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Advances in the Synthesis of Multimetallic Systems: Hydroxyl Group Protection in (Aryldiamine)platinum Species

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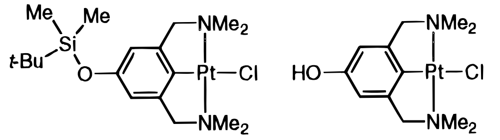
Summary: A multimetallic system containing three platinum atoms has been synthesized through use of an (aryldiamine)platinum complex with a protected hydroxyl group which, after deprotection, is coupled with the trisubstituted aryl molecule 1,3,5-tris(chlorocarbonyl)benzene that provides the core moiety. The resulting trimetallic system is formed in high yield and has been characterized by elemental microanalysis, spectroscopic techniques, and mass spectrometry.

Introduction

Currently there is great interest in the synthesis and properties of molecules which contain more than one covalently bonded (transition) metal atom, so-called "multimetallic systems". Areas of study include electronic communication between the metal centers *via* chemical bonds,[1] photochemical properties,[2] the development of metal-containing dendrimers[3] and other nanoscale systems,[4] and homogeneous catalysis with catalytically active transition metal-containing dendrimers.[5] We are interested in developing methods for the synthesis of multimetallic systems based on the stepwise construction of a target molecule as a pure and well-defined material. Employing this type of approach, we have recently synthesized a novel multimetallic system which contains three platinum atoms per molecule[6] based on the monoanionic *N,C,N′* tridentate $C_6H_3(CH_2NMe_2)_2$-2,6 ligand.[7] Here we describe the synthesis of another new triorganoplatinum system in which three square-planar chloroplatinum moieties are attached by ester linkages to a central benzene ring in a 1,3,5 fashion to form a C_3-symmetric molecule **1**, illustrated in Scheme 2. Complexes such as **1** might show interesting properties as a direct consequence of their multimetallic composition, and we have therefore established a methodology whereby organoplatinum units can be easily employed in the construction of such systems.



9 **10**

Figure 1. Functionalized arylplatinum complexes **9** and **10**.

Our approach is based on the synthesis of an arylplatinum complex which possesses a potentially reactive functional group in the organoaryl part of the chelating ligand. This would then allow attachment of many such organoplatinum units to, for example, an organic core molecule possessing appropriate functional groups and so afford the desired multimetallic systems. We chose the hydroxyl unit as a reactive functional group for the organoaryl ligand of the organoplatinum complex. The hydroxyl group can then be reacted with an acid chloride group of an organic core molecule to form a product in which there are ester groups as the coupling units. This approach has already been demonstrated by Millar *et al.* in the successful construction of well-defined organic dendrimers based on symmetrically substituted benzenetricarboxylic acid esters.[8] The organoplatinum complex employed in the present case is **10** (Figure 1) and this possesses a hydroxyl group *para* to the metalated carbon atom of the aryl ring (C_{ipso}). It was necessary to synthesize this organoplatinum complex with the hydroxyl group protected as a *tert*-butyldimethylsilyl (TBDMS) ether, *i.e.* complex **9** (Figure 1), and then to deprotect it with tetrabutylammonium fluoride before the reaction with an acid chloride.

Results and Discussion

The synthesis of the required TBDMS-protected aryldiamine ligand precursor **7** is shown in Scheme 1 and starts from commercially available 5-hydroxyisophthalic acid (**2**). The synthetic route to the dichloro compound **6** follows procedures reported by other workers,[4] and isolated yields for each step were 99% to form the diester **3**, 69% to form the TBDMS-protected diester **4**, 82% to form the diol **5**, and 89% to form the dichloro compound **6**. The final step in the synthesis of **7** is diamination of **6** by reaction with dimethylamine hydrochloride in dimethylformamide in the presence of triethylamine as a base (91% yield). The ligand precursor **7** was isolated in a 45% overall yield (based on 5-hydroxyisophthalic acid) as a pale yellow oil which slowly crystallized at −30 °C.

