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Nonhelical heterometallic [Mo₂M(npo)₄(NCS)₂] string complexes

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(M = Fe, Co, Ni) with high single-molecule conductance

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Using planar 1,8-naphthyridin-2(1H)-one (Hnpo) ligand, novel nonhelical HMSCs $[Mo_2M(npo)_4(NCS)_2]$ (M = Fe, Co, Ni) were synthesised and they exhibited high single-molecule conductance.

Heteronuclear metal string complexes (HMSCs)¹⁻⁷ attract much attention due to their unique electronic, magnetic, structural properties, and potential applications in molecular electronics. However, preparation of HMSCs are considerably more challenging than those of their homometallic counterparts because of difficulties involved in the purification of many possible combinations of metal atoms which concurrently lead to intriguing and profound properties. During the past few years, examples of HMSCs, supported by prototypical ligands of oligo- α -pyridylamido anions,⁸⁻²² have been increasing yet with frustrating barriers. Hence, an increase of the variety of suitable equatorial ligands is an alternative to realise conceived HMSCs.^{2,13,23-25}

Hnpo (1,8-naphthyridin-2(1H)-one, Scheme 1) is a ligand consisting of coordinating sites of naphthyridinate and ketone. Previous attempts to have Hnpo and its methyl substituted analogue, Hmonp (7-methyl-1,8-naphthyridin-2-one), ligated with metal atoms resulted in *di*metallic complexes of $[Rh_2(npo)_2(CO)_2]$ and $[Mo_2(monp)_4]$.^{26,27} $[Mo_2(monp)_4]$ is in a (2,2)-*trans* form with two non-coordinated oxygen atoms at each terminus. *Tri*nuclear metal strings can, in principle, be obtained if the *trans-tri*dentate ligands can shift in relations to each other to create a coordination site for an additional metal centre. Given the different rigidity and coordinating strength of the oxygen and naphthyridine nitrogen atoms, Hnpo may accommodate various kinds of metal cores and is suitable for developing a new class of HMSCs. Herein, we report a



Scheme 1. Syntheses of Ligand Hnpo and HMSCs 1, 2 and 3.

straightforward method to synthesise npo-based *tri*metal HMSCs, (2,2)-*trans*-[MoMoM(npo)₄(NCS)₂] where M is Fe, Co, or Ni. Utilising $[Mo_2Fe(npo)_4(NCS)_2]$ (**1**) as the precursor by direct substitution of the terminal iron atom with cobalt and nickel (Scheme 1) confers $[Mo_2Co(npo)_4(NCS)_2]$ (**2**) and $[Mo_2Ni(npo)_4(NCS)_2]$ (**3**) with respective high yields of 88% and 86%. In addition to the high electric conductance for the potential applications as molecular wires,²⁸⁻³⁰ these new HMSCs are the first series of non-helical metal strings in which the ligands are co-planar with the metal-atom chain.

To prepare Hnpo, 2-amino-1,8-naphthyridine was obtained by literature procedures³¹ and reacted with $NaNO_2(aq)$ and HCl (2 M) for 30 min. The product was subsequently subjected to chromatographic separation using silica gel as the stationary phase. Hnpo is tautomeric in solution (Scheme 1) and

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becomes naphthyridone in solid. Our strategy for the preparation of Co or Ni-incorporated [MoMoM(npo)₄(NCS)₂] was metal replacement. HMSC 1, also the precursor for 2 and 3, was prepared from a one-pot reaction of the dimer $[Mo_2(OAc)_4]$ which served as both the molybdenum source and source of the base for the deprotonation of the ligand. [Mo₂(OAc)₄], anhydrous FeCl₂, and Hnpo were reacted in a ratio of 1.2 : 2 : 4 in refluxing naphthalene under an argon atmosphere. After 1.5 h the reaction mixture was cooled down to room temperature and NaNCS was added as the source of the axial ligand NCS⁻. The mixture was stirred for another 12 h. The naphthalene solvent was removed by dissolving it in *n*-hexane, followed by the extraction of the product from the precipitate with CH₂Cl₂. 1 was isolated as a red brown polycrystalline product with a yield of 16%. ¹H-NMR spectrum of 1 exhibited 10 proton peaks (Fig. S1, ESI⁺). Because the npo ligand has 5 protons, 10 peaks suggest 2 sets of chemically different environments, consistent with the (2,2)-trans conformation determined by X-ray crystallography (vide infra, Figure 1). Mass spectra confirmed the proportion of two Mo and one Fe ion, while infrared confirmed the presence of two inequivalent NCS⁻ (Figs. S2, S3, and S5, ESI⁺).

