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PAPER

New bimetallic complexes supported by a tetrakis(imino)pyracene (TIP) ligand†‡

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The first examples of palladium dihalide and indium trihalide complexes supported by a tetrakis(imino)pyracene (TIP) ligand have been prepared and structurally characterized.

Introduction

Although the first metal complexes supported by the bis(imino)-acenaphthene (BIAN) ligand were disclosed over four decades ago,[1] it is only much more recently that compounds of this genre have begun to attract significant attention. Since BIAN ligands can be regarded as arising from the fusion of a naphthalene ring to a 1,4-diaza-1,2-butadiene, the rigidity of the resulting ligand framework has rendered this ligand class excellent platforms for the support of a wide range of robust transition metal catalysts that are capable of facilitating a significant number of important transformations such as the homopolymerization of alkenes[2] and the copolymerization of carbon monoxide and alkenes.[3]

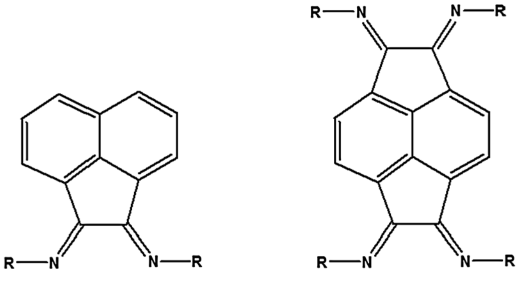

Fig. 1 Mono- and difunctional imino ligands.

Given the foregoing, it was anticipated that bifunctional analogues of the BIAN ligand class might prove to be interesting as *e.g.* bimetallic catalyst supports, metallopolymers and molecular wire models. The first two examples of the so-called tetrakis(imino)pyracene (TIP) ligands were prepared by two different synthetic routes, each of which employed tetraketopyracene as the starting material (Fig. 1).[4] An initial objective of this work was to demonstrate the feasibility of preparing a polymer that incorporated a TIP ligand. This objective was accomplished by layering two equivalents of $CuBr_2$ in ethanol on top of the 2,6-diisopropylphenyl-substituted TIP ligand (dipp-TIP). Crystals of a metallopolymer of overall composition $[BrCu(dipp\text{-}TIP)CuBr]_n$ formed slowly from ethanol/THF solution over a period of 7 days of storage at ambient temperature (Fig. 2).[4] The X-ray crystal structure comprises a chain of essentially planar Cu(dipp)Cu rhomboids that are oriented in a close to orthogonal fashion along the polymer chain. It is clear from the stoichiometry of the product that $CuBr_2$ is reduced to CuBr in the course of polymerization. However, the polymer scaffold itself is not redox active and the Cu···Cu distance of 2.718(1) Å exceeds the sum of covalent radii for Cu(I).

Given the importance of palladium-catalyzed cross-coupling reactions, it is clear that there is a strong interest in the development of new catalysts that feature this and other metals. Accordingly, we have turned our attention recently to the potential usefulness of TIP ligands for the assembly of stable main-chain polymers that are both tunable and recoverable. While no such examples incorporating a BIAN ligand have been reported, an encapsulated pyridyl-substituted BIAN system which is effective for the copolymerization of carbon monoxide and 4-tert-butylstyrene[5] could potentially be used for such systems. For the purpose of generating the desired catalysts, we have recently prepared, structurally characterized and herein report the requisite palladium monomers of the type $X_2Pd(dipp\text{-}TIP)PdX_2$ [X = Cl (**1**); X = Br (**2**)] as well as a series of indium complexes of the form $X_3In(dipp\text{-}TIP)InX_3$ [X = Cl (**3**); X = Br (**4**); X = I (**5**)].

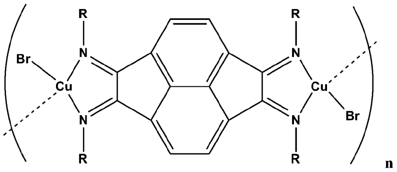

Fig. 2 $(CuBr)_2$TIP polymer.

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† Dedicated with admiration to Professor Didier Astruc on the occasion of his 65th birthday.