Reaction of **7** with *n*-butyllithium in hexane affords the monolithiated species **8** (Scheme 1) in which lithia-

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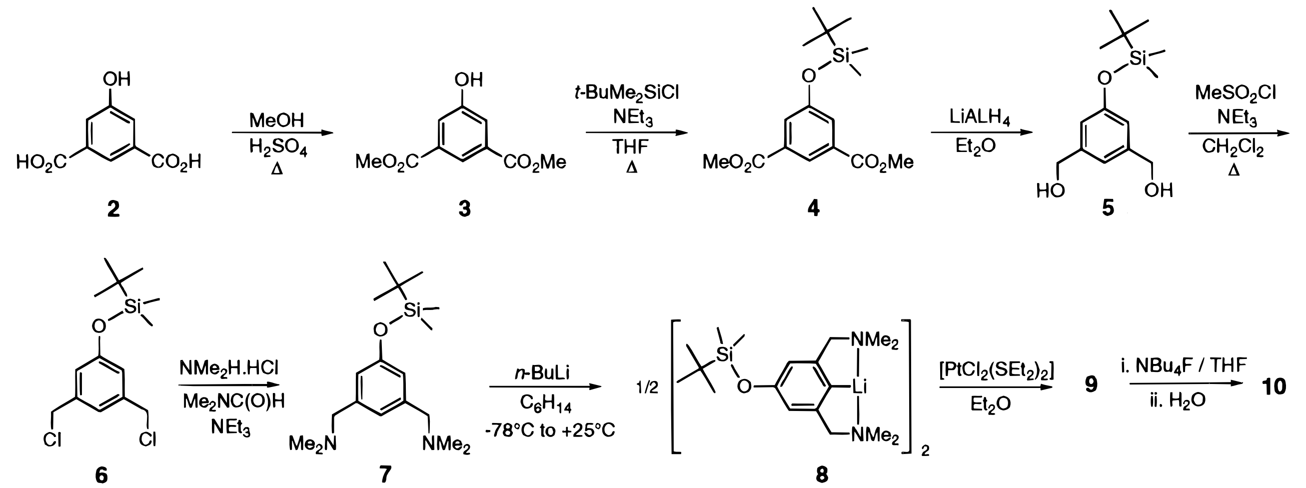
Scheme 1. Synthetic Route to 9 and 10



tion occurs exclusively between the CH_2NMe_2 substituents; this was established by quenching a sample of **8** with D_2O and deducing the position of deuterium incorporation by ^1H NMR spectroscopy.

Organolithium complex **8** probably exists as a dimer in the solid state and in solution by analogy with known structures of related species.[9] Reaction of **8** with $[PtCl_2(SEt_2)_2]$ in diethyl ether affords, *via* transmetalation, the protected (aryldiamine)platinum complex **9** in 32% yield. The TBDMS protecting group has been cleanly removed with tetrabutylammonium fluoride in THF to afford, after the addition of water, the corresponding (*p*-hydroxylaryldiamine)platinum complex **10** which can then be isolated.[10]

However, as shown in Scheme 2, the desired multimetallic system **1** has been synthesized directly from **9** by *in situ* removal of the TBDMS protecting group as described above, followed by the addition of $^1/_3$ equiv of the trifunctional electrophile 1,3,5-tris(chlorocarbonyl)benzene (which served as the starting core molecule in the systems described by Millar *et al.*).[8] From the reaction mixture precipitation of a pale yellow solid occurs over 4 days, and this material was isolated and fully characterized as being the desired symmetrically organoplatinum-substituted benzenetricarboxylic acid ester complex **1**.

