

Synthesis and Characterization of the Bis-Cyclometalating Ligand 3,3',5,5'-Tetrakis[(dimethylamino)methyl]biphenyl and Its Use in the Preparation of Bimetallic M(II), M(IV) (M = Pt, Pd), and Mixed-Valence Pt(II)–Pt(IV) Complexes via a Dilithio-Derivative. Crystal Structure of the Pd Dimer [ClPd{2,6-(Me₂NCH₂)₂C₆H₂}]₂

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The potentially bis-cyclometalating ligand 3,3',5,5'-tetrakis[(dimethylamino)methyl]biphenyl, was prepared from 3,5-(Me₂NCH₂)₂C₆H₃Br in a one-pot synthesis involving lithium–halogen exchange, transmetalation, and reductive-elimination reactions. This ligand undergoes selective dilithiation in the 4 and 4' positions of the biphenyl group to form [Li₂{2,6-(Me₂NCH₂)₂C₆H₂}]₂*n*, which is a versatile precursor to bimetallic complexes via a double transmetalation reaction. The syntheses and characterization of the new homobimetallic Pt(II) and Pd(II) compounds, [(MeCN)Pt{2,6-(Me₂NCH₂)₂C₆H₂}]₂(CF₃SO₃)₂ and [ClPd{2,6-(Me₂NCH₂)₂C₆H₂}]₂, is reported in addition to a novel synthetic route to the complex [ClPt{2,6-(Me₂NCH₂)₂C₆H₂}]₂. The solid-state structure of Pd dimer was determined by single-crystal X-ray diffraction. Oxidative addition of Cl₂ to the latter Pt compound produced the bis-platinum(IV) complex [Cl₃Pt{2,6-(Me₂NCH₂)₂C₆H₂}]₂, which reacts with 2 equiv of Ag(O₃SCF₃) in MeCN solution to form [(MeCN)Cl₂Pt{2,6-(Me₂NCH₂)₂C₆H₂}]₂(CF₃SO₃)₂. This complex could also be obtained directly by reaction of the former Pt^{II} dimer with 2 equiv of Cl₂IPh. ¹H NMR spectroscopic studies show that mixtures of the Pt^{II} and Pt^{IV} dimers in acetonitrile solution are in equilibrium with a mixed-valence (Pt^{II},Pt^{IV}) species [(MeCN)Pt^{II}{2,6-(Me₂NCH₂)₂C₆H₂–C₆H₂(CH₂NMe₂)–2,6}Pt^{IV}Cl₂(NCMe)](CF₃SO₃)₂, which, however, could not be isolated in pure form. The reaction of the Pt^{II} dimer with ≤1 equiv of Cl₂IPh also gave a Pt^{IV} dimer, along with unreacted starting material and the mixed-valence complex. A reversible double C–C bond formation has been achieved by reaction of the Pt^{II} dimer with excess of methyl iodide. This procedure yields the bis(arenonium) species [IPt^{II}{2,6-(Me₂NCH₂)₂–1-MeC₆H₂}]₂(CF₃SO₃)₂ in which both the Me groups derived from I–Me bond cleavage are bound to the C_{ipso} of the aryl rings. The mono(arenonium) compound [IPt^{II}{2,6-(Me₂NCH₂)₂–1-MeC₆H₂–C₆H₂(CH₂NMe₂)–2',6'}Pt^{II}](CF₃SO₃)₂ has been identified as an intermediate in this reaction by ¹H NMR spectroscopy.

Introduction

A variety of bimetallic transition-metal complexes connected by π-delocalized bridging ligands have been prepared during recent years, and the electronic and photophysical properties of these compounds have been reported.^{1–15} Such species are of interest for their

potential use as precursors to conducting organometallic oligomers and polymers ("molecular wires") and to materials exhibiting nonlinear optical and liquid-

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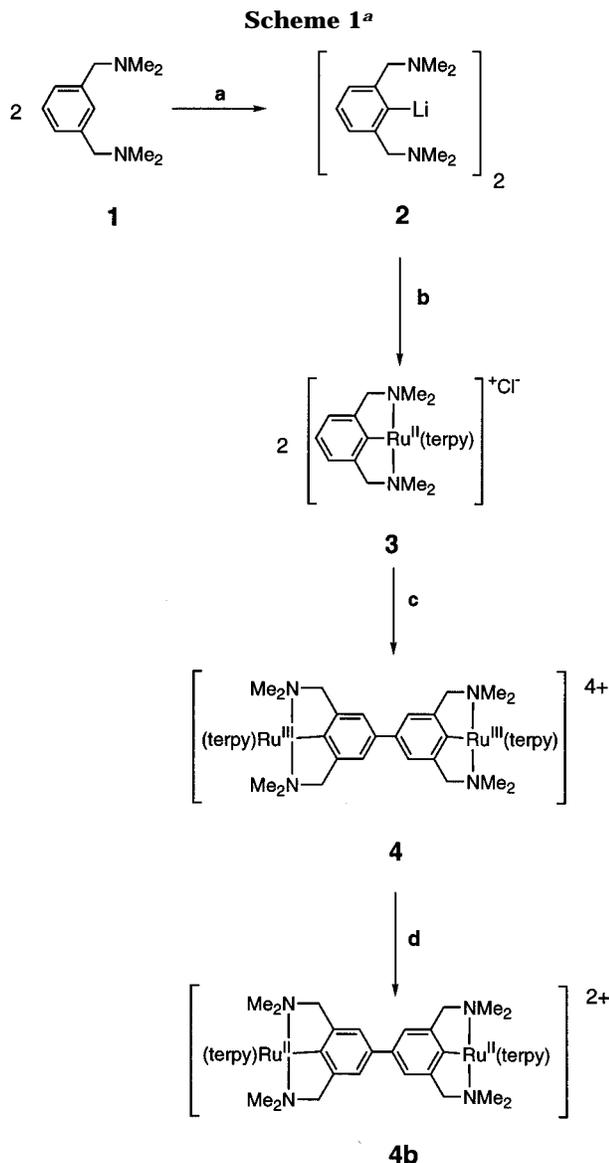
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^a (a) +*n*-BuLi/pentane; (b) (i) + [RuCl₂(PPh₃)₄]THF, -LiCl, -3PPh₃ (ii) + terpy/MeOH, -PPh₃; (c) Cu^{II}Cl₂/MeOH; (d) H₂NNH₂·H₂O.

crystalline behavior. A major objective in this field is the preparation of an appropriate organic framework which is capable of stabilizing well-defined organometallic fragments while concurrently promoting electronic coupling between metal atoms.

During the last decade, the chemistry of the monoanionic aryldiamine ligand 2,6-bis[(dimethylamino)methyl]benzenide (**2**, Scheme 1) has been studied extensively, and this work includes the structural and chemical properties of a number of transition-metal and main-

group complexes. The versatility of this ligand has been demonstrated in a variety of organometallic derivatives containing different ligand bonding modes and structural geometries.^{16,17} In addition, this ligand has the capacity to form chemically robust complexes in unusual oxidation states (e.g., stable Ni(III) organometallic complexes)^{18,19} with synthetically useful catalytic properties.^{20–23} We have begun to expand our investigations to include the use of aryldiamine ligands as organic bridges in bimetallic systems. Thus, the organometallic chemistry of bridging dianionic aryldiamine ligands such as **12** and others (Scheme 2) has been developed.^{24,25} In this regard, the tetracationic diruthenium(III) compound (**4**, Scheme 1) was the first example of a bimetallic complex containing the dianionic ligand **12**.¹ In the solid state, **4** contains a planar 4,4'-biphenyldiyl bridge. The synthesis of this compound involves an oxidative C–C bond-forming reaction between two mononuclear ruthenium complexes.²⁶ The related derivatives containing Ru^{II}/Ru^{II} or mixed-valence Ru^{II}/Ru^{III} metal centers show greatly different electronic intramolecular coupling properties between the metal atoms in addition to distinct ligand structure.^{1,27} Prototypical complexes of the group 10 metals incorporating the aryldiamine fragments **1** or **12** (Schemes 1 and 2) have likewise been previously described.^{16,17}

The oxidative coupling at a Pt metal center is an alternative route to bimetallic complexes incorporating **12**, as outlined in Scheme 2.²⁸ In this procedure, the availability of diamine 3,5-bis[(dimethylamino)methyl]-

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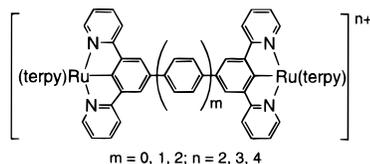
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(26) In addition to **4**, about 10% of the *para*-chlorinated product [(terpy)Ru{2,6-(Me₂NCH₂)₂-4-Cl-C₆H₄}]⁺ is also formed.

