Recovered catalysts 1c crystallographic information

Experimental

Single-crystal X-ray diffraction data were collected on a Bruker KAPPA APEX II DUO diffractometer using graphite-monochromated Mo-Kα radiation (χ = 0.71073 Å). Data collection was carried out at 173(2) K and are shown in Table 1. Temperature was controlled by an Oxford Cryostream cooling system (Oxford Cryostat). Cell refinement and data reduction were performed using the program SAINT.[1] The data were scaled and absorption correction performed using SADABS.[1]

The structure was solved by direct methods and refined by full-matrix least-squares methods based on F^2 using SHELXL version 2014/7 [2] and using the graphics interface program Olex.[3]

Table 1. Single crystal structural information of used catalyst

Compound	Recovered catalyst 1c
Mol. Formula	$C_{40}H_{48}Cl_3F_6IrNP_3$
Mol. Weight	1048.25
Temperature (k)	173(2)
Wavelength (Å)	Mo Kα (0.71073)
Crystal symmetry	orthorhombic
Space Group	Pnma
a (Å)	17.5194(10)
b (Å)	12.9278(8)
c (Å)	18.8945(11)
α, β, γ (°)	90, 90, 90
Volume ($Å^3$)	4279.4(4)
Z	4
Density (g/m^3)	1.627
Absorption coefficient (mm^{-1})	
F(000)	2088
Crystal size (mm)	0.10×0.09 ×0.08
Θ range for data collection	3.17, 56.72
Reflection (collected, independent, R_{int})	46125, 5582, 0.0759
Goodness-of-fit on F^2	1.031
Final R indexes [I>=2σ (I)]	R_1 = 0.0388, wR_2 = 0.0881
Final R indexes [all data]	R_1 = 0.0649, wR_2 = 0.0984
Largest diff. peak, hole (e.$Å^{-3}$)	2.07, -1.50

All non-hydrogen atoms, except those of dichloromethane, were refined anisotropically. The phenyl ring C13-C18 were disordered over two positions with refined site occupancy factors of 0.576 and 0.424. Carbon atoms C20 and C22, and a solvent molecule dichloromethane were disordered over special positions. Anisotropic displacement parameters restraints were applied to the carbon atoms on the disordered phenyl rings and the fluorine atoms. The solvent molecule was refined isotropically due to

their high thermal motions and the hydrogen atoms were excluded from the final model. All other hydrogen atoms were placed in idealised positions and refined in riding models with U_{iso} assigned the values to be 1.2 or 1.5 times those of their parent atoms and the distances of C-H were constrained to 0.95 Å for aromatic hydrogen atoms, 0.99 Å for CH_2 and 0.98 Å for CH_3. The structure was refined to R factor of 0.0349.

Results

Table 2. Selected bond distances and bond angles of the used complex **1c**.

Bond distances (Å)	Recovered Catalyst 1c
M-P(1)	2.2924(12)
M-Cl(1)	2.3888(15)
M-Cp*(1-3)	2.220(6), 2.236(5), 2.248(5)
P(1)-N(1)	1.685(4)
P(1)-C(7)	1.810
P(1)-C(13A)	1.794
N(1)-C(19)	1.513
Bond angles (°)	**Recovered Catalyst 1c**
P(1)-M-P(2)	69.38(6)
P(1)-N(1)-P(1)	101.43
P(1)-M-Cl(1)	85.57

Catalyst **1c** was obtained by allowing the reaction mixture to evaporate upon standing and washed several times with diethyl ether. The suitable crystal was then re-grown by the vapour diffusion method of diethyl ether into a solution of dichloromethane

The selected inter atomic distances and angles for the used catalyst are listed in Table 2. The used catalyst show the iridium centre is distorted octahedrally and the chloride anion is coordinated perpendicular to the strained four membered chelate ring, whilst the Cp* ligand is trans to the PNP nitrogen donor. This catalyst structure is comparable with the fresh catalyst **1c**.

For recycle experiments, the recovered catalyst (**1c** or **2c**) was used instead of fresh catalyst, in the procedure as described in Section 2.3.

References

1. Sheldrick, G. M.; 2.05 ed.; SHELXS-97, SHELXL-97 and SADABS version 2.05, University of Göttingen, Germany: 1997
2. Sheldrick, G. *Acta Crystallogr., Sect. A:*. 2008, **64**, 112.

3.Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* 2009, **42**, 339.