Synthesis of a Configurationally Stable Three-Legged Piano-Stool Complex**

Bruno Therrien and Thomas R. Ward*

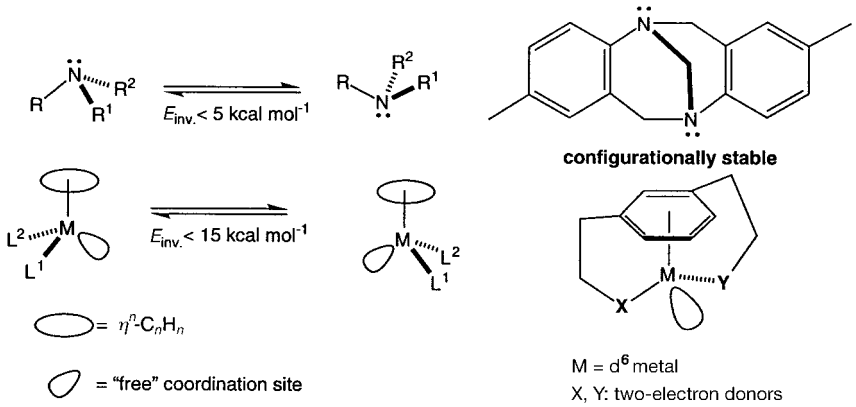
In memory of Vlado Prelog

Metal-based chirality is as old as coordination chemistry itself.[1, 2] To a great extent, A. Werner derived his coordination theory from stereochemical arguments that eventually led to the proof of octahedral coordination of hexacoordinate metals. Seventy years later, H. Brunner revived the interest for metal-based chirality by initiating a systematic study of piano-stool complexes which are chiral at the metal center.[3, 4] Compounds of the type $[(\eta^n\text{-}C_nH_n)ML^1L^2L^3]$ are chiral and have been resolved in many cases. Over the years, a number of groups has focused on applications of enantiopure piano-stool complexes in organic transformations. Several elegant examples of such complexes come from the groups of Brunner,[4–6] Davies,[7] Faller,[8] and Gladysz.[9] To the best of our knowledge, however, compounds that have metal-based and not ligand-based chirality have only found stoichiometric (and not catalytic) applications in organic chemistry.

Recently, piano-stool complexes with a d^6 electron count have been used as Lewis acid catalysts in C–C bond formations, for example, in Diels–Alder and Mukaiyama reactions.[10–13] The prospect of using an asymmetric piano-stool complex devoid of ligand-based chirality as a catalyst for such enantioselective transformations is very appealing. This would allow one to address the role of chirality at the metal in enantioselective catalysis.[14, 15] For this purpose, however, it is imperative to ensure configurational stability of the active catalyst (probably a two-legged piano-stool complex with a vacant site for substrate activation), as racemization at the metal center would have a dramatic effect on the enantiomeric excess of the resulting products. Theoretical[16] as well as mechanistic studies[9, 17–19] on the configurational stability of coordinatively unsaturated two-legged piano-stool complexes of the type $[(\eta^n\text{-}C_nH_n)ML^1L^2]$ ($n = 5-7$) suggest that, although some of these complexes indeed possess pyramidal ground-state geometries (and thus metal-centered chirality), the computed and experimentally determined inversion barriers are low, that is, less than 15 kcal mol^{-1}, thus hampering their use as enantioselective catalysts.

Inspired by Tröger's base, we set out to synthesize a configurationally stable piano-stool complex with chirality at the metal center by anchoring the metal in a rigid "bicyclic" framework (Scheme 1). Inspection of molecular models of such configurationally locked piano-stool complexes suggests that racemization can only occur by arene dissociation, an energetically costly process. Although tethered cyclopentadienyl ligands have received much attention,[20–22] tethered benzene systems have attracted much less consideration.[23–25] We report herein the synthesis of an enantiopure, configurationally stable, three-legged piano-stool ruthenium complex built from a prochiral ligand.

In recent years, "electronically asymmetric" ligands have received enormous attention in asymmetric catalysis. In particular, phosphane-imine-based bidentate ligands have proven superior to C_2-symmetric systems for a variety of enantioselective transformations.[26–29] Tethering a phosphane and an electron-deficient pyrazole to an arene yields a potential ten-electron donor (PArN) with pronounced electronic asymmetry. Upon $\eta^6{:}\eta^1{:}\eta^1$ coordination to Ru^{II}, a three-legged piano-stool complex is formed: $[\{\eta^6{:}\eta^1{:}\eta^1\text{-}(PArN)\}RuL]^{2+}$ (L = weakly bound solvent molecule).