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Experimental section

General considerations

Manipulations involving InX_3 were performed in a dry and oxygen-free argon atmosphere by using standard Schlenk or glove-box techniques. Hexanes and dichloromethane were dried over Na and CaH_2, respectively, and freshly distilled prior to use. Acetonitrile was used as received from Sigma Aldrich. The metal halides PdX_2 and InX_3 were purchased from Strem Chemicals and used without further purification. The ligand dipp-TIP[4] was synthesized according to the published procedure.

Physical measurements

Low-resolution CI mass spectra were collected on a Finnigan MAT TSQ-700 mass spectrometer. High resolution mass spectra were acquired on a VG Analytical ZAB-VE sector instrument. All ^1H NMR spectra were recorded at 295 K on a Varian 300 MHz NMR spectrometer. Deuterated solvents were obtained from Cambridge Isotopes and stored over 4 Å molecular sieves prior to use. The ^1H spectra are reported relative to tetramethylsilane and referenced to solvent. Melting points were obtained on a Fisher–Johns apparatus and are reported uncorrected.

X-Ray crystallography

The X-ray data were collected on a Nonius Kappa CCD diffractometer equipped with an Oxford Cryostream liquid nitrogen cooling system. Samples were covered with mineral oil and mounted on a nylon thread loop prior to data collection. All data collections were performed at 153(2) K using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). A correction was applied for Lorentz-polarization in each case. All structures were solved by direct methods and refined by full-matrix least squares on F^2 using the Siemens SHELXL PLUS 5.0 (PC) software package.[6] All hydrogen atoms were placed in calculated positions ($CH_3 = 0.96$ Å, C–H = 0.98 Å, Ar–H = 0.93 Å) and refined using a riding model and a general isotropic thermal parameter. The program SQUEEZE was used to remove two disordered dichloromethane molecules from structures **1** and **3** and one disordered dichloromethane molecule from structures **4** and **5**.

Preparation of $(PdCl_2)_2$(dipp-TIP) (1)

Acetonitrile (10 mL) was added to a flask charged with dipp-TIP (0.030 g, 0.034 mmol) and $PdCl_2$ (0.012 g, 0.068 mmol) and the resulting mixture was stirred at reflux for 1 h. Cooling of the reaction mixture and stripping of solvent afforded a red solid. The crude solid was washed with deionized water (5 mL) and cold diethyl ether (2 mL) and dried, resulting in an analytically pure red powder. The solid was dissolved in dichloromethane, filtered and allowed to evaporate slowly over 3 days thereby affording a crop of red crystalline blocks. Yield 0.032 g (76%).

MS (CI^+, CH_4): *m*/*z* 1227 $[M + H]^+$; HRMS (CI^+, CH_4): calcd for $C_{62}H_{72}N_4Pd_2Cl_4$ *m*/*z* 1227.3122; found, 1227.3130; ^1H NMR (CD_2Cl_2): δ 0.90 (d, 24H, CH_3), 1.45 (d, 24H, CH_3), 3.31 (sept, 8H, -CH), 6.50 (d, 4H, NapC-H), 7.38 (d, 8H, Ar-H), 7.55 (t, 4H, Ar-H); IR (cm^{-1}): 1771s, 1625s, 1601s, 1586, 1458, 1440, 1300, 1187, 1064; mp 299 °C (d).

Preparation of $(PdBr_2)_2$(dipp-TIP) (2)

Acetonitrile (10 mL) was added to a flask charged with dipp-TIP (0.030 g, 0.034 mmol) following which $PdBr_2$ (0.018 g, 0.068 mmol) was added and the resulting mixture was stirred at reflux for 45 min. Cooling of the reaction mixture and subsequent stripping of the reaction solvent afforded a dark red solid which was washed with deionized water (5 mL) and cold diethyl ether (2 mL) and dried, resulting in an analytically pure red powder. The solid was dissolved in a minimal volume of dichloromethane, filtered and allowed to evaporate slowly for 3 days, affording a crop of dark red crystalline blocks. Yield 0.037 g (77%).

MS (CI^+, CH_4): *m*/*z* 1405 $[M + H]^+$; HRMS (CI^+, CH_4): calcd for $C_{62}H_{72}N_4Pd_2Br_4$ *m*/*z* 1405.2332; found, 1405.2326; ^1H NMR (CD_2Cl_2): δ 0.86 (d, 24H, CH_3), 1.44 (d, 24H, CH_3), 3.29 (sept, 8H, -CH), 6.46 (d, 4H, NapC-H), 7.37 (d, 8H, Ar-H), 7.51 (t, 4H, Ar-H); IR (cm^{-1}): 1722s, 1627s, 1603s, 1586s, 1451, 1441s, 1364, 1296, 1187s, 1065s; mp 291 °C (d).