(27) Subsequent reduction of **4** with hydrazine yields the dicationic species **4b** (Scheme 1). The calculated value of the comproportionation constant (*K_c*) of the equilibrium Ru^{II},Ru^{II} + Ru^{III},Ru^{III} → Ru^{II},Ru^{III} is very large, indicating strongly coupled metal centers. Intense communication between both metal centers was also found in related bis-(bis(2-pyridyl)phenyl) complexes (below), in which the value of *K_c* decreases with the length of the aromatic spacer, see: Beley, M.; Chodorowsky-Kimmes, S.; Collin, J.-P.; Lainé, P.; Launay, J.-P.; Sauvage, J.-P. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1775.



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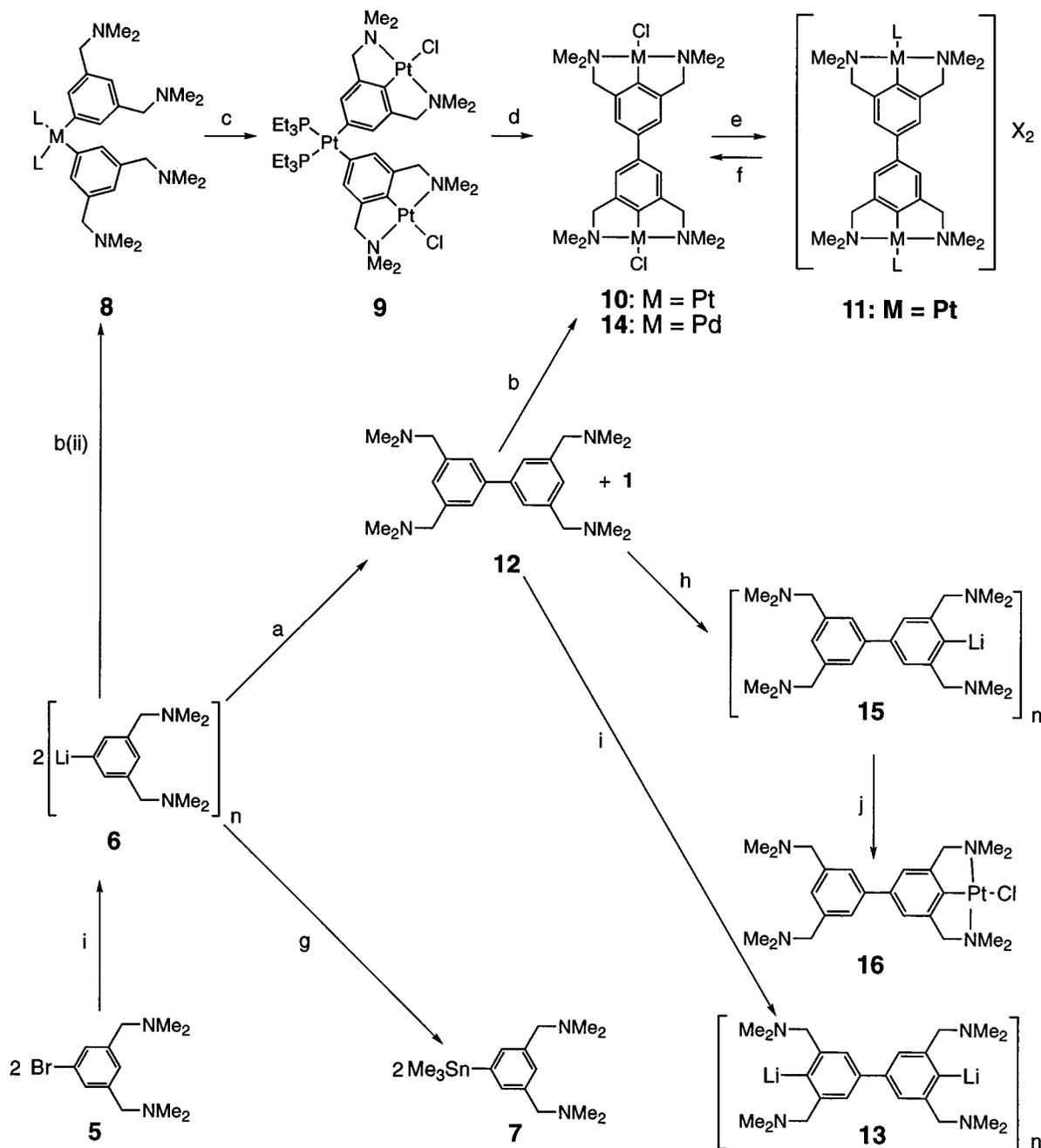
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Scheme 2^a

^a (a) $[MCl_2L_2]$ ($M = Pd, L_2 = cod; M = Ni, L = PMe_3, PBu_3, py$)/ $Et_2O, -2LiCl$. (b) (i) + $2t\text{-BuLi/THF}/-100\text{ }^\circ\text{C}$; (ii) + $cis\text{-}[PtCl_2L_2], -2LiCl, L = PET_3$; (c) (i) + $2t\text{-BuLi/pentane}$; (ii) + $2[PtCl_2(SET_2)_2], -2LiCl, -4SET_2$; (d) In chloroform, $-[PtCl_2(PET_3)_2]$; (e) + $2Ag(O_3SCF_3)/CH_3CN, -2AgCl, X = CF_3SO_3^-$; (f) $NaCl(aq)$; (g) $ClSnMe_3$; (h) $n\text{-BuLi}$; (i) $2n\text{-BuLi}$; (j) $PtCl_2(SET_2)_2, -2LiCl, -2SET_2$.

bromobenzene (5)²⁹ is crucial, as is the quantitative and selective lithiation of the arene rings in the bis(aryl)-platinum precursor 8.

The synthesis of the ligand 3,3',5,5'-tetrakis[(dimethylamino)methyl]biphenyl (12), in addition to its selective dilithiation, is reported here as a route to linear homobimetallic complexes *via* transmetalation reactions and, hence, a general method of preparing bimetallic compounds such as 4, 4b, and 10 (Schemes 1 and 2). Also, the description of the synthesis, characterization, and

structure of symmetrical diplatinum(II) and dipalladium(II) compounds is outlined. The reactivity of these complexes with Cl_2 and MeI to yield dinuclear M(IV) ($M = Pd, Pt$) compounds and bis(arenonium) species is detailed. Of special interest is the observation of a rare mixed-valence (Pt^{II}, Pt^{IV}) species by 1H NMR spectroscopy.³⁰⁻³⁴

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Table 1. Selected NMR Data^a

	¹ H NMR			¹³ C NMR					
	Ar	CH ₂	Me	C-4	C-3	C-2	C-1	CH ₂	Me
7 ^a	7.55 (45) ^b 7.48	3.35	2.13 0.24 (Me ₃ Sn) (52, 54) ^c	130.1 (11) ^d	139.4 (47) ^e	135.3 (37) ^f	141.7	64.7	45.5 -9.6 (Me ₃ Sn) (330, 346) ^g 45.5
12 ^a	7.77 7.52	3.35	2.12	128.6	140.6	126.8	141.8	64.6	45.5
	Ar	CH ₂	Me	C _{ipso}	C _{ortho}	C _{meta}	C _{para}	CH ₂	NMe ₂
10 ^h	6.95	4.06 (45) ⁱ	3.11 (36) ⁱ	143.7	143.8 (73) ^j	118.0 (37) ^k	138.2 (27) ^l	77.7 (61) ^j	54.5
11 ^m	7.06	4.19 (50) ⁱ	3.04 (38) ⁱ	142.5 (984) ⁿ	147.1 (80) ^j	119.3 (31) ^k	140.3	77.4 (62) ^j	55.0
14 ^h	6.98	4.03	2.96	155.5	145.4	118.0	138.7	74.8	53.1
16 ^{h,p}	7.37 7.16 7.07	4.09 (44) ⁱ 3.45	3.10 2.25						
17 ^o	7.19	4.43 (29) ⁱ	3.06 (29) ⁱ						
18 ^h	7.16	4.52	3.24						
19 ^m	7.27	4.47 (31) ⁱ	3.08 (29) ⁱ	141.7	142.0 (19) ^j	123.6	136.6	76.1 (21) ^j	57.1
20 ^{m,p}	7.24	4.45 (31) ⁱ	3.08						
	7.09	4.20 (48) ⁱ	3.05						
26 ^{m,p}	7.60	4.77 (d) ^q	3.02						
	7.57	3.62 (d) ^q	2.97						
		4.49 (48) ⁱ	2.94						
			2.66						
27 ^m	7.92	4.87 (d) ^q	3.14 (Me-C)						
		3.80 (d) ^q	3.08 (26) ⁱ						
			2.72 (26) ⁱ						

