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Selective synthesis of isomeric heterodinuclear complexes with switched metal arrangements *via* proton-induced reversible metal migration†

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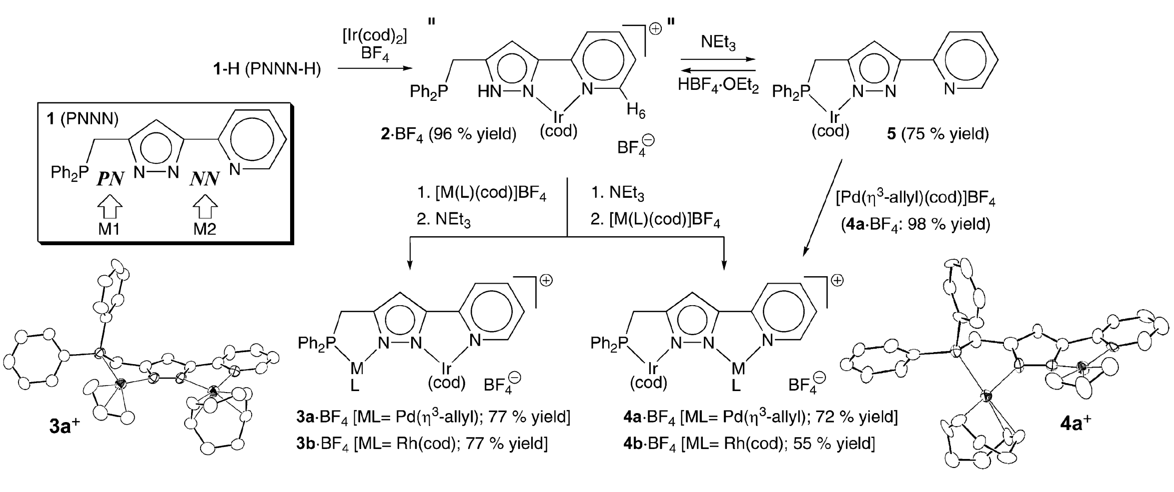
Pairs of isomeric heterodinuclear complexes, [(cod)Ir(μ-PNNN)M(L)]BF$_4$ and [(L)M(μ-PNNN)Ir(cod)]BF$_4$, with switched metal arrangements are prepared in a specific manner by simply changing the addition order of the reagents.

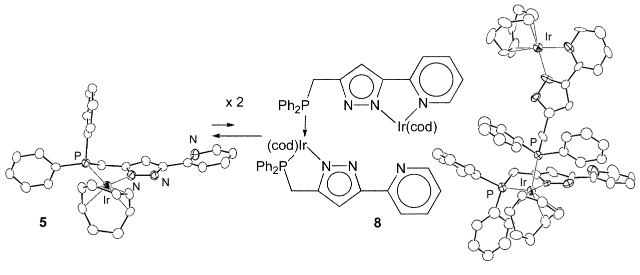
Polynuclear heterometallic complexes are expected to display unique reactivity through cooperation of the metal centers with different characters.[1] But putting different metal fragments on particular coordination sites on a polydentate ligand *in a specific manner* is not always facile. Doubly donor-armed heteroaromatics with two chelating coordination sites are versatile dinucleating ligands.[2] Although a variety of such derivatives have been prepared so far, attempts to prepare heterometallic complexes have been few.[3] We are now carrying out a synthetic study on heterodinuclear complexes with the PNNN ligand **1** (3-diphenylphosphinomethyl-5-pyridylpyrazolate; Scheme 1),[4] which follows that on homometallic polynuclear complexes with a symmetric PNNP ligand.[5,6] The PNNN ligand **1** has one PN- and one NN-coordination site and herein we wish to report the selective synthesis of pairs of isomeric heterodinuclear complexes with a reversed metal arrangement from the same sources by simply changing the addition procedure of the reagents.



Scheme 1 All reactions were carried out in CH$_2$Cl$_2$.