The crystal structure of HMSC **1** is displayed in Fig. 1 as a representative for all three isostructural compounds which crystallise in the monoclinic space group P2₁/c (see Table S1 and Fig. S7, ESI†). The linear metal cores are coordinated with four npo⁻ ligands. Unlike those supported by dpa⁻, these npobased HMSCs are not helical. A smaller dihedral angle of \angle N-Mo-Mo-N is envisaged to be more favourable for intermolybdenum $d_{x^2-y^2}$ interactions, leading to a larger Mo-Mo bond order (*vide infra*).

The unit cells of 1-3 contain one metal string and two dichloromethane solvent molecules. The metal framework consists of one dimolybdenum unit and one 3d metal ion located at one of the terminal positions. The terminal metal centres of 1-3 are disordered with occupancy ratios of 0.540/0.460, 0.522/0.478, and 0.452/0.548, respectively. The Mo-Mo distances of all three HMSCs are in the range of 2.122(8)-2.067(8) Å, typical for Mo₂ quadruple bonds.^{24,32,33} The Mo…M distances of 1-3 (2.710(9)-2.643(10) Å) is shorter for a smaller metal ion (viz., ion size: Fe > Co > Ni), consistent with the trend in their dpa-based HMSC analogues with the distance of Mo…Fe (2.76 Å) 34 being longer than that of Mo… Co (2.62 Å).¹⁵ Similar correlations between the bond length and metal size are found for $M-O_{av}$ and $M-N_{av}$ (see Table 1). Although the metal-metal distances are unreliable due to the disorder of the metal centres, the average bond distance of Moterminal-O (2.060(6) Å) is significantly shorter by as much as 0.156 Å than that of $Mo_{terminal}$ – N_{av} in 1 and those of $Mo_{terminal}$ – N_{py} in $[MoMoM(dpa)_4 \text{Cl}_2]$ analogues. $^{15,34}~$ The shorter and thus stronger Mo-O bonds in 1 is attributed to the larger electronegativity of O atoms which carry a higher charge than that of N atoms.

HMSC **1** reacted with 4 equivalents of $CoCl_2$ in refluxing naphthalene under argon atmosphere, affording **2** with a high yield of 86%. By using anhydrous [Ni(OAc)₂] instead of $CoCl_2$, **3** with a good yield (88%) can be obtained from **1** in the same



Fig. 1 ORTEP view of $[MoMoFe(npo)_4(NCS)_2]$ (50% probability). Hydrogen atoms and interstitial solvents are not shown for clarity.

Table 1. Selected bond distances of HMSCs 1-3 and 3'

distance (Å)	$1.3CH_2Cl_2$	2·2CH ₂ Cl ₂	3·2CH ₂ Cl ₂	3'.CH2Cl2	
M–N _{av}	2.236(8)	2.216(9)	2.187(7)	2.105(3)	
M–O _{av}	2.079(7)	2.077(10)	2.068(8)		
Мо…М	2.710(9)	2.672(14)	2.643(10)	2.546(6)	
Mo Mo	2.122(8)	2.117(11)	2.067(8)	2.105(5)	
Mo–N _{av}	2.216(6)	2.202(7)	2.178(7)	2.199(3)	
Mo–O _{av}	2.060(6)	2.064(7)	2.071(7)		
3' is $[M_0,N_1(dna)_{\ell}(NCS)_{2}]$ an analogue of 3 , where dna is dipyridylamido anion					