^a All constant couplings are given in Hertz and δ in ppm. Unless otherwise indicated, all Me groups correspond to NMe₂ and all signals are singlets; in C₆D₆. ^b ³J(^{117,119}Sn-¹H). ^c ²J(^{117,119}Sn-¹H). ^d ²J(^{117,119}Sn-¹³C). ^e ³J(^{117,119}Sn-¹³C). ^f ⁴J(^{117,119}Sn-¹³C). ^g ¹J(^{117,119}Sn-¹³C). ^h In Cl₃CD. ⁱ ³J(¹⁹⁵Pt-¹H). ^j ²J(¹⁹⁵Pt-¹³C). ^k ³J(¹⁹⁵Pt-¹³C). ^l ⁴J(¹⁹⁵Pt-¹³C). ^m In CD₃CN. ⁿ ¹J(¹⁹⁵Pt-¹³C). ^o In Cl₂CH₂. ^p Not isolated pure, ¹H NMR deduced from a mixture. ^q J(¹H-¹H) = 13 Hz.

Results and Discussion

Synthesis and Characterization of 3,3',5,5'-Tetrakis(dimethylamino)methylbiphenyl (12). Our attempts to prepare ligand **12** from 3,3',5,5'-tetramethylbiphenyl³⁵ or from the bromoarene **5** *via* nickel-³⁶ or copper-mediated³⁷ homocoupling reactions were not successful. The trimethyltin compound 1-SnMe₃-3,5-(Me₂NCH₂)₂C₆H₃ (**7**) was obtained as a colorless liquid in 58% yield from the reaction of 1.4 equiv of Me₃SnCl with a cold ethereal solution of [3,5-(Me₂NCH₂)₂C₆H₃-Li]_n (**6**) (prepared *in situ* from **5** and 2 equiv of *t*-BuLi in Et₂O at -70 °C). Subsequent Pd-catalyzed reaction³⁸ of **7** with **5** afforded the desired compound **12**, but the yields were quite low and the desired compound was also contaminated with at least five other products (see Experimental Section).

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(36) Ni(0)-mediated aryl homocoupling reactions have been successful in the preparation of related complexes.¹¹ In our case, however, complicated mixtures of products, which did not contain the desired compound **12**, were obtained.

(37) (a) Preparation of the Cu(I)-biaryl complex by reaction of **7** with 2 equiv of CuBr₂ was attempted, since subsequent reductive elimination of the copper compound was predicted to yield **12**. However, complicated mixtures of products were obtained using this procedure. (b) For the formation of **12** as a byproduct in Rh chemistry, see: van der Zeijden, A. A. H.; van Koten, G.; Luijk, R.; Vrieze, K.; Slob, C.; Krabbendam, H.; Spek, A. L. *Inorg. Chem.* **1988**, *27*, 1014.

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The indirect synthetic protocol used in the synthesis of **10** (Scheme 2)²⁸ was then employed as a strategy to obtain the free ligand **12** (*i.e.*, a stoichiometric transmetalation reaction of **6** followed by reductive elimination). Since complex **8** (M = Pt) was found to be stable toward reductive elimination, the corresponding Pd(II) and Ni(II) precursors were synthesized *via* the reaction of *in situ*-prepared **6** with 0.5 equiv of MCl₂L₂ (M = Pd, L₂ = cod [cod = cyclo-1,5-octadiene]; M = Ni, L = PMe₃, PBU₃, py) at -70 °C. After the reaction mixture was allowed to warm to room temperature, the biaryl **12** could then be isolated in yields ranging from 30% to 52%. Higher yields were obtained by using [PdCl₂(cod)] or [NiCl₂(PMe₃)₂], but unfortunately the parent diamine **1** (Scheme 1) was often formed as a byproduct, probably *via* protonolysis of **6**. Further purification of **12** was then possible by column chromatography (alumina, 67% MeCOOEt:32% hexane:1% Et₃N as the eluent). However, impure samples of **12** (containing up to 50% impurities) could be successfully used in the preparation of the subsequent diplatinum complex **10** (*vide infra*). The isolation of **10** is facilitated by its inherent low solubility in common organic solvents, and it could be easily separated from other byproducts and impurities such as PtCl[C₆H₃(CH₂NMe₂)₂-2,6] by extraction (*e.g.*, with THF). The intermediate in this reaction was not isolated, but it could be assumed that the reaction follows the same mechanism as established for the formation of the diplatinum compound **10** (*i.e.*, *via* an intermediate of similar structure to **8** where M = Pd, L₂ = cod or M = Ni, L = PMe₃, PBU₃, or py).

Tetraamine **12** and the novel trimethyltin compound **7** were characterized by ¹H and ¹³C{¹H} NMR spectroscopy (see Table 1) and by GC/MS. No impurities could be detected by these analytical techniques, but an

acceptable elemental analysis of **12** could not be obtained. The NMR data of compounds **7** and **12** can be found in Table 1.

Selective Lithiation of 12. Compound **12** was reacted with 2.2 equiv of *t*-BuLi or *n*-BuLi during a 4 h period (in Et₂O or hexane solution, respectively) to yield the dilithio species **13**. The progress of this reaction was followed by deuterolysis (*via* MeOH-*d*₄) of samples taken at various time intervals. Analysis of the resulting samples by ¹H NMR spectroscopy revealed that the singlet at 7.52 ppm assigned to the 4-ArH protons in **12** is not present in the spectrum of the product of this procedure, compound **12-d**₂. The dilithium complex **13** was not isolated but prepared *in situ* and subsequently reacted with an appropriate Pd(II) or Pt(II) precursor (see below). Compound **13** is insoluble in ether and hydrocarbon solvents. This may be a result of a polymeric or oligomeric structure of this material. Related monolithium compounds such as **2** (Scheme 1) are dimeric in both the solid state and in solution.^{29,39–41}

Previous studies have shown that the selectivity of the lithiation of **1** is solvent dependent, *i.e.*, [$\{2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}\text{Li}\}_n$ is obtained quantitatively when the reaction is carried out with *n*-BuLi in pentane or hexane, whereas a 5:1 mixture of [$\{2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}\text{Li}\}_n$ and [$\{2,5-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}\text{Li}\}_n$ results when Et₂O is used as a solvent.⁴² The selectivity in the lithiation of **12**, however, was not affected by the use of Et₂O instead of hexane. Similarly, the use of 20% excess of *t*-BuLi resulted in the same quantitative formation of **13**.

In an attempt to prepare the monolithiated derivative **15**, compound **12** was reacted with 1 equiv of *n*-BuLi in hexane. Subsequent quenching experiments with MeOH-*d*₄ did not give conclusive evidence for the formation of **15**,⁴³ thus the direct conversion of the reaction mixture with [PtCl₂(SEt₂)₂] was attempted. This procedure yielded a mixture of three products: free ligand **12**, the diplatinum compound **10**, and a third compound **16** in *ca.* 1:1:2 molar ratio based on the integrals of the respective ¹H NMR signals of the resulting products. Since a pure sample of **16** could not be obtained, the assignment of its ¹H NMR spectrum in the reaction mixture indicates that two nonequivalent bis[(dimethylamino)methyl]aryl units are present. From this result, it can be concluded that each of the aryl units of **12** can be lithiated independently. This behavior differs from that observed in the reaction of 1,2,4,5-(Me₂NCH₂)₄C₆H₂ with *n*-BuLi or *t*-BuLi, in which only the product of monolithiation can be obtained and a second lithiation step is hampered.²⁶ Apparently the monolithiation of **12** does not provide an effective barrier to a second lithiation step. Consequently, the quantitative monolithiation of **12** will be difficult under the conditions examined.

