Details of X-ray crystallography

Singles crystals were mounted on glass fibers.

Diffraction measurements were made on a Rigaku RAXIS IV imaging plate area detector with Mo Kα radiation (λ= 0.71069 Å). Indexing was performed from 2 oscillation images, which were exposed for 5 min. The crystal-to-detector distance was 110 mm. Data collection parameters were as follows: the oscillation range / the number of oscillation images / the exposed time: 6.0° / 21 / 600 sec / deg (**2**$^{\mathrm{Ni}}$); 6.0° / 16 / 800 sec / deg (**2**$^{\mathrm{Co}}$); 6.0° / 20 / 600 sec / deg (**2**$^{\mathrm{Co}}$**-THF**); 5.0° / 36 / 450 sec / deg (**3**); 4.5° / 40 / 350 sec / deg (**5**$^{\mathrm{Ni}}$); 5.0° / 36 / 350 sec / deg (**6**); 5.0° / 36 / 300 sec / deg (**7**); 2.0° / 90 / 360 sec / deg (**8**); 5.0° / 36 / 400 sec / deg (**9**); 3.0° / 60 / 250 sec / deg (**10**); 5.0° / 36 / 250 sec / deg (**11**$^{\mathrm{Ni}}$); 5.0° / 36 / 400 sec / deg (**12**$^{\mathrm{Ni}}$); 5.0° / 36 / 240 sec / deg (**14a**); 3.0° / 60 / 300 sec / deg (**14b**); 5.0° / 28 / 600 sec / deg (Tp$^{\mathrm{Ph,Me}}$Co-OTf). Readout was performed with the pixel size of 100 μm x 100 μm. Neutral scattering factors were obtained from the standard source. In the reduction of data, Lorentz and polarization corrections and empirical absorption corrections were made.[1] Crystallographic data and results of structure refinements are listed in Table S4.

Diffraction measurements of **2**$^{\mathrm{Ni}}$**-THF**, **4**, **11**$^{\mathrm{Co}}$, and **12**$^{\mathrm{Co}}$ were made on a Rigaku AFC7R automated four-circle diffractometers by using graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The unit cell was determined and refined by a least-squares method using 20 independent reflections (2θ ~ 20°). Data were collected with ω-2θ scan techniques. If σ(F)/F was more than 0.1, a scan was repeated up to three times and the results were added to the first scan. Three standard reflections were monitored at every 150 measurements. The data processing (data collection) was performed on a VENTRIS FX 5133 computer. In the reduction of data, Lorentz and polarization corrections were made. An empirical absorption correction (Ψ scan) was made.

The structural analysis was performed on an IRIS O2 computer using teXsan structure solving program system obtained from the Rigaku Corp., Tokyo, Japan.[2] Neutral scattering factors were obtained from the standard source.[3] In the reduction of data, Lorentz and polarization corrections were made. An empirical absorption correction was also made.[4]

The structures were solved by a combination of the direct methods (SHELXS56 [4] or SAPI91 or SIR92 or MITHRIL90)[5] and Fourier synthesis (DIRDIF94).[6] Least-squares refinements were carried out using SHELXL-97 [4] (refined on F^2) linked to teXsan. All the non-hydrogen atoms were refined anisotropically. Unless otherwise stated riding refinements were applied to the methyl hydrogen atoms [B(H) = B(C)], and the other hydrogen atoms were fixed at the calculated positions. A part of disordered TfO anions and solvate molecules were fixed. Details of the refinements wera as follows. **3**, **9**: Hydrogen atoms attached to MeCN molecules were fixed. **4**, **11^{Co}**, **14b**: All hydrogen atoms were fixed. **6**: The disordered TfO anion and hexane solvate were refined isotropically (S1O1-3 : S2O1a-3a: 0.59 : 0.41; C91-93 : C91a-93a: 0.5 : 0.5) and hydrogen atoms attached to the hexane solvate were not included in the refinement. **7**: The H0 atom included in hydrogen bonding was refined isotropically. **8**: Atoms C71,72, 81-86, Cl1,2,1A,2A and all hydrogen atoms were fixed. Two components (Cl1-Cl2 : Cl1a-Cl2a: 0.70 : 0.30) were taken into account for one of the CH_2Cl_2 solvates. The other atoms in the solvate molecules were refined isotropically and the hydrogen atoms attached to them were not included in the refinement. **10**: The disordered CH_2Cl_2 solvate (Cl1-C50-Cl2 : Cl1A-C50A-Cl2A= 0.64 : 0.36) was fixed at the final stage of the refinement. **11^{Ni}**: The disordered TfO groups (0.5 : 0.5) were refined isotropically. **14a**, Tp^{Ph,Me}Co-OTf: The solvate molecules were refined isotropically and the attached hydrogen atoms were located at the calculated positions and not refined.

References

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