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Intramolecularly Stabilized 1,4-Phenylene-Bridged Homo- and Heterodinuclear Palladium and Platinum Organometallic Complexes Containing *N,C,N*-Coordination Motifs; η^1-SO_2 Coordination and Formation of an Organometallic Arenium Ion Complex with Two Pt−C σ-Bonds[¥]

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The new ligand precursors [1-(Me_3Si)-4-(R){$C_6(CH_2NMe_2)_4$-2,3,5,6}] (**2**, R = Me_3Si; **3**, R = H) have been used for the preparation of ionic 1,4-phenylene-bridged bispalladium(II) and palladium(II)−platinum(II) complexes [1-{M(MeCN)}-4-{M′(MeCN)}{$C_6(CH_2NMe_2)_4$-2,3,5,6}]-$(BPh_4)_2$ (**5b**, M = M′ = Pd; **10**, M = Pd, M′ = Pt). Lithium−halogen exchange of the new ligand precursor $C_6Br_2(CH_2NMe_2)_4$-2,3,5,6, **11**, generates a presumably polymeric organodilithium reagent, **12**, which in a transmetalation reaction with [$PtCl_2(Et_2S)_2$] affords the 1,4-phenylene-bridged bisplatinum complex [1,4-$(PtCl)_2${$C_6(CH_2NMe_2)_4$-2,3,5,6}], **13**. Reaction of colorless **13** with SO_2 affords the unique orange bis-SO_2 adduct [1,4-{PtCl(η^1-SO_2)}$_2${$C_6(CH_2NMe_2)_4$-2,3,5,6}], **16**, of which an X-ray crystal structure has been determined. The ionic derivative [1,4-{Pt(MeCN)}$_2${$C_6(CH_2NMe_2)_4$-2,3,5,6}]$(BPh_4)_2$, **14b**, obtained by reaction of **13** with AgOTf in MeCN followed by addition of $NaBPh_4$, has been the subject of an X-ray crystal structure determination. The X-ray molecular structures of **5b**, **10**, and **14b** have been determined and show intramolecular M···M distances of ca. 6.5 Å. The bistriflate complex [1,4-{Pt(MeCN)}$_2${$C_6(CH_2NMe_2)_4$-2,3,5,6}]$(OTf)_2$, **14a**, has also been used for the synthesis of the organometallic polymer {[1,4-{PtI(μ-I)}$_2${$C_6(CH_2N(H)Me_2)_4$-2,3,5,6}]$_n$}-$(OTf)_{2n}$, **24**. Triflate complex **14a** slowly reacts with iodomethane to afford the dark red air-stable crystalline complex [1,4-{PtI}$_2${C_6Me-1-$(CH_2NMe_2)_4$-2,3,5,6}](OTf), **23**. The X-ray molecular structure of **23** shows it to be a unique arenium ion species with two *para*-oriented σ-bonded iodoplatinum substituents.

Introduction

In the last two decades, several examples of oligophenylene-bridged dinuclear organometallic complexes have been reported,[1] and such bimetallic complexes are of interest due to their potential application in the synthesis of (conducting) organometallic polymers. In particular when heterobimetallic complexes are used as building blocks, directionality in the resulting organometallic polymer can be anticipated. Another feature of bimetallic complexes that is attracting interest is the electronic contact that is possible between two metal centers bridged by an organic unit, since this could afford speciality materials with interesting electronic and/or optical properties.

Despite this wide range of possible applications, the number of different synthetic routes to oligophenylene-bridged bimetallic complexes is very limited. Most reported bimetallic (bis-cyclometalated) complexes are prepared by difficult synthetic pathways that only allow the introduction of a few metals. Therefore, an alternative more general synthetic route, particularly for

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[¥] This work is dedicated to Prof. Dr. Roald Hoffmann (Cornell University, Ithaca, New York) on the occasion of his 60th birthday.

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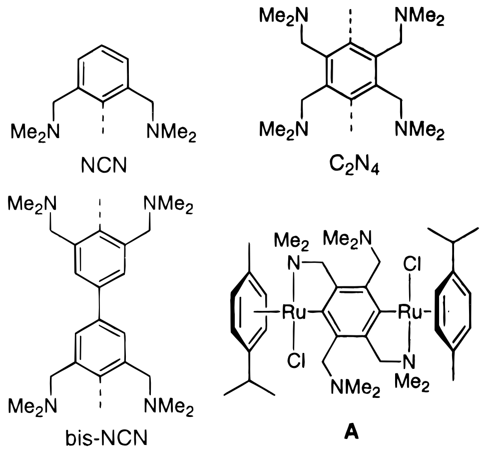

Figure 1. Schematic representation of the monoanionic ligand NCN and the dianionic ligands C_2N_4 and bis-NCN, and of a bis-ruthenium complex derived from C_2N_4.

heterobimetallic complexes, is still required, and this is the theme behind the chemistry described in this paper.

