets and structure refinement details for the two structures is summarised in Table S1. Selected bond lengths and angles for the highly distorted {ReHIO₂P₂} octahedral coordination environments are collected in Table S2.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC-680868 and -680869 (for **1** and **2**, respectively). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 2EZ, U.K. FAX: (+44) 1223 336033. E-mail: deposit@ccdc.cam.ac.uk.

Table S1. Crystal and structure refinement data for (PPh₃)₂(O)(I)Re(H)OBcat·2(C₇H₈) (**1**) and (PPh₃)₂(O)(I)Re(H)OBpin·1.5(C₇H₈) (**2**).

	1	2
Formula	C ₅₆ H ₅₁ BIO ₄ P ₂ Re	C _{52.50} H ₅₅ BIO ₄ P ₂ Re
Formula weight	1173.82	1135.82
Crystal system	Orthorhombic	Orthorhombic
Space group	<i>Pbca</i>	<i>Pbca</i>
Temperature/K	180(2)	150(2)
<i>a</i> /Å	19.2359(8)	19.173(3)
<i>b</i> /Å	18.2151(7)	18.349(3)
<i>c</i> /Å	26.5497(10)	27.388(4)
Volume/Å ³	9302.6(6)	9635(3)
<i>Z</i>	8	8
<i>D_c</i> /g cm ⁻³	1.676	1.566
<i>μ</i> (Mo-Kα)/mm ⁻¹	3.394	3.273
Crystal size/mm	0.35×0.30×0.10	0.28×0.12×0.08
Crystal type	Brown blocks	Brown blocks
<i>θ</i> range	3.53 to 29.13	3.52 to 29.13
Index ranges	-26 ≤ <i>h</i> ≤ 26 -24 ≤ <i>k</i> ≤ 24 -36 ≤ <i>l</i> ≤ 36	-26 ≤ <i>h</i> ≤ 25 -24 ≤ <i>k</i> ≤ 25 -28 ≤ <i>l</i> ≤ 37
Reflections collected	298065	147899
Independent reflections	12505 (<i>R</i> _{int} = 0.0532)	12941 (<i>R</i> _{int} = 0.0835)
Data completeness	up to <i>θ</i> = 29.13° 99.8%	up to <i>θ</i> = 29.13° 99.8%
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] ^{<i>a,b</i>}	<i>R</i> 1 = 0.0613 <i>wR</i> 2 = 0.1347	<i>R</i> 1 = 0.0675 <i>wR</i> 2 = 0.1401
Final <i>R</i> indices (all data) ^{<i>a,b</i>}	<i>R</i> 1 = 0.0720 <i>wR</i> 2 = 0.1398	<i>R</i> 1 = 0.1020 <i>wR</i> 2 = 0.1508
Weighting scheme ^{<i>c</i>}	<i>m</i> = 0.0351 <i>n</i> = 98.1056	<i>m</i> = 0.0367 <i>n</i> = 132.8221
Largest diff. peak and hole	5.445 and -5.076 eÅ ⁻³	5.532 and -2.245 eÅ ⁻³

$$^a R1 = \sum ||F_o| - |F_c|| / \sum |F_o|; \quad ^b wR2 = \sqrt{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]};$$

$$^c w = 1 / [\sigma^2(F_o^2) + (mP)^2 + nP] \text{ where } P = (F_o^2 + 2F_c^2) / 3$$

Table S2. Selected bond lengths (in Å) and angles (in degrees) for the {ReHIO₂P₂} coordination environments present in (PPh₃)₂(O)(I)Re(H)OBcat·2(C₇H₈) (**1**) and (PPh₃)₂(O)(I)Re(H)OBpin·1.5(C₇H₈) (**2**).

	1	2
Re(1)–O(1)	1.732(5)	1.735(6)
Re(1)–O(2)	1.933(5)	1.958(5)
Re(1)–P(1)	2.4766(14)	2.479(2)
Re(1)–P(2)	2.4851(14)	2.4870(19)
Re(1)–I(1)	2.8057(5)	2.8504(7)
Re(1)–H(1)	1.703(10)	1.71(7)
O(1)–Re(1)–O(2)	173.8(2)	172.0(3)
O(1)–Re(1)–P(1)	96.77(16)	95.83(17)
O(1)–Re(1)–P(2)	91.52(16)	92.08(17)
O(1)–Re(1)–I(1)	96.76(19)	97.7(2)
O(1)–Re(1)–H(1)	107(2)	101(2)
O(2)–Re(1)–P(1)	83.08(14)	84.43(16)
O(2)–Re(1)–P(2)	87.95(14)	87.06(16)
O(2)–Re(1)–I(1)	89.41(15)	90.32(17)
O(2)–Re(1)–H(1)	67(2)	71(2)
P(1)–Re(1)–P(2)	169.28(5)	170.72(6)
P(1)–Re(1)–I(1)	93.17(4)	91.94(5)
P(1)–Re(1)–H(1)	86(3)	89(2)
P(2)–Re(1)–I(1)	92.58(4)	91.80(5)
P(2)–Re(1)–H(1)	85(3)	85(2)
I(1)–Re(1)–H(1)	156(2)	161(2)

References

1. T. Kottke and D. Stalke, *J. App. Cryst.*, 1993, **26**, 615-619.
2. APEX2, *Data Collection Software Version 2.1-RC13*, Bruker AXS, Delft, The Netherlands, 2006.
3. Cryopad, *Remote monitoring and control, Version 1.451*, Oxford Cryosystems, Oxford, United Kingdom, 2006.
4. SAINT+, *Data Integration Engine v. 7.23a* ©, 1997-2005, **Bruker AXS, Madison, Wisconsin, USA**.
5. G. M. Sheldrick, *SADABS v.2.01*, Bruker/Siemens Area Detector Absorption Correction Program, 1998, **Bruker AXS, Madison, Wisconsin, USA**.
6. G. M. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112-122.
7. G. M. Sheldrick, *SHELXS-97, Program for Crystal Structure Solution*, University of Göttingen, 1997.
8. G. M. Sheldrick, *SHELXL-97, Program for Crystal Structure Refinement*, University of Göttingen, 1997.
9. F. H. Allen, *Acta Cryst. B*, 2002, **58**, 380-388.
10. F. H. Allen and W. D. S. Motherwell, *Acta Cryst. B*, 2002, **58**, 407-422.
11. P. van der Sluis and A. L. Spek, *Acta Cryst. A*, 1990, **46**, 194-201.
12. A. L. Spek, *Acta Cryst. A*, 1990, **46**, C34.
13. A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7-13.