Complex **1** was isolated in 90% yield based on complex **9** with this crude product showing no indication by ^1H NMR spectroscopy of the presence of possible mono- or disubstituted complexes. Purification to remove traces of tetrabutylammonium salts afforded analytically pure **1** in 75% yield. This high yield synthesis of **1** indicates that the esterification reaction is very efficient. The presence of water (less than 5%) in the THF solution of tetrabutylammonium fluoride employed was found not to interfere with this type of coupling reaction, and accordingly, no evidence of hydrolysis of the acid chloride groups was found. The fact that complex **1** has a pale yellow color both in the solid state and in solution results from tailing of the very strong UV–vis absorptions at 241 and 276 nm that may possibly indicate some weak electron interactions throughout the molecule.

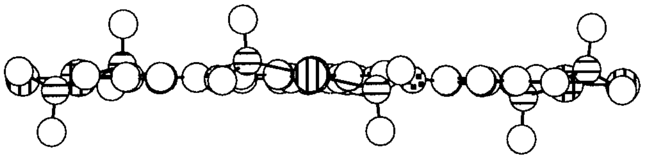
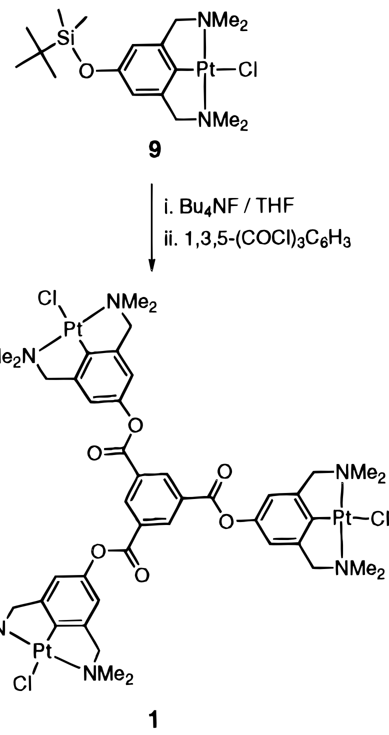


Figure 2. Representation of complex **1** based on molecular modeling (MM2) viewed along a Cl–(Pt)–C_{aryl} vector.

Scheme 2. Synthetic Route from 9 to 1



Molecular modeling calculations of **1** (at the MM2 level) show that in its lowest energy conformation the four aryl rings all lie approximately in the same plane, as shown in Figure 2, and this would be favorable for electron delocalization. The high-resolution FAB mass spectrum of **1** shows molecular envelopes corresponding to the parent molecular ion and for the parent ion with loss of one chloride atom. The isotopic patterns of these ions were in both cases consistent with the isotopic distribution resulting from the presence of three platinum atoms per molecule of **1**.

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[10] The (*p*-hydroxyaryldiamine)platinum complex **10** has been isolated and fully characterized and the X-ray crystal structure solved: *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1959.

In summary we have demonstrated the utility of the organoplatinum complex **9** for the construction of a covalently bonded multimetallic system of a well-defined nature. This methodology therefore provides a possible route for the attachment of organometallic moieties to organic polymers and dendrimers to afford novel metal-containing materials with interesting properties. Further studies of the use of **9** in the synthesis of larger multimetallic systems are currently under investigation.

Experimental Section

General Comments. Syntheses were carried out using standard Schlenk techniques under an atmosphere of purified nitrogen. All solvents were dried and distilled under nitrogen prior to use. Dichlorobis(diethyl sulfide)platinum[11] was prepared quantitatively by addition of excess diethyl sulfide to a suspension of platinum dichloride in benzene followed by filtration and evaporation of all volatiles *in vacuo*. GC-MS was carried out on a Unicam Automass instrument using electron impact (EI, 70 eV). UV spectra were measured using a Carey 1 UV−vis spectrophotometer. Melting points were determined by differential scanning calorimetry (DSC). High-resolution fast atom bombardment mass spectra were recorded in the positive ion mode on a JEOL SX102/102A tandem mass spectrometer. The bombarding atoms were xenon with an energy of 6 keV, and the matrix employed was *m*-nitrobenzyl alcohol.