Preparation of $[(InCl_3)_2$(dipp-TIP)] (3)

Dichloromethane (20 mL) was added to a flask charged with dipp-TIP (0.025 g, 0.029 mmol) and $InCl_3$ (0.013 g, 0.059 mmol) and the resulting orange mixture was stirred for 12 h. The solvent was stripped and the crude solid was dissolved in a minimal volume of a 4 : 1 dichloromethane/hexanes solution. The resulting red solution was filtered and stored at room temperature for 5 days, affording a crop of red crystals. Yield 0.032 g (84%).

MS (CI^+, CH_4): *m*/*z* 1094 (M-$InCl_3$); ^1H NMR ($CDCl_3$): δ 0.69 (d, 24H, CH_3), 1.31 (d, 24H, CH_3), 2.95 (sept, 8H, -CH), 6.54 (d, 4H, NapC-H), 7.30 (b, 8H, Ar-H), 7.45 (t, 4H, Ar-H); IR (cm^{-1}): 1727s, 1631s, 1462, 1362s, 1073s, 748s.

Preparation of $[(InBr_3)_2$(dipp-TIP)] (4)

Dichloromethane (20 mL) was added to a flask charged with dipp-TIP (0.025 g, 0.029 mmol) and $InBr_3$ (0.021 g, 0.059 mmol) and the resulting orange mixture was stirred for 12 h. Removal of the reaction solvent *in vacuo* resulted in the formation of a solid residue that was subsequently recrystallized from a saturated 4 : 1 dichloromethane/hexanes solution stored at room temperature for 5 days. Yield 0.041 g (89%).

MS (CI^+, CH_4): *m*/*z* 1226 (M-$InBr_3$); ^1H NMR ($CDCl_3$): δ 0.75 (d, 24H, CH_3), 1.30 (d, 24H, CH_3), 2.94 (sept, 8H, -CH), 6.58 (d, 4H, NapC-H), 7.35 (b, 8H, Ar-H), 7.49 (t, 4H, Ar-H); IR (cm^{-1}): 1655s, 1617s, 1460s, 1360, 1093, 1020, 797s.

Preparation of $[(InI_3)_2$(dipp-TIP)] (5)

Dichloromethane (20 mL) was added to a flask charged with dipp-TIP (0.025 g, 0.029 mmol) and InI_3 (0.030 g, 0.060 mmol) and the resulting orange mixture was stirred for 12 h. Solvent stripping resulted in the isolation of a red-orange solid. The crude solid was recrystallized from a saturated 4 : 1 dichloromethane/hexanes solution stored at room temperature for 5 days. Yield 0.048 g (87%).

MS (CI^+, CH_4): *m*/*z* 1368 (M-InI_3); ^{1}H NMR ($CDCl_3$): δ 0.66 (d, 24H, CH_3), 1.35 (d, 24H, CH_3), 2.95 (sept, 8H, -CH), 6.61 (d, 4H, NapC-H), 7.40 (b, 8H, Ar-H), 7.53 (t, 4H, Ar-H); IR (cm^{-1}): 1660s, 1611s, 1584, 1459s, 1365, 896, 739s.

Results and discussion

As detailed above, compounds **1** and **2** were prepared by treatment of the dipp-TIP ligand with two equivalents of the appropriate Pd(II) dihalide in hot acetonitrile solution. Both compounds were structurally authenticated by single crystal X-ray diffraction, the details of which are presented in Table 1. A listing of selected metrical parameters for **1** and **2** is presented in Table 2 and the overall structure of **2** is illustrated in Fig. 3. Both **1** and **2** are located on an inversion center and, within experimental error, both molecular frameworks are planar and the dipp substituents are arranged in an orthogonal fashion with respect to the rest of the molecule. Akin to the BIAN ligand, the TIP ligand is redox-active, hence a number of bonding modes are possible. In the cases of compounds **1** and **2**, however, no redox reaction has taken place and the nitrogen atoms function in a purely donor fashion. Such a conclusion is evident from the C(1)–N(1) and C(5)–N(2) bond lengths of 1.281(5) and 1.290(5) Å, respectively, for **2** which correspond to double bonds. Moreover, the C(1)–C(5) separation of 1.506(5) Å is consistent with the presence of a single bond. As expected, the Pd^{2+} cation adopts a square planar coordination environment. The sum of bond angles at this center is 360.12°.