Scheme 1. Anchoring a configurationally labile chiral center in a bicyclic framework results in a configurationally stable complex.

The synthesis of the ligand, outlined in Scheme 2, is straightforward. Nucleophilic substitution with 3,5-bis(trifluoromethyl)pyrazole on 3-bromobenzyl bromide followed by a Stille vinylation and a radical addition of $HPPh_2$ on the resulting double bond affords PArN (**3**) in 79% overall yield. Coordination of phosphane to $[\{(\eta^6\text{-}C_6H_5CO_2Et)RuCl_2\}_2]$[30] and subsequent thermal displacement of the arene ligand affords $[\{\eta^6{:}\eta^1\text{-}(PArN)\}RuCl_2]$ (**5**). Upon η^6 coordination of the disubstituted arene to ruthenium, a planar chiral complex results. After many unsucessful derivatization and crystallization experiments, we were pleased to find that the racemate could be resolved by preparative HPLC (800 mg of *rac*-**5** on a Chiralpak AD column with ethanol as eluent), affording a quasi-baseline separation of the enantiomers (*R*)-**5** (317 mg, 99.5% *ee*) and (*S*)-**5** (341 mg, 91% *ee*). Recrystallization from ethanol of the second enantiomer to be eluted affords enantiopure (HPLC) crystals suitable for anomalous X-ray diffraction, allowing unambiguous assignment of the absolute configuration. The molecular structure of (*S*)-**5** is depicted in Figure 1.[31]

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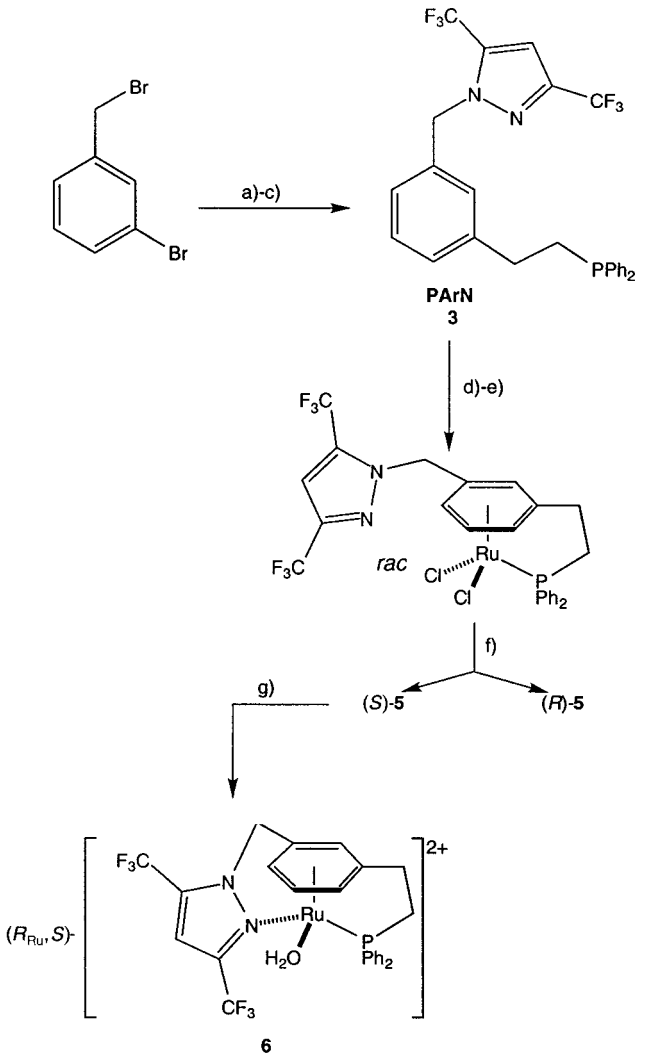