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(43) The ¹H NMR spectrum in C₆D₆ of the deuterolysis product showed, in the aromatic region, two singlets at 7.80 (2,6-ArH) and 7.5 (4-ArH) ppm of relative intensity 4:1, which may correspond to the deuterolysis of the pure monolithiated species (**15**).

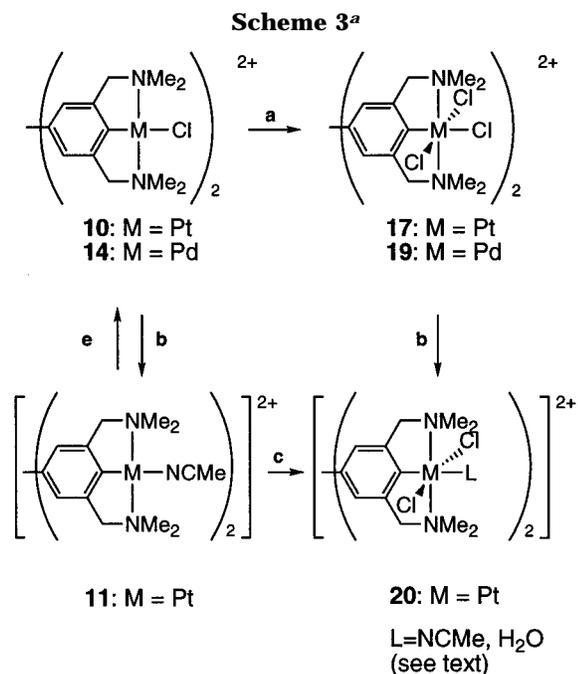
Synthesis of Diplatinum(II) and Dipalladium(II) Complexes. [ClM{2,6-(Me₂NCH₂)₂C₆H₂}-]₂ (M = Pt (**10**), Pd (**14**)) were prepared by addition of 2 equiv of [MCl₂L₂] (M = Pt, L = SEt₂; M = Pd, L = PhCN or SMe₂) to a Et₂O suspension of the dilithium compound **13** prepared *in situ* (Scheme 2). The diplatinum(II) and dipalladium(II) compounds are insoluble in Et₂O, THF, and hydrocarbon solvents, which enables their purification (*i.e.*, by removal of L, LiCl, MCl[C₆H₃(CH₂NMe₂)₂-2,6], etc.) by filtration and subsequent washing. The dipalladium compound **14** was obtained in 30% yield using [PdCl₂(SMe₂)₂], while a lower yield was found (14%) starting from [PdCl₂(NPh)₂]. The products can be readily recrystallized from a dichloromethane solution. The diplatinum compound **10** could not be purified by recrystallization due to its inherent low solubility in chlorinated hydrocarbons. The crude product, which contains traces of Pt(0), can, however, be used in further reactions. Thus, the addition of excess of Ag(O₃SCF₃) to a suspension of crude **10** in acetonitrile resulted in the formation of the dicationic complex [(MeCN)Pt{2,6-(Me₂NCH₂)₂C₆H₂}-]₂(CF₃SO₃)₂ (**11**). This compound is highly soluble in acetonitrile. Recrystallization from this solvent gave **11** as an orange crystalline solid (32% yield). Interestingly, **11** is also soluble in water and/or acetone. Although we did not investigate the nature of the species present in these solutions, exchange between the coordinated acetonitrile and solvent molecules (H₂O or acetone) is likely to occur.

The dicationic complex **11** could be reconverted in good yield to the neutral dichloride **10** by adding a solution of NaCl (2 equiv) in water to compound **11** in acetone/water. The reaction product, **10**, readily precipitates as a white solid from this solvent mixture (Schemes 2 and 3).

Compounds **10**, **11**, and **14** are air and moisture stable in the solid state and in solution for a period of a few hours, but they should be kept under nitrogen atmosphere when stored for longer periods.

Synthesis of Diplatinum(IV) and Dipalladium(IV) Complexes. Complexes [Cl₃M{2,6-(Me₂NCH₂)₂C₆H₂}-]₂ (M = Pt (**17**), Pd (**19**)) were obtained by adding 2 equiv of Cl₂IPh to a chloroform solution of **10** or **14**, respectively (Scheme 3). Upon addition of Cl₂IPh, the initially colorless reaction mixtures become deep orange. The diplatinum(IV) compound **17** is air and moisture stable and could also be prepared by adding excess of Cl₂ (saturated solution in CCl₄) to a Et₂O suspension of **10**. Selective oxidation of the metal center was not accompanied by any detectable C–Pt bond cleavage or chlorination of the organic skeleton.

As expected, the corresponding dipalladium(IV) compound **19** is much less stable than the related Pt(IV) species. Decomposition of **19** in dichloromethane or chloroform solution occurs in the course of a few minutes. A ¹H NMR spectrum recorded immediately upon addition of Cl₂IPh to a chloroform solution of **14** showed the sole presence of the double oxidative-addition compound **19** with the expected formation of IPh. Precipitation of a solid takes place after a few minutes, and the ¹H NMR spectrum of the supernatant solution, which has a reduced color intensity, revealed that the concentration of **19** had decreased considerably. Presumably, chlorination across the Pd–C bond takes



^a (a) + 2Cl₂IPh/Cl₃CH; (b) + 2Ag(O₃SCF₃)/MeCN, -2AgCl; (c) + 2Cl₂IPh/MeCN; (d) M = Pt, +2NaCl/Me₂CO·H₂O, -2Na(O₃SCF₃).

place, although no attempt to identify the decomposition products was made. Work-up of the reaction (see Experimental Section) gave samples of **19** (pure by ¹H NMR) in low yields. However, its instability prevented the further characterization of the compound by other techniques (e.g., ¹³C{¹H} NMR, IR, elemental analysis).

The stabilizing effect of the ligand toward Pd(IV) is no doubt a consequence of the fact that the Pd(IV) state is stabilized by bidentate nitrogen ligands,^{44–46} in addition to the proven ability of strongly electron-donating aryldiamine ligands to support high-oxidation-state complexes. For example, ligand **1** (Scheme 1) forms stable Pt(IV)^{16,17} and Ni(III)^{18,20,21} complexes, and the isomeric CNN' ligand {C₆H₄CH₂N(Me)CH₂CH₂NMe-2}⁻ has been shown to form stable Pd(IV) organometallic complexes.⁴⁷

Like its precursor (**10**), the diplatinum(IV) compound **17** exhibits low solubility in common organic solvents. To increase the solubility of **17** in polar solvents, the dicationic solvento complex, *trans*-**20**, was prepared. This complex can be obtained from the reaction of **17** and Ag(O₃SCF₃) in acetonitrile, following an analogous procedure discussed for **10**, or by a double oxidative-addition reaction of dicationic **11** with Cl₂IPh (2 equiv). In both cases, only the *trans*-Cl₂ isomer was obtained, as indicated by ¹H NMR (a *cis* arrangement would force the two CH₂ benzylic protons to be diastereoisomeric regardless of the relative arrangement (*cis* or *trans*) of the Pd-bound acetonitrile ligands; there is no NMR evidence for such inequivalence).⁴⁸ The *trans* disposi-

tion of the halide ligands is typical for the oxidative addition of dihalogens to square-planar complexes,⁴⁹ except in situations where dihalide M(IV) (M = Pd, Pt) products would place two strongly *trans*-influencing ligands (e.g., two formally carbanionic ligands) in a *trans* arrangement. An example of this can be found in the product of X₂ addition to [Pt(NCN)R] (R = phenyl or *p*-tolyl) which forms *cis*-[PtX₂(NCN)R].⁴⁸ In the case studied here, acetonitrile appears to act as a weak σ -donor ligand and, hence, *trans* products are formed (*vide supra*). It is assumed that in acetonitrile solution both Pt(IV) centers are coordinated to MeCN, although as in the case of **11**, exchange between the coordinated acetonitrile and other (solvent) molecules may take place. The structure of **20** in the solid state appears to be different, as its elemental analysis indicates that one molecule of H₂O has substituted one MeCN ligand. The source of this water is probably due to exposure of the complex to air or water present in the acetonitrile or in the Et₂O used in the work-up procedures (see Experimental Section). The IR spectra of **20** and its precursor **11** were carried out in Nujol mull to clarify this point. Complex **20** yields one broad O–H stretching band in the region 3150–3300 cm⁻¹ and an H–O–H bending vibration at 1627 cm⁻¹, both of which strongly suggest the presence of water. Two weak bands at 2317 and 2283 cm⁻¹ are assigned to the CN group. The IR spectrum in Nujol of the diplatinum(II) compound **11** shows two ν (CN) bands at the same position, in addition to four bands associated with the triflate group at 1124, 1150, 1221, and 1273 cm⁻¹. Complex **20** shows five bands in this region (1107, 1163, 1224, 1249, and 1282 cm⁻¹). It is unclear how these bands are modified in the case of mono- or dicoordination of the triflate anion. In the solid state, compound **20** may contain water and a coordinated acetonitrile molecule may have been partially replaced by coordinated triflate.^{16b}