fashion. Due to the very stable quadruple bond of the Mo Mo dimer, Fe ion was the only metal replaced. HMSCs 2 and 3 thus inherit the (2,2)-trans form and are isostructural to 1 as evidenced by crystallographic data (Fig. S7, ESI⁺). The purity was interrogated by ¹H-NMR spectroscopy which would reveal more than 10 proton peaks if the samples of 2 and 3 were inadequately purified and thus contained the initial reactant (i.e., HMSC 1) or mixtures of conformational isomers, such as (4,0), (3,1), and (2,2)-cis forms. MALDI-TOF high-resolution mass spectrometry and voltammetry also showed no indication of residual 1 in purified samples of 2 and 3. (Figs. S2-4, ESI⁺). Vibrational peaks, $v_{C=N}$ of the –NCS axial ligands, at *ca*. 2035-2082 cm⁻¹ are split, suggesting that the termini metal centres are different and that the axial ligands remained intact after the replacement reaction (Fig. S5 ESI⁺). Attempts to directly synthesise 2 and 3 in a one-pot reaction similar to that for 1 were of limited success, leading to mixed compounds and low yields (4–5%). The metal substitution method improves not only the purity but also the yield. The discrepancy might be due to the coordination affinity of npo- to the metal centres. The stronger tendency of Ni^{2+} and Co^{2+} than Fe^{2+} on the formation of square planar or octahedral structures might impede the formation of Mo₂M strings and lead to unwanted complexes. In addition, the stronger bond strength of Fe-O (410 KJ/mol) than those of Co-O (370 KJ/mol) and Ni-O (390 KJ/mol)³⁵ might favour the formation of **1** over the latters although the experimental conditions could be equally crucial. Also prepared in this study is HMSC 3' ([MoMoNi(dpa)₄(NCS)₄]), an analogue of **3** by utilising the prototypical ligand, dpa-(dipyridylamido anion). It is worth noting the difficult timing of

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terminating the reaction; a short reaction time would not produce **3'** and a slightly longer period yields *tri*nickel one, $[Ni_3(dpa)_4(NCS)_4]$. The results show the advantages of npo⁻ ligand in the formation of heterometal string complexes.

Measurements of the magnetic properties were carried out on a SQUID magnetometer (Fig. S8, ESI[†]). The magnetic moments of HMSCs **1**, **2** and **3** were, respectively, 4.96, 4.65, and 3.11 μ_{B} at 300 K, consistent with the theoretical spin-only value (4.89 μ_{B} (**1**), 3.87 μ_{B} (**2**) and 2.83 μ_{B} (**3**)) where the discrepancy in **2** was larger than the other two because of more substantial spin-orbital coupling involved in Co.¹⁵ The magnetic behaviours of **1–3** are similar to those reported [MoMoM(dpa)₄Cl₂] complexes, in which the diamagnetic Mo₂ units are coupled with terminal high-spin 3d metal ions.^{15,34}

The conductance of the complexes was studied by the method of STM-BJ (scanning tunnelling microscopy-based break junction)³⁶⁻³⁸ in which the molecular junctions of electrode-molecule-electrode configurations were generated by breaking the fused tip-substrate contact. The tip and substrate were both gold to which the axial ligands of NCS exhibited strong affinity³⁶ and the experiments were carried out in propylene carbonate containing the molecule of interest.³⁸ The junction can, therefore, be bridged by the complexes via the -NCS termini upon the formation of nanometre-sized tip-substrate gaps. During the course of measurements, the junctions were repeatedly created by having the tip hit into and retracted from the substrate while the conductance of the contact was monitored at a fixed E_{bias} of 50 mV. The acquired conductance values of conductancetip displacement traces (G-s traces) were expressed in terms of quantum conductance (10⁰ G₀ = $2e^2/h \approx 77.5 \ \mu$ S or (12.9 $(k\Omega)^{-1}$ which represents the conductance for a single conducting channel or the cross-section of the contact being a single gold atom. Pooling together the acquired G-s traces results in the conductance histograms (Fig. 2 and Fig. S9, ESI⁺).