Scheme 2. Preparation of enantiopure complex **6**. a) 3,5-bis(trifluoromethyl)pyrazole, NaH, DMF, 2 h at room temperature (RT) then 48 h at 60 °C (86 %); b) $[Pd(PPh_3)_4]$, $Bu_3Sn(CH{=}CH_2)$, toluene, 100 °C, 8 h (92 %); c) $HPPh_2$, azobisisobutyronitrile (AIBN), CH_2Cl_2, RT, *hv*, 24 h (quant.); d) $[\{(\eta^6\text{-}C_6H_5CO_2Et)RuCl_2\}_2]$ (0.5 equiv), CH_2Cl_2, RT, 0.5 h (82 %); e) CH_2Cl_2, 110 °C, 24 h (quant.); f) HPLC (Chiralpak AD), EtOH; g) excess $AgOSO_2CF_3$, THF/H_2O, RT, 24 h (quant.).

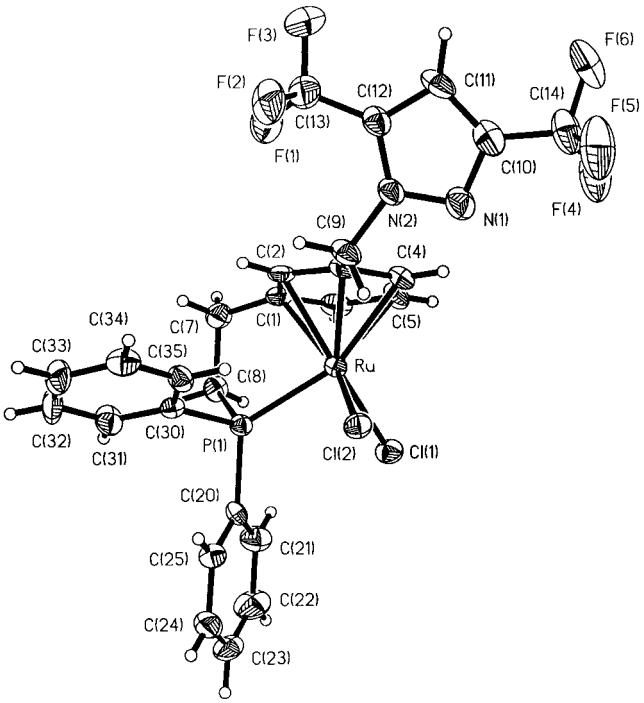

Figure 1. Molecular structure of (*S*)-**5**. Thermal ellipsoids are at the 50 % probability level. Selected bond lengths [Å] and angles [°]: Ru–C_{Ar} 2.212 (mean), Ru–$arene_{centroid}$ 1.697(7), Ru–P 2.322(1), Ru–Cl(1) 2.408(1), Ru–Cl(2) 2.414(1); P(1)-Ru-Cl(2) 90.28(4), Cl(1)-Ru-Cl(2) 89.90(4), P(1)-Ru-Cl(1) 88.29(4).

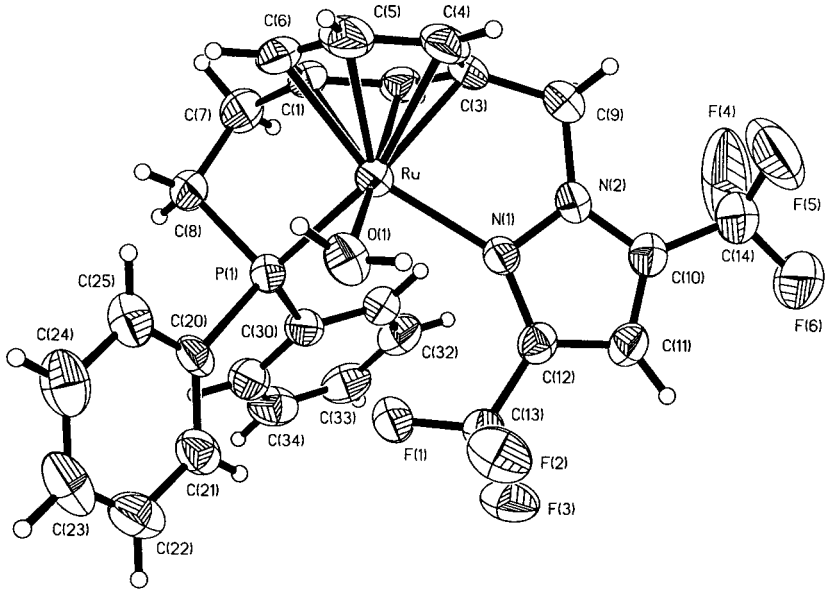

Figure 2. Molecular structure of **6**. Thermal ellipsoids are at the 50 % probability level (triflate molecules omitted for clarity). Selected bond lengths [Å] and angles [°]: Ru–C_{Ar} 2.186 (mean), Ru–$arene_{centroid}$ 1.667(9), Ru–P 2.387(2), Ru–O(1) 2.134(4), Ru–N(1) 2.163(4); P(1)-Ru-O(1) 88.6(1), O(1)-Ru-N(1) 88.8(2), P(1)-Ru-N(1) 102.0(1).