Mixed-Valence Pt(II)–Pt(IV) Complexes. The reaction between **11** and 1 equiv of Cl₂IPh in acetonitrile yielded, after 30 min and appropriate work up, a mixture of three products in 1:1:2 molar ratio, as indicated by ¹H NMR. Two of these products were identified as unreacted **11** and **20** by comparison of the spectrum with those of authentic samples, while the third pattern was assigned to a species having two nonequivalent bis[(dimethylamino)methyl]aryl units, i.e., to the mixed-valence complex [(MeCN)Pt^{II}{2,6-(Me₂NCH₂)₂C₆H₂-C₆H₂(CH₂NMe₂)₂-2,6}Pt^{IV}Cl₂(NCMe)](CF₃-SO₃)₂ (**21**) (see Scheme 3). Complex **21** could also be obtained by reacting equimolar amounts of **11** and **20** (cf. Scheme 3) in solution (CD₃CN), as monitored by ¹H NMR. The amount of the mixed-valence compound slowly increased with time. However, after 72 h, the same 1:1:2 (**11**:**20**:**21**) statistical distribution of products was reached, as found in the reaction of **11** and Cl₂IPh in a 1:1 mol ratio.

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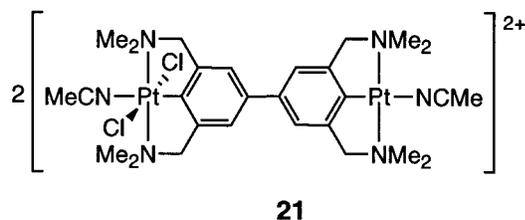
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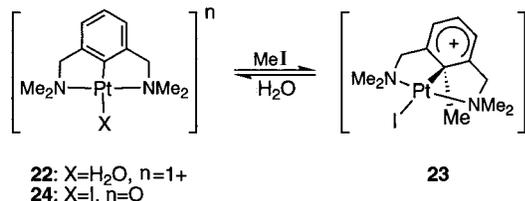
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Scheme 4



Scheme 5. Reverse Formation of Monoarenonium Platinum(II) Complexes

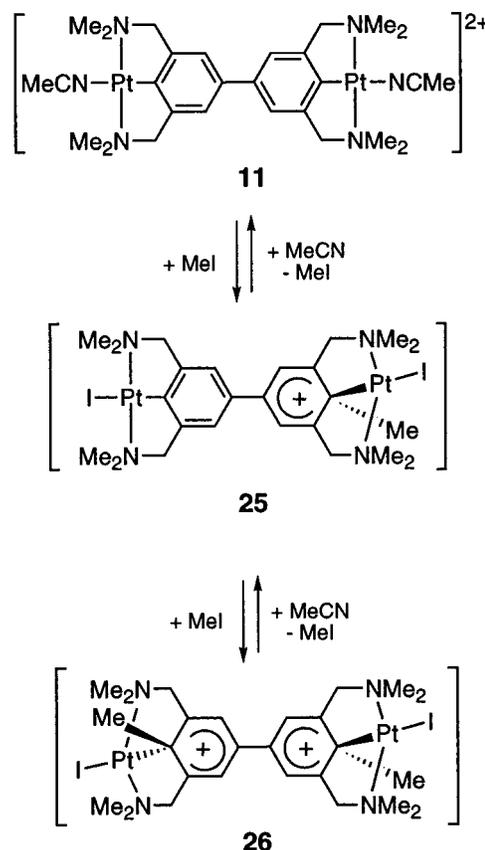


The reaction of complex **11** with a stoichiometric deficit of Cl₂IPh (0.2 equiv) was also examined by ¹H NMR spectroscopy. The initial ¹H NMR spectrum that was run immediately upon this addition showed a mixture of three products: **11**, **20**, and **21** (ca. 14:1:1 ratio). Over time, a simultaneous increase of the relative amount of **21** and an appropriate decrease of the amount of **11** and **20** was observed. After 20 h, only **11** and **21** (ca. 6:1) were present in the reaction mixture. This ratio appeared to be the thermodynamic equilibrium, as no further changes were noted. Thus, **21** appears to be more stable than **20** with respect to reductive elimination of Cl₂. Unfortunately, the attempts to obtain a pure sample of **21** from the latter reaction mixture were unsuccessful.

Reaction of 11 with MeI. Synthesis of the Bis-(arenonium) Compound [IPt^{II}{2,6-(Me₂NCH₂)₂-1-MeC₆H₂-C₆H₂Me-1-(CH₂NMe₂)₂-2',6'}Pt^{II}](CF₃SO₃)₂ (26**).** We have observed the independent reactivity of each of the aryldiamine units in ligand **12** (i.e., toward lithiation, *vide supra*), as well as to the metal centers bound to them (i.e., the formation of the mixed-valence Pt^{II}-Pt^{IV} species). We extended this study by reacting the Pt^{II}-Pt^{II} compound **11** with MeI, since it is known that the reaction between cationic Pt^{II} complexes containing an aryldiamine ligand derived from **1** (**22**) and MeI yields the unique mono(arenonium)-Pt^{II} compounds (**23**). The Me group of the alkyl halide is bound to the C_{ipso} of the aryl ring in these products (Scheme 5).^{25,50} Reversibility of this process was shown by addition of water or halide to [IPt^{II}-1-MeC₆H₃(CH₂NMe₂)₂-2,6]⁺ (**23**), which yielded the cationic or neutral, homonuclear Pt(II) compound [PtX{C₆H₃(CH₂NMe₂)₂-2,6}]ⁿ⁺ (**22**, X = H₂O, n = 1; **24**, X = I, n = 0), respectively.

A suspension of **11** in MeI was stirred in the dark for 17 days, over which time the mixture became deep red, and upon removal of the excess of MeI *in vacuo*, a mixture of the mono- (25%, **25**) and the bis(arenonium) (75%, **26**) compounds was formed. This was indicated by ¹H NMR of the dark-red solid in CD₃CN. This solid

Scheme 6. Reversibility of C-C Bond Formation



was thereafter suspended in MeI and reacted for a further 8 days. ¹H NMR analysis in CD₃CN indicated that the reaction had yielded a single product, **26**. The rate of this reaction is much slower than that of **22** with MeI, but it is comparable to that of compound **25**, in which only one of the two metal centers is reacted (Scheme 6). In this case, the low solubility of the platinum complexes in MeI may be responsible for the slow reaction rate. Also, the addition of drops of acetonitrile to a suspension of **25** and **26** (1:1) in MeI resulted in the formation of a mixture of **25** and compound **11**. Unfortunately, the arenonium compounds were only briefly stable in CD₃CN solution (<10 min), thus allowing only ¹H NMR measurements to be made. Decomposition to nonidentified products also takes place in acetone solution in the course of a few hours, and the very low solubility of **26** in chloroform and dichloromethane precluded the use of such solvents in NMR studies. The precise geometry of complex **26** could not be determined from spectroscopic studies. A rigid planar biaryl bridge between the two Pt metal centers would allow for the formation of *cis*- and *trans*-diarenonium complexes (Scheme 6, *trans* isomer is shown; with respect to the orientation of the Me groups derived from MeI across the biaryl bridge).