The conductance of metal strings was found correlated strongly with metal-metal interactions or bond orders.^{29,38-40} For example, prior to this study, the most conductive *tri*metal string (Table 2) was [Cr₃(dpa)₄(NCS)₂] with formerly the largest bond order of 1.5 with electrons delocalised between the three chromium centres. HMSCs 1-3 appear more conductive than $[Cr_3(dpa)_4(NCS)_2]$. The conductance values of 1–3 are quite similar, suggesting that the electron transport associated strongly with the dimolybdenum moiety and relatively independent on whether the third metal centre is Fe, Co or Ni. To explore the effect of nonhelical npo ligand on conductance, [Mo₂Ni(dpa)₄(NCS)₂] (3'), an analogue of $[Mo_2Ni(npo)_4(NCS)_2]$ (3), was prepared by the prototypical ligand and it was found less conductive (Fig. 2). The helical dpa⁻ ligands of **3'** led to a significant dihedral angle of $\angle N_{nv}$ -Mo-Mo-N_{amido} (ca. 12.4°) and presumably weakens the δ bond of Mo₂.⁴¹ The proposed stronger δ bond of **3** relative to **3'** is supported by (1) the crystallographic findings with a shorter Mo-Mo distance (2.067(8) Å for **3** versus 2.104(5) Å for **3**'), (2) UV/vis spectra with a shorter wavelength of the δ -to- δ^* transition and thus a more stable δ bond (483 nm for ${\bf 3}$ and 495 nm for 3', Fig. S6, ESI \dagger), and (3) a larger bond order of Mo₂ elucidated by single-point DFT calculations (bond order of 3.10 for 3 and 2.80 for the helical 3', Figs. S10-12, ESI⁺).



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Fig. 2 Conductance histograms of HMSCs (red) **3** and (black) **3'** which have the same metal chains yet have, respectively, nonhelical npo⁻ and helical dpa⁻ equatorial ligands. Except the apex, the STM tip was insulated with a layer of ethylene vinyl acetate to minimise the background current. Other conditions: solutions, saturated HMSCs in propylene carbonate; E_{blass} 50 mV; numbers of *G*-s traces: red, 1183 for **3**; black, 1521 for **3'**.

Table 2. Single-molecule conductance of trimetal strings

	Conductance (× 10 ^{−3} G₀)	Resistance (MΩ) ⁴²	reference		
[Mo ₂ Fe(npo) ₄ (NCS) ₂], 1	20 (±12)	0.63 (±0.39)	this work		
[Mo ₂ Co(npo) ₄ (NCS) ₂], 2	16 (±10)	0.83 (±0.53)	this work		
[Mo ₂ Ni(npo) ₄ (NCS) ₂], 3	18 (±14)	0.73 (±0.55)	this work		
[Mo ₂ Ni(dpa) ₄ (NCS) ₂], 3'	6.2 (±5.4)	2.1 (±1.9)	this work		
[Cr ₃ (dpa) ₄ (NCS) ₂]	14 (±2)	0.9 (±0.1)	39		
[Ru ₃ (dpa) ₄ (NCS) ₂]	9.8 (±2.0)	1.3 (±0.3)	29		
[Co ₃ (dpa) ₄ (NCS) ₂]	6.8 (±0.4)	1.9 (±0.1)	39		
[Ni ₃ (dpa) ₄ (NCS) ₂]	3.8 (±0.6)	3.4 (±0.5)	39		
[Ni ₃ (dzp) ₄ (NCS) ₂]	3.3 (±0.9)	3.9 (±1.0)	43		
[Ni₃(mpta)₄(NCS)₂]	1.8 (±0.4)	7.1 (±1.5)	44		
dzn: 1.9-diazanhenovazine: ⁴³ mnta: 1-methylpyridylthiazolylamido anion ⁴⁴					