Synthesis of $C_6H_3(CH_2NMe_2)_2$-1,3-(OSiMe$_2$-*t*-Bu)-5 (7). 1,3-Bis(chloromethyl)-5-((*tert*-butyldimethylsilyl)oxy)benzene (**6**) (5.16 g, 17.0 mmol) was dissolved in *N*,*N*-dimethylformamide (130 mL). Dimethylamine hydrochloride (25.2 g, 0.311 mol) and triethylamine (73.3 g, 100.8 mL, 0.726 mol) were added, and the mixture was stirred at room temperature for 18 h. The mixture was poured on to 600 mL of 1 N sodium hydroxide and extracted with hexane (3 × 100 mL). The combined organic extracts were dried over anhydrous magnesium sulfate, and the solvent was removed *in vacuo* to yield the title product as a pale yellow liquid (5.0 g, 91% based on **6**). Anal. Calcd for $C_{18}H_{34}N_2OSi$: C, 67.02; H, 10.62; N, 8.68%. Found: C, 66.88; H, 10.60; N, 8.94. ^{1}H NMR (200 MHz, CDCl$_3$, TMS): δ 0.18 (s, 6H, Me), 0.97 (s, 9H, *t*-Bu), 2.21 (s, 12H, NMe$_2$), 3.34 (s, 4H, C*H*$_2$NMe$_2$), 6.69 (s, 2H, aromatic), 6.84 (s, 1H, aromatic). ^{13}C NMR (50 MHz, CDCl$_3$, TMS): δ 155.5, 140.1, 123.0, 119.6 (aromatics), 64.2 (*C*H$_2$NMe$_2$), 45.3 (NMe$_2$), 25.7 (*t*-Bu), 18.2 (*t*-Bu), −4.4 (Me). GCMS [*m*/*z* (rel intensity)]: 322 (3, M), 279 (63, M − NMe$_2$), 234 (85, M − 2NMe$_2$), 220 (5), 177 (50), 163 (15), 73 (32), 58 (100).

Synthesis of [Pt{$C_6H_2(CH_2NMe_2)_2$-2,6-(OSiMe$_2$-*t*-Bu)-4}-Cl] (9). 1,3-Bis(dimethylamino)methyl)-5-((*tert*-butyldimethylsilyl)oxy)benzene (**7**) (1.0 g, 3.11 mmol) was dissolved in hexane (40 mL) and the solution cooled to −78 °C. After addition of a solution of *n*-butyllithium in hexane (1.6 M, 1.90 mL, 3.11 mol) the solution was allowed to warm to room temperature and was then stirred at room temperature for 18 h. The hexane was removed *in vacuo* to leave a pale yellow solid which was redissolved in diethyl ether (20 mL). This solution was added in one portion to a suspension of dichlorobis(diethyl sulfide)platinum (1.34 g, 3.00 mmol) in diethyl ether (10 mL) at room temperature. The mixture was stirred at room temperature for 18 h, and the precipitated solids were isolated by centrifugation and decantation of the solvent. The solid material was washed once with diethyl ether (50 mL). Dichloromethane (100 mL) was added, and the undissolved lithium chloride was removed by centrifugation and decantation of the mother liquor. The dichloromethane solution was concentrated to *ca.* 5 mL, and addition of diethyl ether (30 mL) caused precipitation of the title complex as a white powder which was collected and dried *in vacuo*. Recrystallization from dichloromethane/diethyl ether yielded colorless crystals (0.55 g, 32% based on **7**). Mp: 312−313 °C (dec). Anal. Calcd for $C_{18}H_{33}ClN_2OPtSi$: C, 39.16; H, 6.02; N, 5.07; Cl, 6.42. Found: C, 38.98; H, 6.06; N, 5.01; Cl, 6.37. ^{1}H NMR (200 MHz, CDCl$_3$, TMS): δ 0.16 (s, 6H, Me), 0.96 (s, 9H, *t*-Bu), 3.07 (s, $^3J_{PtH} = 38.0$ Hz, 12H, NMe$_2$), 3.96 (s, $^3J_{PtH} = 46.5$ Hz, 4H, C*H*$_2$-NMe2), 6.35 (s, 2H, aromatic). ^{13}C NMR (50 MHz, CDCl$_3$, TMS): δ 152.6 (C$_{para}$), 143.8 ($^2J_{PtC} = 82.0$ Hz, C$_{ortho}$), 136.2 ($^1J_{PtC}$ not observed, C$_{ipso}$), 111.4 ($^3J_{PtC} = 37.7$ Hz, C$_{meta}$), 77.7 ($^2J_{PtC} = 53.2$ Hz, CH$_2$), 54.5 ($^2J_{PtC} = 15.5$ Hz, NMe$_2$), 25.7 (*t*-Bu), 18.1 (*t*-Bu), −4.4 (Me).