Our attempts to observe the presence or absence of stable isomers of **26** have unfortunately been hampered by its low solubility and instability. The reversibility of the C-C bond formation process was observed *via* ¹H NMR spectroscopy of a solution of **26** in CD₃CN at given time intervals (see Table 2). The initially red solution became colorless during the study. After 5 days, total consumption of the starting compound **26** was observed and the reaction mixture contained **25** (ca.

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Table 2^a

<i>t</i>	26	25	11
0	100%	0%	0%
1 day	27%	73%	0%
5 days	0%	75%	25%
6 days	0%	67%	33%

^a Relative amounts of products based on the integrals of the respective ¹H NMR patterns of the compounds in the reaction mixture.

75%) and **11** (ca. 25%). After 6 days, gas chromatography experiments indicated the presence of MeI (and not MeOH) in the reaction mixture. After 8 days, formation of other nonidentified decomposition products was observed. Total consumption of **25** took place after 11 days. At this stage of the reaction, the mixture that was formed included **11** together with other unidentified products.

NMR Spectroscopy of the Platinum and Palladium Complexes. The NMR spectra of the compounds **10**, **11**, **14**, **17–19**, **25**, and **26** (see Table 1) are fully consistent with the proposed structures and exhibit similar chemical shift and coupling features known for the related mononuclear platinum and palladium complexes.^{51–54} The NMR data reveal a high degree of symmetry of all the homobimetallic complexes in solution (e.g., a singlet ¹H NMR resonance is found for the four aryl protons of the ligand system). As in the free ligand, equivalence between the two bis[(dimethylamino)methyl]aryl units is attributed to either free rotation around the *para* C–C bond or planarity of the biaryl unit. In addition, each aryldiamine unit possesses rigid C₂-symmetric coordination to the metal centers (except in **25**). This pattern excludes the *cis*-Cl₂ isomer as a possible structure for **20**.

¹H NMR Spectra. The aryl protons in **10**, **11**, **14**, **17**, **18**, and **20** are shifted relative to the free ligand and appear as one singlet, whereas the CH₂N(CH₃)₂ protons appear as two singlets which exhibit a pronounced downfield shift and in the case of **10**, **11**, **17**, and **20** have ¹⁹⁵Pt (*I* = 1/2, 34% abundance) satellite resonances. The increase of the oxidation state of the coordinated metal (from +2 to +4) and its coordination number (from 4 to 8) results in a characteristic downfield shift of the CH₂ protons and a decrease of the ¹⁹⁵Pt–¹H coupling constant to both CH₂ and Me protons (cf., for example, **11** and **20**). Complexes **11** and **20** show broad singlets at 2.39 and 2.23 ppm, respectively, corresponding to the coordinated acetonitrile molecules which are in rapid exchange with the solvent (see above).

The CH₂ protons of complex **16** (in CDCl₃) appear as two singlets at 3.45 and 4.09 ppm, the latter having ¹⁹⁵Pt satellites (³*J*(¹⁹⁵Pt–¹H) = 44 Hz). This is consis-

tent with the presence of a noncoordinated aryldiamine unit (as in **12**) and a Pt-coordinated one (as is **10**). Accurate values for the ¹⁹⁵Pt–¹H coupling to the N(CH₃)₂ coordinated to Pt^{II} could not be obtained due to overlapping with other signals of the compounds present in the mixture (**10** and **12**).

The ¹H NMR spectrum of the Pt^{II},Pt^{IV} compound **21** in CD₃CN shows six singlets which by comparison with the parent compounds **11** and **20**, are assignable to a Pt^{II}-coordinated aryldiamine unit and a Pt^{IV}-coordinated one (Table 1). The values of the ¹⁹⁵Pt–¹H coupling constants observed for the CH₂ protons (48 and 31 Hz, respectively) also support this view.

The general appearance of the ¹H NMR spectrum of the mono(arenonium) species **25** is similar to that of the symmetric compounds **10** and **26**. Thus, the CH₂ protons appear as a singlet with ¹⁹⁵Pt satellites (³*J*(¹⁹⁵Pt–¹H) = 48 Hz) closest to the Pt^{II} metal center and two doublets for the diastereotopic CH₂ protons in proximity to the Pt^{IV} center.

The ¹H NMR spectrum of **26** shows diastereotopic CH₂ and NMe₂ groups (δ CH₂ = 4.87 and 3.80, *J*(¹H–¹H) = 13 Hz; δ NMe₂ = 2.72 and 3.08, ³*J*(¹⁹⁵Pt–¹H) = 26 Hz), as expected from the molecular symmetry with respect to the two nonequivalent aryldiamine units. A singlet resonance at 3.14 ppm accounts for the Me group bound to the *ipso* carbon atom at the aromatic ring.

¹³C NMR Spectra. The ¹³C{¹H} NMR data of the pure homobimetallic complexes are given in Table 1, except for that of compound **17** (low solubility), **18**, and **26** (the latter two are both unstable in solution). The ¹³C{¹H} NMR spectra of complex mixtures of the compounds previously discussed were not measured. The magnitude of the ¹⁹⁵Pt–¹³C coupling constants are given only when accurate measurements could be made. As expected, we observe downfield shifts for the ¹³C{¹H} NMR resonances of the atoms close to the metal (C_{*ipso*}, CH₂, Me, C_{*ortho*}) with respect to those of the free ligand. The ¹³C{¹H} NMR spectrum of the diplatinum(IV) complex **20** does not show significant differences in chemical shift when compared to those of the diplatinum(II) species, but it does yield smaller ¹⁹⁵Pt–¹³C coupling constants (Table 1). The ¹³C{¹H} resonances of the coordinated acetonitrile molecules in complexes **11** and **20** were not visible at room temperature (a solvent exchange mechanism may be operating, as mentioned above).

Crystal Structure of [ClPd{2,6-(Me₂NCH₂)₂C₆H₂}]₂ (14**).** Pale yellow octahedral crystals of **14** obtained from a dichloromethane:benzene (3:1) solution were found to be suitable for X-ray crystal structure determination. The molecular structure and atom-numbering scheme are shown in Figure 1, and selected bond lengths and angles are listed in Table 3. The structure determination reveals that the complex crystallizes in an orthorhombic system with *Fddd* space group symmetry. Three mutually perpendicular 2-fold axes intersect at the mid-point of the *para* C–C bond. This symmetry is enforced by two circumstances: (i) the rigidity of each aryldiamine terdentate unit which strains the Pd(II) atom in a distorted square-planar geometry, with the two N-donor atoms in trans positions (N(1)–Pd(1)–N(1)c = 161.9(3)°); and (ii) the distinct

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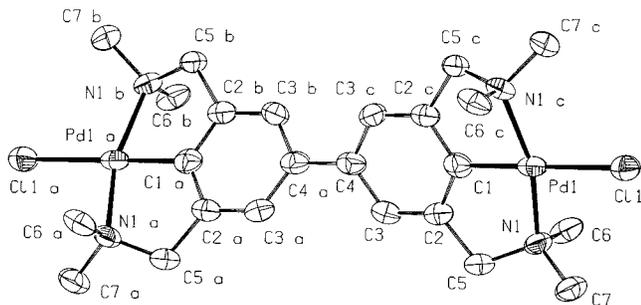


Figure 1.