Treatment of PNNN-H (**1**-H) with [Ir(η^4-cod)$_2$]BF$_4$ in CH$_2$Cl$_2$ gave a pale yellow precipitate **2**·BF$_4$‡ (Scheme 1). Subsequent addition of another labile metal component [M(L)(cod)]BF$_4$ [M(L) = Pd(η^3-allyl), Rh(η^4-cod)] followed by a base (NEt$_3$) furnished the heterodinuclear complexes **3**·BF$_4$.‡ In **3**·BF$_4$ the Ir and Pd fragments occupied the NN- and PN-coordination site, respectively, as determined for **3a**·BF$_4$ by X-ray crystallography.§ To our surprise, simply reversing the addition order of the second metal reagent and the base exclusively brought about formation of the isomeric species **4**·BF$_4$,‡ where the metal arrangement is switched as also determined for **4a**·BF$_4$ by X-ray crystallography (Scheme 1).§

Low solubility of **2**·BF$_4$ in organic solvents hampered full spectroscopic characterization but upfield shift of the H$_6$ signal, which was a sign of NN-coordination,‡ led to tentative assignment of the structure shown in Scheme 1. It is notable that deprotonation of **2**·BF$_4$ with NEt$_3$ afforded the neutral species **5**, where the iridium atom was incorporated into the PN-site as confirmed by (i) the deshielded ^{31}P signal [δ_P 30.1; *cf.* **1**-H: −20.1], (ii) downfield shift of the doublet H$_6$ signal and (iii) X-ray crystallography (Scheme 2).§ Protonation of **5** with HBF$_4$·OEt$_2$ immediately caused quantitative precipitation of **2**·BF$_4$.



Scheme 2

These results suggest that the deprotonation–protonation processes bring about reversible migration of the Ir fragment between the NN- and PN-coordination sites, which can account for the selective formation of **3**·BF$_4$ and **4**·BF$_4$. Coordination of the P atom in **2**·BF$_4$ to the second metal species followed by deprotonation leads to **3**·BF$_4$, whereas a deprotonation–migration–coordination sequence from **2**·BF$_4$ affords the other isomer **4**·BF$_4$ by way of **5**. Accordingly, treatment of **5** with [Pd(η^3-allyl)(cod)]BF$_4$ gave **4a**·BF$_4$ quantitatively.

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† Electronic supplementary information (ESI) available: experimental details, spectroscopic and crystallographic data. See http://www.rsc.org/suppdata/cc/b4/b409514f/

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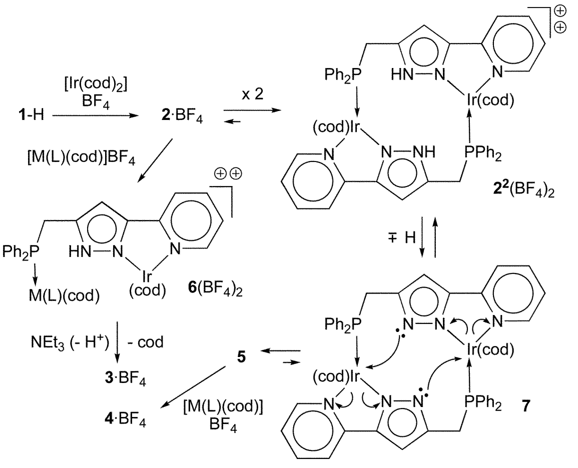
Few metal migration reactions on a polynucleating ligand have been reported and their reaction mechanisms remain to be clarified. For example, Oro *et al.*[7] reported a σ-1,2-metallotropic shift on dirhodium μ-pyrazolato complexes, which was interpreted in terms of a μ–η^1:η^2-pyrazolato intermediate. Further examination of the reaction mechanism reveals that the present migration process is not unimolecular but that metal migration occurs in a dimeric intermediate. The ^{31}P NMR signal for **2**·BF$_4$ appears at δ_P −5.3, which is distinct from those of the free ligand **1**-H as well as chelated species (*e.g.* **5**: δ_P 31.2), but suggests some coordination. No dynamic behavior is applicable, because solid ^{31}P NMR measurements also give a single resonance in the same region (δ_P 0.6). On the basis of the ESI-MS data containing peaks at m/z = 1376 [**2** × 2 + BF$_4$ (^{193}Ir)] and 1288 [**2** × 2 – H (^{193}Ir)], we propose an oligomeric structure, most likely a dimeric one [**2**^{2}·(BF$_4$)$_2$],[8] and the present intriguing selective formation of the isomeric species can be explained by the mechanisms shown in Scheme 3.