Treating (*R*)-**5** or (*S*)-**5** with an excess of $AgOSO_2CF_3$ (AgOTf) in THF affords, after aqueous workup, the piano-stool complexes (R_{Ru},S)-$[\{\eta^6{:}\eta^1{:}\eta^1\text{-}(PArN)\}Ru(OH_2)](OTf)_2$ ((R_{Ru},S)-**6**) and (S_{Ru},R)-**6**, respectively, which show chirality at the metal center. Upon $\eta^6{:}\eta^1{:}\eta^1$ coordination of PArN, the ^{31}P NMR signal is shifted from $\delta = +45.7$ for **5** to $\delta = +59.3$ for **6**. The presence of a unique signal suggests that a single diastereomer is formed upon coordination of the pyrazole nitrogen atom to ruthenium, locking its configuration. This was confirmed by an X-ray analysis of single crystals of **6** (Figure 2).[31] Comparing the molecular structures of **5** and **6**, we note that, upon coordination of the pyrazole tether to yield a "bicyclic structure", the Ru–P bond lengthens by 0.065 Å, while the Ru–$arene_{centroid}$ length shortens by 0.03 Å. The piano-stool geometry around ruthenium in **6** is slightly distorted (P-Ru-N 102.0(1)°), reflecting the large bite angle imposed by the 1,3-substitution pattern of the tethers on the arene. As

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observed for related η^6-arene–ruthenium complexes with tethered ligands, the coordinated arene deviates from planarity.[25] (The greatest deviation from the least square plane of the arene is shown by C(2) for **5** (0.035(3) Å) and by C(3) for **6** (0.026(4) Å).)

The stereochemical stability of **5** and **6** is remarkable. All attempts to racemize enantiopure complexes **5** and **6** have failed, eventually yielding decomposition rather than racemization products. When **6** is dissolved in CH_2Cl_2 in the presence of an excess of a coordinating solvent (DMSO, benzaldehyde, methacrolein, water, ethanol, and acetonitrile), the CD trace is practically unaltered over a period of 48 h at room temperature. Upon heating, the slow appearance of decomposition products is observed by ^{31}P NMR and UV/Vis spectroscopy. The CD spectra of **5** and **6** are depicted in Figure 3. It appears that the configuration at the ruthenium