Table 2 Selected metrical parameters (Å) for $(PdCl_2)_2$-TIP·2 CH_2Cl_2 (**1**), $(PdBr_2)_2$-TIP (**2**), $(InCl_3)_2$-TIP·2 CH_2Cl_2 (**3**), $(InBr_3)_2$-TIP·CH_2Cl_2 (**4**) and $(InI_3)_2$-TIP·CH_2Cl_2 (**5**)

Bond	1	2	3	4	5
C(1)–C(5)	1.503(7)	1.506(5)	1.542(5)	1.530(5)	1.519(9)
C(1)–N(1)	1.288(7)	1.281(5)	1.277(4)	1.275(4)	1.273(8)
C(5)–N(2)	1.289(7)	1.290(5)	1.261(4)	1.271(5)	1.267(8)
N(1)–M(1)	2.061(4)	2.050(3)	2.309(3)	2.411(3)	2.366(5)
N(2)–M(1)	2.068(4)	2.051(3)	2.438(3)	2.381(3)	2.483(5)
M(1)–X(1)	2.3889(8)	2.2692(12)	2.3468(13)	2.5047(12)	2.7060(14)
M(1)–X(2)	2.3949(9)	2.2703(13)	2.3864(15)	2.5058(8)	2.7118(11)
M(1)–X(3)			2.3579(12)	2.5041(9)	2.7301(9)

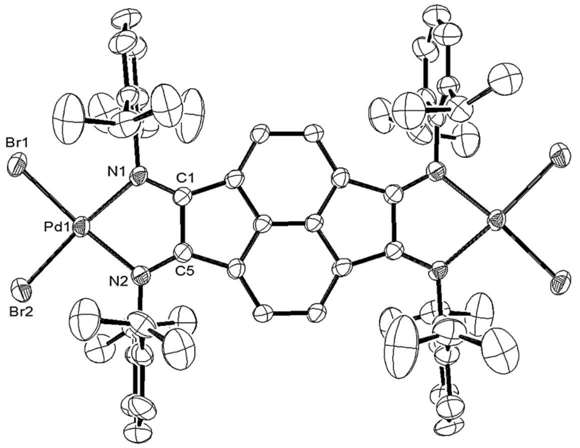

Fig. 3 ORTEP view of **2** with thermal ellipsoids shown at 40% probability. All hydrogen atoms have been omitted for clarity.

The main group chemistry of the TIP ligand is also proving to be fruitful. In earlier work, it was found that treatment of the dipp-TIP ligand with four equivalents of BCl_3 resulted in the formation of $[Cl_2B(dipp\text{-}TIP)BCl_2][BCl_4]_2$ which represented the first example of a dicationic species supported by a TIP ligand.[4] Examination of the X-ray crystal structure of this compound revealed that the diimine groups are linked to BCl_2^+ moieties at either end of the dication by donor–acceptor bonds. No comparable reactions have been explored with the heavier congeneric Group 13 trihalides with respect to the TIP ligand. However, it has been demonstrated that the reaction of the mesityl-substituted BIAN ligand with $InCl_3$ in THF solution results in the formation of [mes-BIAN-$InCl_3$(THF)] which possesses a distorted octahedral geometry at the indium center.[7]

Table 1 Selected crystal data, data collection and refinement parameters for $(PdCl_2)_2$-TIP·2 CH_2Cl_2 (**1**), $(PdBr_2)_2$-TIP (**2**), $(InCl_3)_2$-TIP·2 CH_2Cl_2 (**3**), $(InBr_3)_2$-TIP·CH_2Cl_2 (**4**) and $(InI_3)_2$-TIP·CH_2Cl_2 (**5**)