Scheme 3 BF$_4^-$ is omitted for clarity.

Coordination of **1** to [Ir(cod)$_2$]BF$_4$ gives the NN-coordinated species **2**·BF$_4$, which is in equilibrium with the five-coordinate dimeric form **2**^{2}(BF$_4$)$_2$, and the equilibrium is shifted to the dimer, which precipitates out. This can be explained by the Lewis acidity of the cationic Ir center, which should prefer five-coordination to four-coordination. The second metal species interacts with **2**·BF$_4$ present as a minor component in the solution to give the adduct **6**(BF$_4$)$_2$, which is converted to **3**·BF$_4$ upon deprotonation. On the other hand, initial deprotonation of **2**·BF$_4$ should give the intermediate **7**, which dissociates into the mononuclear species **5**, because the metal center in a neutral species is less Lewis acidic and may not be coordinated by a fifth donor. Subsequent NN-coordination to the second metal species furnishes the other isomer **4**·BF$_4$. It should be noted that, in the metal migration process (**7** → **5**), the iridium fragments are transferred to the other ligand and as a result, the coordination site is switched. Intervention of a five-coordinated species is supported by formation of **8**, a dimer of **5** (Scheme 2).[9]

Notable features of the present selective isomer formation are that (i) the flexible coordination structure (four- *vs.* five-coordination), charge (neutral *vs.* cationic) and Lewis acidity of the metal center are switched by the deprotonation–protonation process and (ii) the supramolecular intermediate **7** undergoes interligand metal migration accompanying the shift from the NN- to the PN-coordination site.

Thus pairs of regioisomers of heterodinuclear species are synthesized with perfect selectivity from the same sources by simply changing the addition procedure of the reagents and the present study provides a new concept of combinatorial approach to a variety of transition metal complexes. The reactivity of the isomeric heteronuclear complexes with the two organic ligands being located in close proximity is now being studied.

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Notes and references

‡ Selected spectroscopic data: **1**-H: δ_H 6.48 (pz), 8.56 (H$_6$). **2**·BF$_4$: δ_H 5.10 (pz), 7.98 (H$_6$). **3a**·BF$_4$: δ_P 34.0; δ_H 6.76 (pz), 7.73 (H$_6$). **3b**·BF$_4$: δ_P 38.8 (d, $J_{P\text{–}Rh}$ = 154.6 Hz); δ_H 6.71 (pz), 7.87 (H$_6$). **4a**·BF$_4$: δ_P 37.7; δ_H 6.83 (pz), 8.53 (H$_6$). **4b**·BF$_4$: δ_P 38.1; δ_H 6.80 (pz). **5**·BF$_4$: δ_P 31.2; δ_H 6.73 (pz), 8.50 (H$_6$). For cod complexes, the NN-coordination can be confirmed by a combination of δ_H(H$_6$) and δ_P data. The H$_6$ signal appears in higher field.