Conclusions

In summary, the novel HMSCs 1-3, $[Mo_2M(npo)_4(NCS)_2]$ (M = Fe (1) Co (2), Ni (3)), supported by ketone containing npo ligands were designed and characterised. From 1, HMSCs 2 and 3 were synthesised through metal substitution and resulted in high yields and purity. The single crystal X-ray diffraction analysis revealed, three isostructural 2,2-trans structures for 1-3 with Mo-O bonds that are comparably stronger than the Mo-N bonds. The members of this new series of HMSCs are paramagnetic due to the terminal 3dmetal ions. HMSCs 1-3 exhibit higher conductance than homometallic predecessors like [Ni₃(dpa)₄(NCS)₂] and $[Cr_3(dpa)_4(NCS)_2]$. The increase can be attributed to the Mo Mo guadruple bond of these complexes. 1 represents the highest conductance value measured in metal string complexes. Further experiments are currently in progress to extend the scope of heterometallic species synthesised by 1,8naphthyridin-2(1H)-one ligands and metal exchange methods.

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Notes and references

‡Crystal data for 1: $C_{37}H_{26}Cl_6FeMo_2N_{10}O_4S_2$, M_w = 1199.23, monoclinic, space group P2₁/c, a = 11.4437(8) Å, b = 9.1690(7) Å, c = 40.646(3) Å, β = 90.2274(12)°, V = 4264.9(5) Å³, Z = 4, d_(calcd) = 1.868 mg·m⁻³, T = 150(2) K, 25574 reflections collected, 9705 independent, $R_{int} = 0.0354$, $R_1 = 0.0774$, $wR_2 = 0.1884$ for all data. Crystal data for **2**: $C_{36}H_{24}CI_4COMo_2N_{10}O_4S_2$, $M_w = 1117.38$, monoclinic, space group $P2_1/c$, a = 11.4447(5) Å, b = 9.1848(4) Å, c = 40.5341(18) Å, β = 90.2579(9)°, V = 4260.8(3) Å³, Z = 4, d_(calcd) = 1.742 mg·m⁻³, T = 150(2) K, 27002 reflections collected, 9705 independent, $R_{int} = 0.0478$, $R_1 = 0.0741$, $wR_2 = 0.2356$ for all data. Crystal data for **3**: $C_{36}H_{24}Cl_4NiMo_2N_{10}O_4S_2$, $M_w = 1117.16$, monoclinic, space group P2₁/c, a = 11.4015(15) Å, b = 9.1595(12) Å, c = 40.310(5) Å, β = 90.2269(11)°, V = 4209.7(10) Å³, Z = 4, $d_{(calcd)} = 1.763 \text{ mg} \cdot \text{m}^{-3}$, T = 150(2) K, 20655 reflections collected, 7705 independent, $R_{int} = 0.0165$, $R_1 = 0.0775$, $wR_2 = 0.2273$ for all data. Crystal data for **3'**: $C_{43}H_{34}Cl_2Mo_2N_{14}NiS_2$, $M_w = 1132.45$, Triclinic, space group P-1, a = 11.9978(2) Å, b = 12.8594(2) Å, c = 16.6250(3) Å, $\alpha = 97.5181(11)^\circ$, $\beta = 105.8370(8)^\circ$, γ 112.0839(8)°, $V = 2206.79(7) \text{ Å}^3$, Z = 2, $d_{(calcd)} = 1.704 \text{ mg} \cdot \text{m}^{-2}$, T = 150(2) K, 29946 reflections collected, 10086 independent, $R_{int} =$ 0.0502, $R_1 = 0.0489$, $wR_2 = 0.1252$ for all data.