	1 (812612)	**2** (812611)	**3** (812614)	**4** (812615)	**5** (812613)
Empirical formula	$C_{64}H_{76}N_4Pd_2Cl_8$	$C_{62}H_{72}N_4Pd_2Br_4$	$C_{64}H_{76}N_4In_2Cl_{10}$	$C_{63}H_{74}N_4In_2Br_6Cl_2$	$C_{63}H_{74}N_4In_2I_6Cl_2$
M	1397.69	1405.68	1485.43	1667.26	1949.20
T/K	153(2)	153(2)	153(2)	153(2)	153(2)
Color	Red	Red	Red	Orange	Red-orange
Crystal system	Orthorhombic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	*Pbca*	*Pbca*	$P2_1/n$	$P2_1/n$	$P2_1/n$
a/Å	19.460(5)	19.605(5)	11.676(5)	10.178(5)	10.370(2)
b/Å	15.257(5)	15.173(5)	17.250(5)	21.687(5)	22.405(5)
c/Å	23.428(5)	23.927(5)	18.117(5)	15.394(5)	15.448(3)
β/°	90.0	90.0	91.994(5)	92.761(5)	95.681(5)
V/Å^3	6956(3)	7117(3)	3647(2)	3394(2)	3572(2)
Z	4	4	2	2	2
D_c/Mg m^{-3}	1.335	1.312	1.353	1.631	1.353
μ/mm^{-1}	0.863	2.785	1.037	4.329	1.037
Crystal size/mm	0.25 × 0.17 × 0.15	0.15 × 0.12 × 0.10	0.19 × 0.14 × 0.06	0.17 × 0.16 × 0.06	0.13 × 0.11 × 0.05
Reflections collected	25 734	26 799	14 713	12 781	13 664
R_{int}	0.0941	0.0623	0.0443	0.0461	0.0558
Data/restraints/parameters	7958/0/333	8177/0/333	8317/0/342	7768/0/342	8143/0/342
R_1 [$I > 2(I)$]	0.0557	0.0672	0.0478	0.0510	0.0545
wR_2 (all data)	0.1456	0.1906	0.1377	0.1049	0.1168
Largest peak, hole/e Å^{-3}	0.697, −1.849	2.508, −1.527	0.796, −0.833	1.281, −1.130	1.267, −1.084

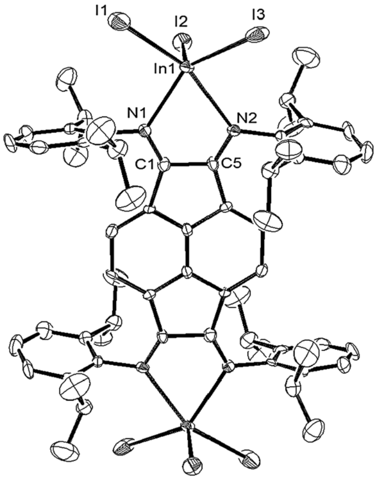

Fig. 4 ORTEP view of **5** with thermal ellipsoids shown at 40% probability. All hydrogen atoms have been omitted for clarity and one molecule of disordered dichloromethane was removed using SQUEEZE.

Interestingly, treatment of the dipp-BIAN ligand with $InMe_3$ in non-coordinating solvents results in the isolation of (Me–dipp-BIAN–$InMe_2$) which possesses a chiral center at one of the carbon atoms of the diazabutadiene moiety due to the attachment of a methyl group.[8] We were therefore curious about the outcome(s) of the reactions of the dipp-TIP ligand with the heavier congeneric indium trihalides, InX_3 (X = Cl (**3**), Br (**4**), and I (**5**)). However, it was found that **3–5** exhibited C(1)–C(5) and average C–N bond distances in the ranges of 1.510–1.550 Å and 1.260–1.285 Å, respectively (Fig. 4). Thus, it is evident that all three trihalides react with the dipp-TIP ligand in the same fashion, that is by donor–acceptor bonding between the dipp-TIP nitrogen atoms and the indium atom. As observed in the cases of **1** and **2**, all three complexes possess an inversion center. Lastly, contrary to the analogous BIAN compounds, the geometry around each indium center is best described as distorted trigonal bipyramidal.

Conclusions

In conclusion, we have prepared a series of bimetallic TIP-supported palladium dihalide and indium trihalide complexes as precursors for applications such as new catalysts and novel polymeric materials. All five new complexes exhibit nitrogen → metal donor–acceptor bonding as evidenced by single crystal X-ray diffraction studies.

Acknowledgements

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