§ X-Ray data collections were carried out with a Rigaku RAXIS-IV imaging plate area detector at −60 °C. **3a**·BF$_4$: $C_{32}H_{34}BN_3F_4PPdIr$, M_w = 877.04, triclinic, space group $P\bar{1}$, a = 10.898(6) Å, b = 11.791(8) Å, c = 12.960(8) Å, α = 96.74(2)° β = 11.63(2)°, γ = 95.51(2)°, V = 1519(1) Å^3, Z = 2, d_{calcd} = 1.916 g cm^{-3}, $R1$ = 0.073 (refined on F^2) for 4754 data ($I > 2\sigma(I)$) and 388 parameters. **4a**·BF$_4$·(CH$_2$Cl$_2$)$_{0.5}$: $C_{32.5}H_{35}BN_3F4PPdIr$, M_w = 919.47, triclinic, space group $P\bar{1}$, a = 13.877(9) Å, b = 14.786(13) Å, c = 16.189(14) Å, α = 83.74(4)° β = 79.66(3)°, γ = 88.57(3)°, V = 3248(5) Å^3, Z = 2, d_{calcd} = 1.88 g cm^{-3}, $R1$ = 0.063 (refined on F^2) for 3480 data ($I > 2\sigma(I)$) and 737 parameters. **5**: $C_{29}H_{62}N_6P_2Ir_2$, M_w = 642.72, triclinic, space group $P\bar{1}$, a = 9.341(5) Å, b = 9.958(5) Å, c = 13.571(9) Å, α = 92.45(5)°, β = 102.39(4)°, γ = 98.18(2)°, V = 1216.9(13) Å^3, Z = 2, d_{calcd} = 1.754 g cm^{-3}, $R1$ = 0.058 (refined on F^2) for 2686 data ($I > 2\sigma(I)$) and 307 parameters. **8**·(CH$_2$Cl$_2$)$_2$: $C_{60}H_{62}N_6P_2Cl_4Ir_2$, M_w = 1455.30, triclinic, space group $P\bar{1}$, a = 11.130(18) Å, b = 14.56(2) Å, c = 18.75(2) Å, α = 78.51(6)° β = 85.37(6)°, γ = 71.38(6)°, V = 2823(7) Å^3, Z = 2, d_{calcd} = 1.712 g cm^{-3}, $R1$ = 0.0727 (refined on F^2) for 2858 data ($I > 2\sigma(I)$) and 627 parameters. CCDC 243413–243416. See http://www.rsc.org/suppdata/cc/b4/b409514f/ for crystallographic data in .cif or other electronic format.

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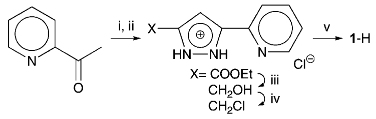
3 See for example M. Konrad, S. Wuthe, F. Meyer and E. Kaifer, *Eur. J. Inorg. Chem.*, 2001, 2233; J. C. Röder, F. Meyer, R. F. Winter and E. Kaifer, *J. Organomet. Chem.*, 2002, **641**, 113; S. Baitalik, U. Flörke and K. Nag, *Inorg. Chim. Acta*, 2002, **337**, 439.

4 The PNNN-H ligand (**1**-H), which was a mixture of PN- and NN-protonated tautomers, was prepared following the conventional reaction sequence. (i) (COOEt)$_2$/NaOEt. (ii) N$_2$H$_4$·H$_2$O. (iii) LiAlH$_4$. (iv) SOCl$_2$. (v) LiPPh$_2$. (See ESI.)



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5 PNNP = 3,5-bis(diphenylphosphinomethyl)pyrazolate: T. G. Schenck, J. M. Downes, C. R. C. Milne, P. B. Mackenzie, H. Boucher, J. W. Whelan and B. Bosnich, *Inorg. Chem.*, 1985, **24**, 2334.

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7 Y. Yuan, M. V. Jiménez, E. Sola, F. J. Lahoz and L. A. Oro, *J. Am. Chem. Soc.*, 2002, **124**, 752; C. Tejel, J. M. Villoro, M. A. Ciriano, J. A. López, E. Eguizábal, F. J. Lahoz, V. I. Bakhmutov and L. A. Oro, *Organometallics*, 1996, **15**, 2967.

8 Recently we found that the symmetrical PNNP ligand also gave an intermediate analogous to **2**^{2}·(BF$_4$)$_2$, which showed two doublet ^{31}P-NMR signals coupled with each other suggesting coordination of two phosphorous atoms in different environments to the iridium center. C. Dubs, A. Inagaki and M. Akita, unpublished data.

9 While only monomer **5** was detected by spectroscopic analyses of a solution sample, two forms of single crystals (**5** and **8**) were isolated from a solid sample and characterized by X-ray crystallography.§ The formation of **8** suggests that the present system consists of a network of equilibria and another metal migration process should be involved in the formation of **8** from **5**.