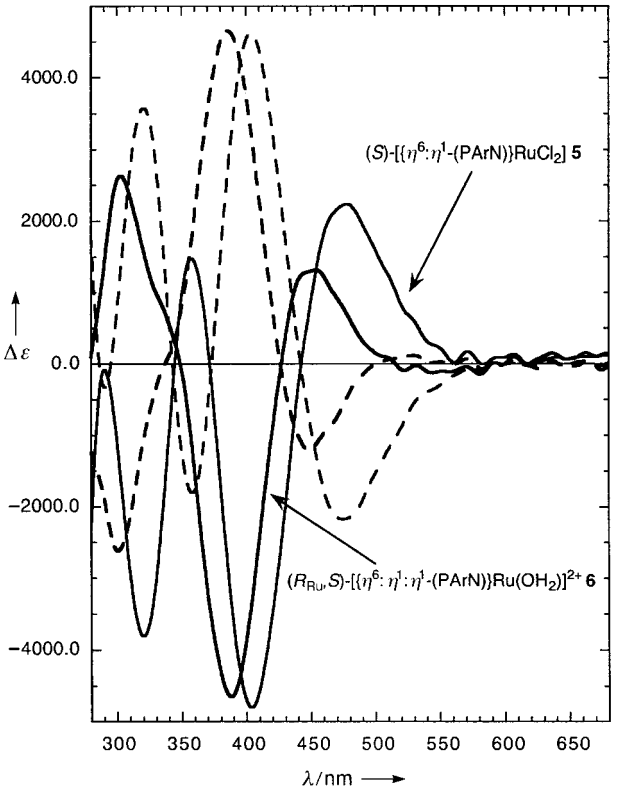

Figure 3. Circular dichroism spectra in CH_2Cl_2 of **5** ([(*S*)-**5**] = 0.195 mM, thin solid line; [(*R*)-**5**] = 0.227 mM, thin dashed line) and **6** ([(R_{Ru},*S*)-**6**] = 0.339 mM, thick solid line; [(S_{Ru},*R*)-**6**] = 0.435 mM, thick dashed line).

center is encoded by the planar chirality resulting from the η^6 coordination of the prochiral arene. Even in the event of phosphane *and* pyrazole decomplexation, the chirality at the metal can be reversibly recovered, thus allowing one to probe the role of chirality at the metal in enantioselective catalysis. We are currently investigating the catalytic properties of **6** in various C–C bond forming reactions.

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[31] Crystal structure analysis of (*S*)-**5** and (*rac*)-**6**:[32] Siemens SMART CCD diffractometer, $T = 200$ and 220 K, respectively, $Mo_{K\alpha}$ radiation (0.71073 Å). A complete hemisphere of data was scanned on ω (0.30° per frame) with a run time of 20 s for (*S*)-**5** and 60 s for (*rac*)-**6**, at the detector resolution of 512×512 pixels and a detector distance of 5.18 cm. A total of 1271 frames were collected for each data set; the collected frames were processed with the SAINT program,[32] which automatically performs Lorentz and polarization corrections. The structure was solved by direct methods and refined by full-matrix least square of F^2 (SHELXL96,[33] β test version). (*S*)-**5**: $C_{26}H_{21}Cl_2F_6N_2PRu$, $M_r = 678.39$; orthorhombic, space group $P2_12_12_1$; $a = 7.2072(1)$, $b = 13.5782(1)$, $c = 27.4530(3)$ Å, $V = 2686.57(5)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.677$ g cm^{-3}, $F(000) = 1352$, $\mu = 0.903$ mm^{-1}, crystal size $0.04 \times 0.14 \times 0.32$ mm; of 13697 reflections measured ($-6 \le h \le 8$, $-17 \le k \le 16$, $-34 \le l \le 29$), 5143 were unique; L_p and absorption corrections (psi scans); refinement of 346 variables with anisotropic displacement parameters for all non-hydrogen atoms gave $R = 0.0354$, $R_w = 0.0806$, and $S = 1.175$; modified statistical weight sug-

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gested by SHELX; absolute structure parameter = −0.05 (4); max./min. residual electron density 0.524/−0.501 e Å^{-3}. Since all attempts to obtain X-ray quality crystals of enantiopure **6** failed, (*rac*)-**6** was analyzed: $C_{28}H_{23}F_{12}N_2O_7PRuS_2$, $M_r = 923.64$; orthorhombic, space group *Pbca*; $a = 19.4161(3)$, $b = 15.9196(2)$, $c = 22.0340(3)$ Å, $V = 6810.6(2)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.802$ g cm^{-3}, $F(000) = 3680$, $\mu = 0.744$ mm^{-1}, crystal size $0.09 \times 0.20 \times 0.32$ mm; of 34713 reflections measured ($-19 \le h \le 24$, $-19 \le k \le 19$, $-27 \le l \le 25$), 6697 were unique; refinement of 485 variables with anisotropic thermal parameters for all non-hydrogen atoms gave $R = 0.0567$, $R_w = 0.1317$, and $S = 1.109$; max./min. residual electron density 0.731/−0.709 e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-102025 ((*S*)-**5**) and CCDC-102024 ((*rac*)-**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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$[Co^{II}_2L(NCS)_2(SCN)_2]$: The First Cobalt Complex to Exhibit Both Exchange Coupling and Spin Crossover Effects**

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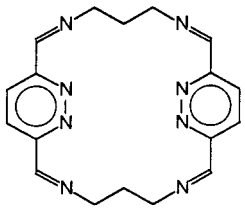
The preparation of molecular materials with possible nanotechnological applications is an area of intense interest.[1, 2] To produce molecules which can act as switches, detectors, or memory devices, the property of bistability is required. Classic examples of bistability are provided by spin-crossover compounds in which the transition from low to high spin is accompanied by a measurable change in magnetism and often also in color.[1–5] Such a signal is vital as it indicates that a change has occurred. To be of use as components there are numerous requirements to be met. One requirement is that the spin crossover should be sharp and occur close to room temperature, ideally with reproducible hysteresis loops (memory) arising from a polymeric structure.[1] Most of the work done in this area has involved iron(II) compounds (d^6), but other transition metals are also known to undergo spin transitions under appropriate conditions, and of interest to us here are cobalt(II) compounds (d^7).