Table 3. Selected Bond Lengths and Angles of Complex 14

bond lengths (Å)		bond angles (deg)	
Pd(1)–Cl(1)	2.425(5)	Cl(1)–Pd(1)–N(1)	99.1(2)
Pd(1)–N(1)	2.109(9)	Cl(1)–Pd(1)–C(1)	180.00
Pd(1)–C(1)	1.920(15)	Cl(1)–Pd(1)–N(1)c	99.1(2)
N(1)–C(5)	1.481(15)	N(1)–Pd(1)–C(1)	80.9(2)
N(1)–C(6)	1.470(15)	N(1)–Pd(1)–N(1)c	161.9(3)
N(1)–C(7)	1.473(14)	C(1)–Pd(1)–N(1)c	80.9(2)
C(1)–C(2)	1.390(13)	Pd(1)–N(1)–C(5)	108.9(6)
C(2)–C(3)	1.370(17)	Pd(1)–N(1)–C(6)	107.2(6)
C(2)–C(5)	1.512(15)	Pd(1)–N(1)–C(7)	114.6(7)
C(3)–C(4)	1.412(13)	C(5)–N(1)–C(6)	109.0(9)
C(4)–C(4)a	1.46(2)	C(5)–N(1)–C(7)	108.7(8)
		C(6)–N(1)–C(7)	108.3(8)
		Pd(1)–C(1)–C(2)	118.9(7)
		Pd(1)–C(1)–C(2)c	118.9(7)
		C(2)–C(1)–C(2)c	122.2(12)
		C(1)–C(2)–C(3)	118.6(10)
		C(1)–C(2)–C(5)	113.7(10)
		C(3)–C(2)–C(5)	127.6(9)
		C(2)–C(3)–C(4)	121.1(10)
		C(3)–C(4)–C(4)a	121.0(7)
		C(3)–C(4)–C(3)c	118.0(12)
		C(4)a–C(4)–C(3)c	121.0(7)
		N(1)–C(5)–C(2)	109.3(8)
		C(2)–C(3)–H(31)	119(5)
		N(1)–C(5)–H(51)	109.9(14)

puckering of the two five-membered chelate rings of each aryldiamine unit with the two NMe₂ groups on opposite sides of the aryl plane (average torsion angle = 16.9°). These two characteristic features, as well as the bond distances and angle values around Pd, are similar to those found in related mononuclear complexes.⁵¹ Unlike the diruthenium(III) complex **4**, which possesses a planar biphenyl bridge and complete conjugation between the two Ru(III) centers,¹ the dipalladium(II) compound **14** presents a dihedral angle of 37.0(6)° between the two aryl rings, which prevents strong electronic communication between the two metal atoms on each molecule. This value is slightly higher than that found in the diruthenium(II) complex **4b** (dihedral angle ~34°)⁵⁴ and in the phenyl *para*-substituted aryldiamine compound [Li{2,6-(Me₂NCH₂)₂-4-Ph-C₆H₄}]₂ (dihedral angle ~31.8°)²⁹ but lies within the normal range for 4,4'-disubstituted (organic) biphenyls.^{55–57} All the molecules in the crystal are packed with their long axes parallel to the *c* axes, forming linear channels along it. However, there is no evidence for strong intermolecular interactions in the crystal to account for such a symmetric packing.

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Conclusions

The new bis-cyclometalating ligand 3,3',5,5'-tetrakis-[(dimethylamino)methyl]biphenyl (**12**) can be induced to form stable bimetallic palladium and platinum organometallic compounds in the M₂²⁺, M₂⁴⁺, or mixed-valence M²⁺M⁴⁺ oxidation states. A bis(arenonium) Pt₂^{II} complex was also found to be accessible. The selective dilithiation of **12** establishes a general route to other bimetallic compounds and provides a potential gateway to multimetallic systems and polymers. The structural characterization of compound **14** reveals a nonplanar biaryl unit in contrast to a Ru^{III} analogue (**4**).⁵⁸ We are currently expanding these investigations to include other metals in a variety of oxidation states, the results of which will be reported in due course.

Experimental Section

General Comments. All experiments were conducted under a dry dinitrogen atmosphere using standard Schlenk techniques. Solvents were dried over appropriate materials and distilled prior to use. Elemental analyses were performed by Dornis und Kolbe, Mikroanalytisches Laboratorium (Mülheim, Germany); ¹H, and ¹³C{¹H} NMR spectra were recorded at 298 K on a Bruker AC200 or AC300 NMR spectrometer. Infrared spectra samples were recorded as Nujol mulls between KBr plates (4000–600 cm⁻¹) on a Perkin-Elmer model 2000 FT-IR spectrometer. The instrument was flushed with nitrogen before spectral recording. Melting (decomposition) points were determined by using a Büchi melting point apparatus. GC/MS analyses were recorded with a Unicam Automass instrument using electron impact (EI). Starting materials: 3,5-(Me₂NCH₂)₂C₆H₃Br (**5**);²⁹ [NiCl₂(PMe₃)₂];⁵⁹ [PdCl₂(NCPPh)₂];⁶⁰ [PtCl₂(SEt₂)₂];⁶¹ and Cl₂IPh⁶² were prepared according to literature procedures. Ag(O₃SCF₃), *t*-BuLi and *n*-BuLi (in hydrocarbon solvents), and methyl iodide (neat) were purchased commercially.

Synthesis of Me₃Sn[3,5-(Me₂NCH₂)₂C₆H₃] (7). A solution of *t*-BuLi in hexane (12 mL, 18.1 mmol) was added dropwise to a solution of 3,5-(Me₂NCH₂)₂C₆H₃Br (**5**; 2.23 g, 8.22 mmol) in Et₂O at -70 °C. After 1 h, a solution of Me₃SnCl (2.39 g, 11.9 mmol) in Et₂O was added and the reaction mixture was allowed to warm to room temperature. The resulting suspension was stirred for 2 h and subsequently filtered. The solvent from the organic layer was then removed *in vacuo*, and the residue was extracted with several portions of dry hexane. The extractions were then combined and concentrated to dryness to give a colorless oil which was heated (60 °C) in *vacuo* for 4 h to remove volatile components. Distillation of the residue at 105 °C and 0.005 mmHg gave compound **7** as a colorless liquid (1.7 g, 58% yield). MS (EI, 70 eV): *m/z* (relative intensity) 355 (M⁺, 0.5), 311 (12.5), 268 (20), 255 (40), 105 (20.8), 58 (100). Anal. Calcd for C₁₅H₂₈N₂Sn: C, 50.74; H, 7.95; N, 7.89. Found: C, 50.59; H, 7.94; N, 7.87.

Pd(II)-Catalyzed Coupling Reaction of 5 and 7. To a solution of **5** (0.24 g, 0.88 mmol) and **7** (0.32 g, 0.92 mmol) in THF was added a suspension of [PdCl₂(PPh₃)₂] (0.04 g, 0.056 mmol) in THF. The resulting yellow solution was refluxed. After 12 and 16 h, separate GC/MS and ¹H NMR analyses of

(58) The crystallographic evidence suggests that the planarity of the 4,4'-biaryl unit (and hence increased metal–metal interactions) may be preferred by high oxidation state metals (*e.g.*, d⁵ Ru^{III}, **4**) with low formal d-electron counts.(59) Jensen, K. A.; Nielsen, P. H.; Pederson, C. T. H. *Acta Chem. Scand.* **1963**, *17*, 1115.(60) Kharasch, M. S.; Seyler, R. C.; Mayo, F. R. *J. Am. Chem. Soc.* **1938**, *60*, 882.(61) Kauffman, G. B.; Cowan, D. O. *Inorg. Synth.* **1960**, *6*, 211.(62) Lucas, H. J.; Kennedy, E. R. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 483.

the reaction mixture were carried out and it was found to contain, in both cases, traces of the desired coupling product (**12**) together with both starting materials (as main components of the mixture) and three other minor byproducts. More [PdCl₂(PPh₃)₂] catalyst (0.06 g, 0.08 mmol) was added, and the reaction mixture was refluxed for a further 48 h. The GC/MS analysis of the mixture at this time indicated that compound **7** was no longer present in the mixture, although traces of **5** still remained. The solvent was then removed *in vacuo*, and the residue was extracted with hexane. The extracts were combined and concentrated to dryness. The residue was treated with a basic aqueous solution, and the aqueous layer was extracted with Et₂O. The combined organic layers were then dried over MgSO₄, and the solvent removed *in vacuo* to give an oil formed by **12** and five other byproducts (as indicated by GC/MS). Attempts to purify **12** by column chromatography were not successful.

Synthesis of 3,3',5,5'-Tetrakis[(dimethylamino)methyl]biphenyl (12). A solution of *t*-BuLi in hexane (20.5 mL, 31 mmol) was added dropwise to a solution of **5** (3.8 g, 14 mmol) in Et₂O (10 mL) at -70 °C. After 1 h, [NiCl₂(PMe₃)₂] (1.9 g, 7 mmol) was added to the reaction mixture in the form of a solid. The resulting orange suspension was warmed to room temperature and then stirred for 1 h. The solvent was removed *in vacuo*, and degassed H₂O was added to the residue, and the resulting aqueous layer was extracted with Et₂O (3 × 10 mL). The combined organic layers were then dried over MgSO₄, and the solvent was removed *in vacuo*. The resulting yellow oil was extracted with pentane (3 × 5 mL), and the pentane solution was concentrated to dryness to give the product **12** as a pale yellow oil (1.4 g, 52% yield). Bp: 48–50 °C (0.06 mmHg). MS (EI, 70 eV): *m/z* (relative intensity) 382 (M⁺, 18.3), 339 (11.5), 294 (8.6), 251 (23.1), 208 (15.4), 148 (7.7), 58 (100). Anal. Calcd for C₂₄H₃₈N₄: C, 75.34; H, 10.01; N, 14.64. Found: C, 74.31; H, 9.10; N, 13.75.