Synthesis of 1,3,5-{Pt[$C_6H_2(CH_2NMe_2)_2$-2,6-O(CO)-4]-Cl}$_3$C$_6$H$_3$ (1). [Pt{$C_6H_2(CH_2NMe_2)_2$-2,6-(OSiMe$_2$-*t*-Bu)-4}Cl] (**9**) (0.179 g, 0.33 mmol) was dissolved in THF (20 mL). A solution of tetrabutylammonium fluoride (1 M, 0.33 mL, 0.33 mmol) in THF was added, and the solution stirred at room temperature for 2 h. 1,3,5-Tris(chlorocarbonyl)benzene (0.029 g, 0.11 mmol) was added and the solution stirred at room temperature for 4 days during which time a yellow precipitate formed. The precipitate was isolated by centrifugation and decantation of the mother liquor, washed twice with diethyl ether, and dried *in vacuo*. The yellow solid was redissolved in dichloromethane (10 mL) and precipitated by the addition of diethyl ether (30 mL). The solid was then stirred in THF (30 mL) and dichloromethane (15 mL) for 1 h. The solid dissolved partially, and then a precipitate slowly formed. After 1 h the solid product was isolated by centrifugation and decantation of the mother liquor. The solid was dried *in vacuo* to yield the title complex as a yellow solid (0.12 g, 75% based on **6**). Mp: 318−319 °C (dec). Anal. Calcd for $C_{45}H_{57}Cl_3N_6O_6Pt_3$: C, 36.78; H, 3.91; N, 5.72. Found: C, 36.99; H, 4.29; N, 5.53. UV (chloroform): λ_{max}/nm (ϵ) = 241.2 (31 390), 276.0 (26 450). ^{1}H NMR (200 MHz, CDCl$_3$, TMS): δ 3.10 (s, $^3J_{PtH} = 31.7$ Hz, 36H, NMe$_2$), 4.05 (s, $^3J_{PtH} = 41.4$ Hz, 12H, CH$_2$), 6.72 (s, 6H, aryldiamine aromatics), 9.15 (s, 3H, core aromatics). ^{13}C NMR (50 MHz, CDCl$_3$, TMS): δ 163.7 (carbonyl), 147.3 (C$_{para}$), 144.1 (C$_{ortho}$), 143.1 (core aromatic), 135.8 (core aromatic), 131.3 (C$_{ipso}$), 112.8 (C$_{meta}$), 77.6 (CH$_2$), 54.5 (NMe$_2$). Slightly broadened platinum satellites are visible on several signals but their intensity was insufficient to resolve and accurately determine $^nJ_{PtC}$. High-resolution FABMS [*m*/*z* (rel intensity)]: calcd for $C_{45}H_{57}Cl_3N_6O_6Pt_3$, 1466 (51), 1467 (77), 1468 (97), 1469 (100), 1470 (92), 1471 (73), 1472 (54), 1473 (34), 1474 (21), 1475 (11), 1476 (6), 1477 (2); found, 1466 (57), 1467 (80), 1468 (98), 1469 (100), 1470 (93), 1471 (73), 1472 (55), 1473 (38), 1474 (25), 1475 (16), 1476 (11), 1477 (7); 1433 ([M − Cl]$^+$).

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