We are studying complexes of chelating ligands based on 3,6-diformylpyridazine.[6–9] To date, very few pyridazine- or phthalazine-bridged dicobalt(II) complexes have been studied,[10] and all of these have contained high-spin cobalt(II) ions throughout the temperature ranges studied. The structure and electrochemistry of the first macrocyclic pyridazine-bridged dicobalt complex was reported very recently.[8] We report here on an air-stable dicobalt(II) complex of the Schiff-base macrocyclic ligand L, which exhibits unique magnetic properties for a cobalt complex and represents a first step towards the development of a "usable" spin-transition polymer.[1]



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The dicobalt(II) complex $[Co_2L(NCS)_2(SCN)_2]$ (**1**) is readily crystallized in quantitative yield by diffusion of a solution of $[Co_2L(MeCN)_4](ClO_4)_4$ (**2**)[8] in acetonitrile into a solution of sodium thiocyanate. The infrared spectrum of **1** shows that the macrocycle has remained intact during this reaction. The structure determination was carried out at 160 K on a crystal obtained from the reaction mixture (Figure 1). The asymmetric unit consists of half of a macrocyclic complex with the other half of the molecule generated by inversion. The

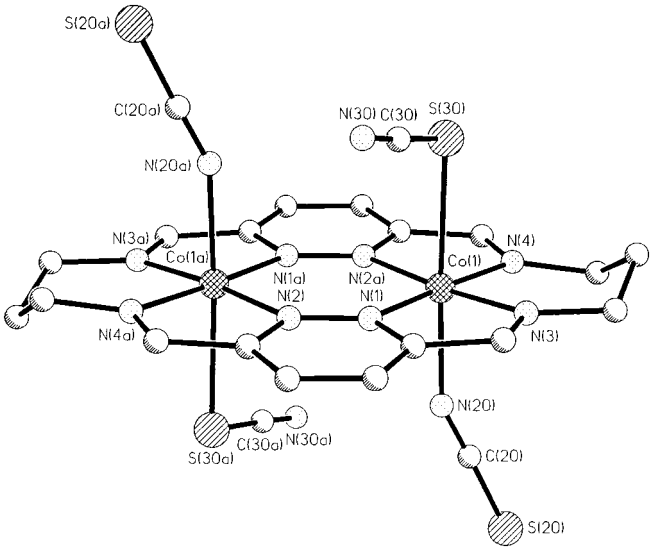

Figure 1. Perspective view of **1**. Selected interatomic distances [Å] and angles [°]: Co(1)–N(4) 1.922(3), Co(1)–N(3) 1.933(3), Co(1)–N(1) 1.966(3), Co(1)–N(2a) 1.983(3), Co(1)–N(20) 2.115(3), Co(1)–S(30) 2.5843(10), Co(1)···Co(1a) 3.813(1); N(4)-Co(1)-N(3) 93.80(12), N(4)-Co(1)-N(1) 175.87(11), N(3)-Co(1)-N(1) 82.07(11), N(4)-Co(1)-N(2a) 81.94(11), N(3)-Co(1)-N(2a) 174.70(11), N(1)-Co(1)-N(2a) 102.19(11), N(4)-Co(1)-N(20) 88.59(12), N(3)-Co(1)-N(20) 90.28(12), N(1)-Co(1)-N(20) 91.21(11), N(2a)-Co(1)-N(20) 92.76(11), N(4)-Co(1)-S(30) 87.49(9), N(3)-Co(1)-S(30) 89.87(9), N(1)-Co(1)-S(30) 92.69(8), N(2a)-Co(1)-S(30) 86.80(8), N(20)-Co(1)-S(30) 176.08(9), N(2)-N(1)-Co(1) 128.5(2), N(1)-N(2)-Co(1a) 129.3(2).

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