Synthesis of [CIPt{2,6-(Me₂NCH₂)₂C₆H₂}]₂ (10). To a solution of **11** (129 mg, 0.112 mmol) in 3 mL of H₂O/acetone (1:1) was added a solution of NaCl (14 mg, 0.224 mmol) in 2 mL of water. A white solid precipitated immediately. The solid was filtered, washed with water, acetone, and Et₂O in succession, and then dried, first *in vacuo* and then on P₂O₅. (Yield 65 mg; 70%). Mp: >240 °C. Anal. Calcd for C₂₄H₃₆Cl₂N₄Pt₂: C, 34.25; H, 4.31; N, 6.65. Found: C, 34.09; H, 4.24; N, 6.33.

Synthesis of [CIPd{2,6-(Me₂NCH₂)₂C₆H₂}]₂ (14). To a solution of **12** (0.11 g, 0.288 mmol) in Et₂O (5 mL) was added a hexane solution of *t*-BuLi (0.51 mL, 0.76 mmol). The resulting orange suspension was stirred at room temperature for 4 h, and then [PdCl₂(SMe₂)₂] (0.26 g, 0.85 mmol) was added as a solid. After 19 h, the mother liquor was decanted, the residue washed with Et₂O (3 × 50 mL) and extracted with CH₂-Cl₂, and the combined extractions filtered through Celite. The filtrate was concentrated *in vacuo*, and Et₂O added to precipitate the product **14** as a pale yellow solid (0.07 g, 31% yield). Mp: 110–112 °C (dec). Anal. Calcd for C₂₄H₃₆Cl₂N₄Pd₂: C, 43.39; H, 5.46; N, 8.43. Found: C, 43.48; H, 5.58; N, 8.28.

Synthesis of [(MeCN)Pt{2,6-(Me₂NCH₂)₂C₆H₂}]₂(CF₃SO₃)₂ (11). To a solution of **12** (0.8 g, 2.08 mmol) in Et₂O (5 mL) was added a hexane solution of *t*-BuLi (3.4 mL, 5.20 mmol). After 4 h, [PtCl₂(SEt₂)₂] (2.1 g, 4.70 mmol) was added to the orange suspension and the reaction mixture stirred for 20 h. The solvent was decanted, and the residue was washed with Et₂O (2 × 10 mL) and THF (4 × 5 mL) and dried *in vacuo*. The resulting brown solid was identified by ¹H NMR as compound **10** (0.5 g) contaminated with a black material that was presumably Pt(0). To a suspension of this residue in MeCN was added Ag(O₃SCF₃) (0.52 g, 2.02 mmol), and the mixture was stirred for 18 h in the absence of light. The suspension was then filtered through a pad of Celite, and the filtrate was concentrated to dryness. The solid was washed repeatedly with Et₂O and then dried *in vacuo*. Compound **11**

was, thus, obtained as a pale yellow solid (yield 0.78 g; 32%). IR (cm⁻¹): [ν(CN)] 2318, 2283 cm⁻¹. Mp: 90 °C (dec). Anal. Calcd for C₃₀H₄₂F₆N₆O₆Pt₂S₂: C, 31.31; H, 3.68; N, 7.30. Found: C, 31.28; H, 3.75; N, 7.36.

Synthesis of [Cl₃Pt{2,6-(Me₂NCH₂)₂C₆H₂}]₂ (17). Addition of excess of Cl₂ (0.5 mL, saturated solution in CCl₄) to a suspension of **10** in Et₂O (25 mg, 0.029 mmol) yielded a deep orange suspension. After 15 min, the mother liquor was decanted and the residual solid washed with Et₂O and dried *in vacuo*. Yield: 19 mg; 67%. Mp: 232–235 °C (dec). Anal. Calcd for C₂₄H₃₆Cl₆N₄Pt₂: C, 29.31; H, 3.69; N, 5.70. Found: C, 29.01; H, 3.89; N, 5.44.

Synthesis of [Cl₃Pd{2,6-(Me₂NCH₂)₂C₆H₂}] (19). Addition of 2 equiv of Cl₂IPh to a solution of **14** in chloroform (10 mg, 0.015 mmol) immediately produced an orange solution. The solvent was removed *in vacuo*, and the resulting orange solid was washed with Et₂O and dried. The solid was then extracted with CDCl₃ for ¹H NMR measurement (Table 1).

Synthesis of [(MeCN)Cl₂Pt{2,6-(Me₂NCH₂)₂C₆H₂-C₆H₂-(CH₂NMe₂)₂-2',6'}PtCl₂(OH₂)](CF₃SO₃)₂ (20). Method 1: Ag(O₃SCF₃) (0.06 g, 0.22 mmol) was added to a suspension of **17** (0.10 g, 0.10 mmol) in MeCN (5 mL). The resulting orange suspension was stirred for 22 h in the dark. The mixture was then filtered through Celite, and the filtrate was concentrated to dryness. The orange solid thus obtained was washed with Et₂O (2 × 20 mL) and dried *in vacuo*, yielding 0.11 g (85%) of **20**.

Method 2: To a solution of **11** (55 mg, 0.047 mmol) in acetonitrile (5 mL) was added Cl₂IPh (26.3 mg, 0.095 mmol). The resulting orange solution was stirred for 30 min, followed by the removal of the solvent *in vacuo*. The residue was washed with Et₂O and dried. Compound **20** was obtained as an orange solid. Yield: 55.3 mg; 90%. IR (cm⁻¹): [ν(OH)] 3150–3300 (br), 1627; [ν(CN)] 2317, 2283. Mp: 138–140 °C (dec). Anal. Calcd for C₂₈H₄₁Cl₄F₇N₅O₆Pt₂S₂: C, 26.49; H, 3.25; N, 5.52. Found: C, 26.35; H, 3.56; N, 5.22.

Synthesis of [IPt^{III}{2,6-(Me₂NCH₂)₂-1-MeC₆H₂}]₂(CF₃SO₃)₂ (26). A suspension of **11** (20 mg, 0.017 mmol) in MeI (10 mL) was stirred in the dark for 25 days. The resulting dark-red suspension was concentrated to dryness *in vacuo* to give **26** as a red solid. Yield: 21 mg; 89%. Mp: 45 °C (dec). Anal. Calcd for C₂₈H₄₂F₆I₂N₄O₆Pt₂S₂: C, 24.86; H, 3.13; N, 4.14. Found: C, 25.19; H, 3.27; N, 4.28.

X-ray Structure Determination of Complex 14. X-ray data were collected at 150 K on an Enraf-Nonius CAD4T on a rotating anode for a yellowish transparent crystal glued on a fiber. Numerical details have been collected in the Supporting Information. Unit cell dimensions were derived from the SET4 setting angles⁶³ of 23 reflections in the range 8° < θ < 25°. The space group was uniquely determined from the observed systematic extinctions. Reflection profiles were found to be split. The ANIVEC⁶³ option of the CAD4 data collection software was used to collect intensity data at the ψ-angles with minimal reflection profile splitting.

The structure was solved by direct methods using SIR92⁶⁴ and refined on *F*² by full-matrix least-squares using SHELXL96.⁶⁵ Hydrogen atoms were taken into account at calculated positions and refined riding on their carrier atoms. A final difference map showed no significant residual features. All other calculations (including ORTEP illustration) were done with PLATON.⁶⁶

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Supporting Information Available: Tables of crystal data, fractional coordinates of the non-hydrogen atoms, anisotropic thermal parameters, fractional coordinates of the hydrogen atoms, bond distances and angles of the non-hydrogen atoms, and bond distances and angles of the hydrogen atoms (10 pages). Ordering information is given on any current masthead page.

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