In our group, we have been recently investigating the synthesis of catalytically active organometallic Ru(II), Ni(II), and Pd(II) complexes derived from the potentially *N,C,N′*-terdentate coordinating monoanionic aryl ligand $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$ (NCN; see Figure 1).[2] Moreover, this ligand has provided Ni(II), Pd(II), and Pt(II) complexes which are useful substrates for the development of new bonding arrangements in organometallic chemistry.[3]

In such M(NCN) organometallic species, terdentate *N,C,N′*-bonding to the metal center results from a M−C σ-bond involving the aryl nucleus together with intramolecular N-donor coordination to the metal of both *ortho*-CH_2NMe_2 substituents.

Recently, we have also explored the synthesis of multimetallic systems using π-conjugated bridging ligands that provide *N,C,N′*- and related coordination motifs. Our aim in this area is to prepare bimetallic complexes in which the metal centers are bridged by the shortest possible aromatic (spacer) group containing two *N,C,N′*-coordination moieties. The spacer group employed here is the 1,4-monophenylene bridging ligand $[C_6(CH_2NMe_2)_4\text{-}2,3,5,6]^{2-}$ (C_2N_4), a dianionic ligand formally derived from $C_6H_2(CH_2NMe_2)_4$-1,2,4,5, **1**; see Figure 1. Platinum group metal complexes of the 4,4′-biphenylene-bridging bis-NCN ligand (see Figure 1)[1i,4a] have recently been prepared, and it could be anticipated that the dianionic ligand C_2N_4 should provide bimetallic complexes with an intermetallic electronic contact that is more efficient than in related oligophenylene-bridged dinuclear organometallic species.[4] In addition, this chosen C_2N_4 system contains tertiary amine groups that provide intramolecular coordination to the metal centers exclusively through σ-donation, and as a result, electron delocalization will be concentrated in the 1,4-phenylenediyl system. Note that in 1993, Loeb and Shimizu[5] reported the first structurally characterized 1,4-phenylene-bridged bispalladium(II) complex that was obtained from $C_6H_2(CH_2SPh)_4$-1,2,4,5; this sulfur-based compound is clearly closely related to the aryltetramine **1** from which C_2N_4 is derived.

Very recently, we briefly communicated on a novel route to homodinuclear 1,4-phenylene-bridged bis-Pd(II) complexes and heterodinuclear Pt(II)−Pd(II) complexes.[6] The general synthetic route to the intramolecularly stabilized 1,4-phenylene-bridged bimetallic complexes described there leads to a new class of dinuclear organometallic species. The methodology used involves combinations of directed aromatic C−H bond ortholithiation,[7] lithium−halogen exchange,[8] and transmetalation reactions[9] together with a new application of the recently reported electrophilic C−Si bond palladation reaction.[6,10] This allows the synthesis not only of the known 1,4-phenylene-bridged bis-Ru(II) complex **A** (Figure 1; note that this is the first compound in its class that shows bis-η^2-*C,N*-bonding)[9c] but also of homo- and heterobimetallic complexes of Pd(II) and Pt(II). The development of this indirect but very effective and general methodology to C_2N_4 bimetallic species was required since direct cyclometalation routes[10d,11] are not yet available for tetramine **1**. In this paper some reactions described for Pt(II) complexes of NCN have been applied to the new 1,4-bis-Pt(II) complexes of C_2N_4 to study possible cooperative effects between the two metal centers. This has resulted in the preparation and isolation of a number of novel bimetallic SO_2 and MeI complexes with interesting bonding arrangements.[12,13]