- A. L. Balch, V. J. Catalano, B. C. Noll and M. M. Olmstead, J. Am. Chem. Soc., 1990, 112, 7558-7566.
- K. Mashima, Y. Shimoyama, Y. Kusumi, A. Fukumoto, T. Yamagata and M. Ohashi, *Eur. J. Inorg. Chem.*, 2007, 2007, 235-238.
- M. Ohashi, A. Shima, T. Rüffer, H. Mizomoto, Y. Kaneda and K. Mashima, *Inorg. Chem.*, 2007, 46, 6702-6714.
- 4. T. Yamada, M. Ebihara and K. Uemura, *Dalton Trans.*, 2016, **45**, 12322-12328.
- L. J. Clouston, R. B. Siedschlag, P. A. Rudd, N. Planas, S. Hu, A. D. Miller, L. Gagliardi and C. C. Lu, *J. Am. Chem. Soc.*, 2013, **135**, 13142-13148.
- W.-C. Hung, M. Sigrist, S.-A. Hua, L.-C. Wu, T.-J. Liu, B.-Y. Jin, G.-H. Lee and S.-M. Peng, *Chem. Commun.*, 2016, **52**, 12380-12382.
- E. Goto, R. A. Begum, C. Ueno, A. Hosokawa, C. Yamamoto, K. Nakamae, B. Kure, T. Nakajima, T. Kajiwara and T. Tanase, Organometallics, 2014, 33, 1893-1904.
- M.-M. Rohmer, I. P.-C. Liu, J.-C. Lin, M.-J. Chiu, C.-H. Lee, G.-H. Lee, M. Bénard, X. López and S.-M. Peng, *Angew. Chem. Int. Ed.*, 2007, 46, 3533-3536.
- G.-C. Huang, M. Bénard, M.-M. Rohmer, L.-A. Li, M.-J. Chiu, C.-Y. Yeh, G.-H. Lee and S.-M. Peng, *Eur. J. Inorg. Chem.*, 2008, 2008, 1767-1777.
- X. López, M.-M. Rohmer and M. Bénard, J. Molecular Struct., 2008, 890, 18-23.
- J. F. Berry, in *Metal-Metal Bonding*, ed. G. Parkin, Springer Berlin Heidelberg, Berlin, Heidelberg, 2010, DOI: 10.1007/978-3-642-05243-9_1, pp. 1-28.
- 12. D. Aydin-Cantürk and H. Nuss, Z. Anorg. Allgem. Chem., 2011, 637, 543-546.
- 13. B. S. Dolinar and J. F. Berry, Inorg. Chem., 2013, 52, 4658-4667.
- 14. M. Nippe and J. F. Berry, J. Am. Chem. Soc., 2007, **129**, 12684-12685.
- M. Nippe, E. Victor and J. F. Berry, *Eur. J. Inorg. Chem.*, 2008, 2008, 5569-5572.
- M. Nippe, G. H. Timmer and J. F. Berry, Chem. Commun., 2009, 4357-4359.
- M. Nippe, J. Wang, E. Bill, H. Hope, N. S. Dalal and J. F. Berry, J. Am. Chem. Soc., 2010, **132**, 14261-14272.

