Dimetallated Thioether Complexes as Building Blocks for Organometallic Coordination Polymers and Aggregates

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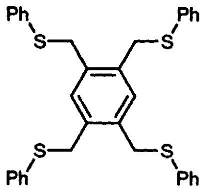
The thioether ligand, 1,2,4,5-tetrakis(phenylthiomethyl)benzene, **L**, can be doubly palladated at the central fragment to form a complex, which, upon reaction with aromatic *N*-donors (pyrazine, 4,4′-bipyridyl), forms linear organometallic coordination polymers.

The assembly of multimolecular metallic arrays in an organized fashion offers an extensive body of applications ranging from organometallic polymers[1,2] or coordination polymers,[3,4] to metallomesogens,[5,6] to 'molecular metals'.[7–9] The thioether ligand, 1,2,4,5-tetrakis(phenylthiomethyl)benzene, **L**, can be metallated at both unsubstituted ring positions of the central durene fragment to form a convenient rigid precursor to linear organometallic oligomers and polymers. We report herein the synthesis and double palladation of **L**, subsequent reactions with pyrazine or 4,4′-bipyridine to form organometallic



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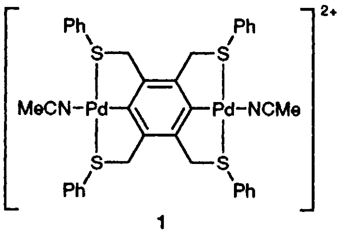

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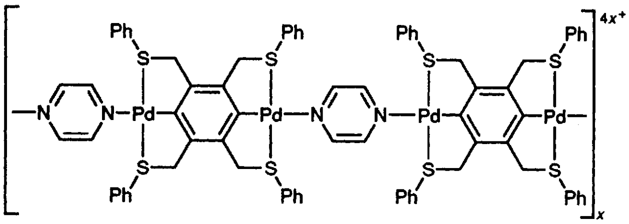

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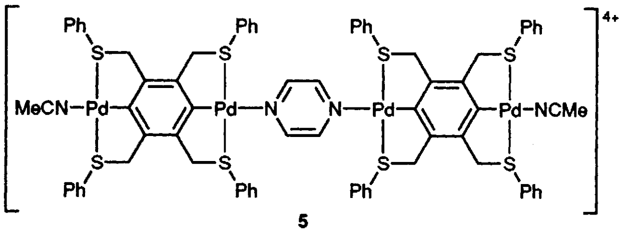

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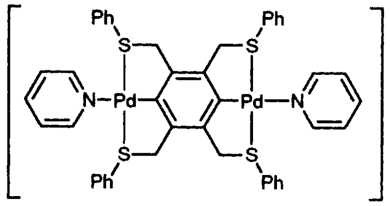

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coordination polymers and aggregates and the structure of $[Pd_2L(pyridine)_2][BF_4]_2$, a model for the repeating unit of the 4,4′-bipyridine polymer.†

L was obtained in nearly quantitative yield as a white crystalline solid from the reaction of 4 equiv. of NaSPh with 1 equiv. of tetrabromodurene in refluxing anhydrous ethanol. The doubly palladated complex **1** is an air-stable, yellow solid and was easily prepared in high yield (95%) by the reaction of 2 equiv. of $[Pd(MeCN)_4][BF_4]_2$ with 1 equiv. of **L** in refluxing MeCN. The presence of two labile acetonitrile ligands in **1** make it an ideal building block for synthesizing higher order structures. Reaction of **1** with 1 equiv. of 4,4′-bipyridine in MeCN resulted in the immediate precipitation of a white solid, $\{[Pd_2L(\mu\text{-}4,4'\text{-bipyridine})][BF_4]_2\}_x$, **2**. The ^1H NMR spectrum indicated a connectivity of two at the nitrogen ligand and the low solubility of the product was consistent with a polymeric material. An analogous reaction employing 1 equiv. of pyrazine afforded similar results to yield $\{[Pd_2L(\mu\text{-pyrazine})][BF_4]_2\}_x$, **3**.

If the stoichiometry of the reaction is altered so that 0.5 equiv. of 4,4′-bipyridine or pyrazine are added to a solution of 1 equiv. of **1**, the discrete aggregates $[(\mu\text{-}4,4'\text{-bipyridine})\{Pd_2L(MeCN)\}_2][BF_4]_4$, **4** and $[(\mu\text{-pyrazine})\{Pd_2L(MeCN)\}_2][BF_4]_4$, **5** are obtained.

For complexes **4** and **5**, the ^1H NMR spectra also showed the *N*-ligands to function in a symmetrical bidentate fashion, however, in both cases, there were two separate sets of resonances observed for the benzylic protons of the metallated fragments. The benzylic protons associated with the Pd–(MeCN) ends of the molecules were observed to resonate at *ca.* 0.1 ppm higher field than the benzylic protons associated with the Pd–(N-donor) core.‡

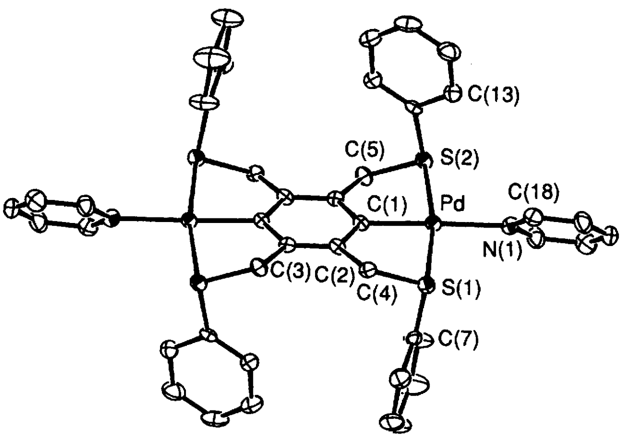

Fig. 1 Perspective ORTEP view of the $[Pd_2L(pyridine)_2]^{2+}$ cation. Selected bonding parameters: Pd–S(1) 2.318(3), Pd–S(2) 2.306(3), Pd–C(1) 2.02(1), Pd–N(1) 2.17(1) Å; S(1)–Pd–S(2) 169.1(1), S(1)–Pd–C(1) 85.0(3), S(2)–Pd–C(1) 84.1(3), S(1)–Pd–N(1) 96.8(3), S(2)–Pd–N(1) 94.1(3), C(1)–Pd–N(1) 178.0(4)°; Pd···Pd′ 6.576(2) Å.