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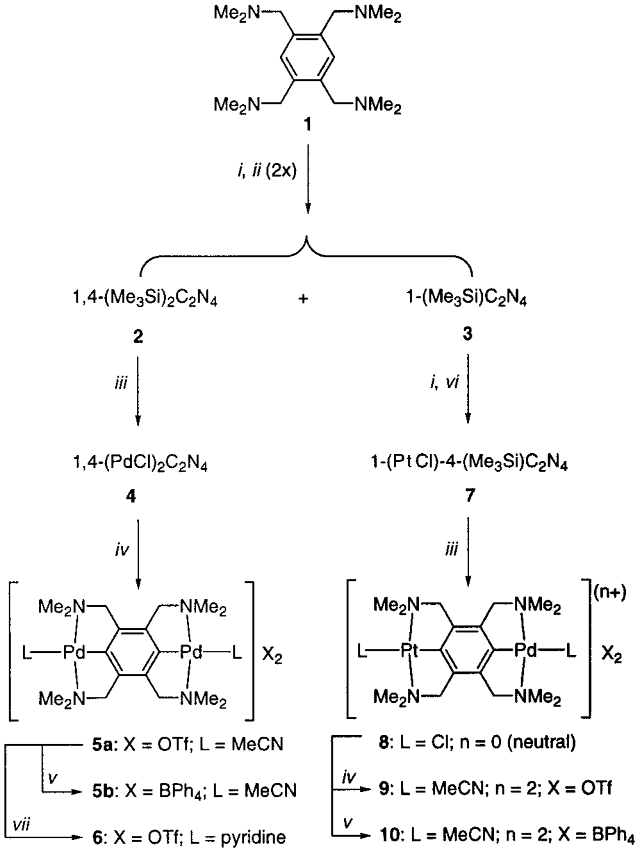
Scheme 1. Synthesis and Subsequent Metalation Reactions of 2 and 3 Yielding Neutral and Cationic Dipalladium(II) and Heterobimetallic Platinum(II)−Palladium(II) Complexes 4 and 5 and 8−10[a]



[a] Conditions: (*i*) *n*-BuLi, hexane, room temp, 18 h; (*ii*) Me_3SiOTf, THF, room temp, 5 min; (*iii*) $[Pd(OAc)_2]$, MeOH (18 h) and LiCl, MeOH (15 min), room temp; (*iv*) AgOTf, MeCN (20 min); (*v*) $NaBPh_4$, MeCN (5 min), room temp; (*vi*) $[PtCl_2(SEt_2)_2]$, THF, 3 h, room temp; (*vii*) pyridine, MeCN, room temp.

Results

Synthesis of Bimetallic C_2N_4 Complexes 4−10. In Scheme 1 the synthetic pathways are outlined to new bimetallic complexes **4**−**10** containing the C_2N_4 ligand system starting from the tetramine $C_6H_2(CH_2NMe_2)_4$-1,2,4,5, **1**, as precursor. The route to the neutral bispalladium(II) complex $[1,4\text{-}(PdCl)_2\{C_6(CH_2NMe_2)_4\text{-}2,3,5,6\}]$, **4** ($=[(PdCl)_2(C_2N_4)]$), and the corresponding ionic species $[1,4\text{-}(PdL)_2\{C_6(CH_2NMe_2)_4\text{-}2,3,5,6\}](X_2)$ (L = MeCN; **5a**, X = OSO_2CF_3 = OTf; **5b**, X = BPh_4) involves the disilylated tetraamine $[1,4\text{-}(Me_3Si)_2\{C_6(CH_2NMe_2)_4\text{-}2,3,5,6\}]$, **2** ($=[(Me_3Si)_2(C_2N_4)]$),[14] obtained directly from **1**.[6]

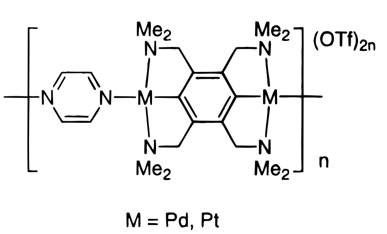


Figure 2. Schematic representation of the organometallic polymers that are formed when bimetallic complexes **5a** and **14a** are treated with an equimolar amount of pyrazine.

2 is first reacted with $[Pd(OAc)_2]$ in MeOH for 20 h at room temperature to afford an intermediate neutral acetato species (not illustrated) which is the result of two successive C−Si bond cleavage reactions.[6,10] Addition of LiCl then affords the bis(chloropalladium) complex $[1,4\text{-}(PdCl)_2(C_2N_4)]$, **4**. Complex **4** has poor solubility in common organic solvents. To aid solution studies and characterization, **4** was converted into the more soluble ionic derivative $[1,4\text{-}\{Pd(MeCN)\}_2(C_2N_4)](OTf)_2$, **5a** (see Experimental Section). The NMR spectroscopic and elemental analysis data of **5a** were in agreement with the bimetallic structure proposed (Scheme 1). The ^1H NMR spectrum of **5a** shows only one singlet for the coordinated and the uncoordinated MeCN ligands, which points to a ligand exchange process that is fast on the NMR time scale.