- D. W. Brogden, J. H. Christian, N. S. Dalal and J. F. Berry, *Inorg. Chim. Acta*, 2015, **424**, 241-247.
- 19. M. Nippe, Y. Turov and J. F. Berry, *Inorg. Chem.*, 2011, **50**, 10592-10599.
- I. P.-C. Liu, G.-H. Lee, S.-M. Peng, M. Bénard and M.-M. Rohmer, Inorg. Chem., 2007, 46, 9602-9608.
- M.-C. Cheng, C.-L. Mai, C.-Y. Yeh, G.-H. Lee and S.-M. Peng, Chem. Commun., 2013, 49, 7938-7940.
- 22. S.-A. Hua, M.-C. Cheng, C.-h. Chen and S.-M. Peng, Eur. J. Inorg. Chem., 2015, 2015, 2510-2523.
- 23. K. Mashima, H. Nakano and A. Nakamura, J. Am. Chem. Soc., 1996, **118**, 9083-9095.
- 24. K. Mashima, Bull. Chem. Soc. Japan, 2010, 83, 299-312.
- 25. B. S. Dolinar and J. F. Berry, *Polyhedron*, 2016, **103, Part A**, 71-78.
- 26. M. A. Ciriano, B. E. Villarroya and L. A. Oro, *Inorg. Chim. Acta*, 1986, **120**, 43-48.
- 27. W. S. Sheldrick and M. Mintert, *Inorg. Chim. Acta*, 1994, **219**, 23-29.
- 28. C.-H. Ko, M.-J. Huang, M.-D. Fu and C.-h. Chen, J. Am. Chem. Soc., 2010, **132**, 756-764.
- 29. K.-N. Shih, M.-J. Huang, H.-C. Lu, M.-D. Fu, C.-K. Kuo, G.-C. Huang, G.-H. Lee, C.-h. Chen and S.-M. Peng, *Chem. Commun.*, 2010, **46**, 1338-1340.
- M.-J. Huang, S.-A. Hua, M.-D. Fu, G.-C. Huang, C. Yin, C.-H. Ko, C.-K. Kuo, C.-H. Hsu, G.-H. Lee, K.-Y. Ho, C.-H. Wang, Y.-W. Yang, I-C. Chen, S.-M. Peng and C.-h. Chen, *Chem.–Eur. J.*, 2014, **20**, 4526-4531.
- C. Reichardt and W. Scheibelein, *Tetrahedron Lett.*, 1977, 18, 2087-2090.
- G. Holste and H. Schäfer, Z. Anorg. Allgem. Chem., 1972, 391, 263-270.
- 33. F. A. Cotton and J. G. Norman, J. Coordination Chem., 1972, 1, 161-171.
- M. Nippe, E. Bill and J. F. Berry, *Inorg. Chem.*, 2011, 50, 7650-7661.
- 35. J. A. Dean, *Lange's Handbook of Chemistry*, McGraw-Hill Companies, 15th edn., 1998.
- M.-D. Fu, I-W. P. Chen, H.-C. Lu, C.-T. Kuo, W.-H. Tseng and C.-h. Chen, J. Phys. Chem. C, 2007, 111, 11450-11455.
- 37. C.-T. Kuo, L.-C. Su and C.-h. Chen, J. Chin. Chem. Soc., 2014, 61, 101-114.
- 38. T.-C. Ting, L.-Y. Hsu, M.-J. Huang, E.-C. Horng, H.-C. Lu, C.-H. Hsu, C.-H. Jiang, B.-Y. Jin, S.-M. Peng and C.-h. Chen, *Angew. Chem. Int. Ed.*, 2015, **54**, 15734-15738.
- 39. I-W. P. Chen, M.-D. Fu, W.-H. Tseng, J.-Y. Yu, S.-H. Wu, C.-J. Ku, C.-h. Chen and S.-M. Peng, *Angew. Chem. Int. Ed.*, 2006, 45, 5814-5818.
- I. P.-C. Liu, M. Benard, H. Hasanov, I-W. P. Chen, W.-H. Tseng, M.-D. Fu, M.-M. Rohmer, C.-h. Chen, G.-H. Lee and S.-M. Peng, *Chem.-Eur. J.*, 2007, **13**, 8667-8677.
- F. A. Cotton, C. A. Murillo and R. A. Walton, eds., *Multiple Bonds* between Metal Atoms, Springer-Verlag New York, 2005.
- 42. Regarding the discrepancy in the relative standard deviations, it could be due to (1) the different criteria for the exclusion of unreasonable conductance traces and (2) the logarithmic scale plotted for the conductance histograms in this study while the previous ones were in the linear scale.
- M.-C. Cheng, I. P.-C. Liu, C.-H. Hsu, G.-H. Lee, C.-h. Chen and S.-M. Peng, *Dalton Trans.*, 2012, **41**, 3166-3173.
- 44. C.-C. Yang, I. P.-C. Liu, Y.-J. Hsu, G.-H. Lee, C.-h. Chen and S.-M. Peng, *Eur. J. Inorg. Chem.*, 2013, **2013**, 263-268.

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