If complex **1** is stirred with 2 equiv. of pyridine, the acetonitrile ligands are readily displaced to yield $[Pd_2L(pyridine)_2][BF_4]_2$, **6**. This complex can be considered to be a model for the repeating unit of the 4,4′-bipyridine polymer and crystals suitable for X-ray analysis were grown by the slow diffusion of diethyl ether into an acetonitrile solution of the complex.

The X-ray structure§ of **6** (Fig. 1) confirms that **L** is indeed doubly palladated with each Pd^{II} centre in a square-planar CS_2N environment; Pd–S(1) 2.318(3), Pd–S(2) 2.306(3), Pd–C(1) 2.02(1), Pd–N(1) 2.17(1) Å. The metallated ring system is completely planar, including the supporting S-donors and the Pd···Pd distance across the central metallated ring is 6.576(2) Å. The S-phenyl rings of each Pd-coordination sphere are positioned in a *syn*-orientation and overall the molecule has a centre of symmetry. The S-phenyl rings are

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† In all complexes with L bonded to Pd, the designation L is meant to represent L − 2H in which L is doubly palladated and contains two Pd–C bonds.

‡ *NMR data* (δ, 300 K). **L**: ($CDCl_3$), ^1H NMR (300 K) δ 7.1–7.3 (m, 20H, S–Ph), 6.99 (s, 2H, Ar), 4.08 (s, 8H, benzylic); $^{13}C\{^1H\}$: 136.00, 134.90, 132.77, 130.54, 128.91, 126.72 (Ar), 36.34 (benzylic). **1**: (CD_3CN), ^1H: 7.80 (m, 8H, S–Ph), 7.51 (m, 12H, S–Ph), 4.60 (br s, 8H, benzylic), 1.94 (s, 6H, MeCN); $^{13}C\{^1H\}$: 155.36 (Pd–C), 145.86 (Ar), 132.24, 131.56, 131.17, 130.77 (S–Ph), 49.76 (benzylic). **2**: (CD_3CN), 1H: 8.81 (br s, 4H, bipy), 8.07 (br s, 4H, bipy), 7.78 (m, 8H, S–Ph), 7.49 (m, 12H, S–Ph), 4.61 (br s, 8H, benzylic). **3**: (CD_3CN), ^1H: 8.56 (s, 4H, pyrazine), 7.78 (m, 8H, S–Ph), 7.52 (m, 12H, S–Ph), 4.82 (br s, 8H, benzylic). **4**: (CD_3CN), ^1H: 8.86 (br s, 4H, bipy), 8.19 (br s, 4H, bipy), 7.80 (m, 16H, S–Ph), 7.51 (m, 24H, S–Ph), 4.80 [br s, 8H, benzylic(bipy)], 4.64 [br s, 8H, benzylic-(MeCN)]. **5**: (CD_3CN), ^1H: 8.55 (s, 4H, pyrazine), 7.80 (m, 16H, S–Ph), 7.53 (m, 24H, S–Ph), 4.82 [br s, 8H, benzylic(pyr)], 4.60 [br s, 8H, benzylic(MeCN)]. **6**: (CD_3CN), ^1H: 8.15 (br s, 10H, py), 7.63 (m, 8H, S–Ph), 7.39 (m, 12H, S–Ph), 4.70 (br s, 8H, benzylic); $^{13}C\{^1H\}$: 155.74 (Pd–C), 151.14 (py), 145.79 (Ar), 139.76 (py), 132.48, 131.71, 131.23, 130.85 (S–Ph), 126.64 (py), 50.80 (benzylic). Satisfactory elemental analyses were obtained for compounds **1**–**6**.

§ *Crystal data* for **6**, $[C_{44}H_{38}N_2Pd_2S_4][BF_4]_2$: monoclinic *C2/c*, a = 22.694(5), b = 10.974(3) c = 19.136(2) Å, β = 102.57(1)°, U = 4575(2) Å^3, Z = 4, D_c = 1.61 g cm^{-3}, μ(Mo-Kα) = 10.158 cm^{-1}. Rigaku AFC6S diffractometer, 1909 unique reflections with $F_o^2 > 3\sigma F_o^2$, R = 6.32, R_w = 6.00%. Atomic coordinates, bond distances and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

positioned well away from the pyridine ligand and there are no stabilizing or destabilizing interactions between the pyridine and the phenyl groups of **L**. The orientation of the four S-phenyl rings in the solid state is presumably a phenomenon of crystal packing as the four rings are observed to be fluxional in solution with a coalescence temperature of 280 K.

Although other metallated thioether complexes have been observed[10–12] and other doubly metallated complexes reported[13–18] to the authors' knowledge **6** represents the first structurally characterized example of a 1,4-dimetallated aromatic ring. The relative ease of synthesis of compound **1** coupled with the vast diversity of available aromatic *N*-donor ligands makes **1** an extremely versatile building block for larger and more elaborate supramolecular systems. Work in this area continues and attempts to use **1** in the synthesis of wholly organometallic polymers is currently being investigated.

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