Treatment of an MeCN solution of the Pd/Pd complex **5a** with $NaBPh_4$ dissolved in MeCN resulted in the precipitation of the corresponding colorless bis(tetraphenylborate) salt $[1,4\text{-}\{Pd(MeCN)\}_2(C_2N_4)](BPh_4)_2$, **5b**. Recrystallization of **5b** from hot MeCN gave crystals that were suitable for an X-ray crystallographic study, and the molecular geometry found (see ref 6 for figure) is discussed later.

Addition of excess pyridine to a solution of the bisacetonitrile complex **5a** in MeCN results in the formation of a new bispyridine analogue $[1,4\text{-}\{Pd(py)\}_2(C_2N_4)](OTf)_2$, **6** (Scheme 1), which has been isolated as pale yellow crystals in high yield after appropriate workup (see Experimental Section). This reaction was used as a model reaction for the synthesis of an organopalladium(II) polymer (Figure 2).

In an attempt to prepare the latter, a titration of a solution of **5a** in CD_3CN with pyrazine was performed, as recently described for a related bis-Pd(II) complex by Loeb and Shimizu.[5] This reaction was followed by ^1H NMR spectroscopy. Upon addition of pyrazine, the resonances of the CH_2NMe_2 groups of the C_2N_4 ligand of **5a** become slightly broadened when the point of equivalence in the titration is reached. At the same time, new resonances appear that were attributed to the concomitant formation of the bimetallic bispyrazine complex $[1,4\text{-}\{Pd(pyz)\}_2(C_2N_4)](OTf)_2$. Addition of an excess of pyrazine resulted in complete conversion of **5a**, but a pure product could not be isolated from the mixture. The ^1H NMR spectrum of the latter clearly showed the presence of $[1,4\text{-}\{Pd(pyz)\}_2(C_2N_4)](OTf)_2$ together with free pyrazine, but the appearance of

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[12] For related platinated cyclohexadienyl arenium ion species, see: (a) van Koten, G.; Timmer, K.; Noltes, J. G.; Spek, A. L. *J. Chem. Soc., Chem. Commun.* **1978**, 250. (b) Grove, D. M.; van Koten, G.; Ubbels, H. J. C. *Organometallics* **1982**, *1*, 1366. (c) Grove, D. M.; van Koten, G.; Louwen, J. N.; Noltes, J. G.; Spek, A. L.; Ubbels, H. J. C. *J. Am. Chem. Soc.* **1982**, *104*, 6609. (d) Terheijden, J.; van Koten, G.; Vinke, I. C.; Spek, A. L. *J. Am. Chem. Soc.* **1985**, *107*, 2891. For a description of the 1,2-sigmatropic Me-shift, see: (e) Ortiz, J. V.; Havlas, Z.; Hoffmann, R. *Helv. Chim. Acta* **1984**, *67*, 1.

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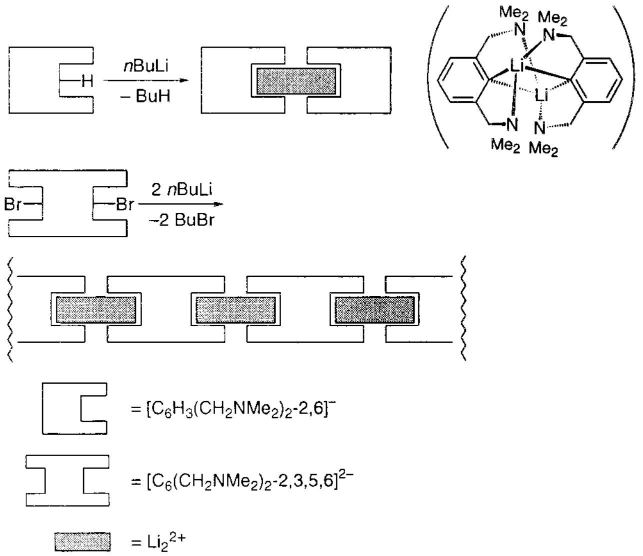


Figure 3. Schematic representation of the dimeric structures of NCN−Li compounds and of the polymeric organodilithium species derived from the C_2N_4 ligand.

coordinated and noncoordinated pyrazine as one singlet indicates a fast exchange at the metal center, as described above for the acetonitrile complex **5a**.

The route to the neutral heterobimetallic species $[1\text{-}(PtCl)\text{-}4\text{-}(PdCl)\{C_6(CH_2NMe_2)_4\text{-}2,3,5,6\}]$, **8** (=[(PtCl)(PdCl)($C_2N_4$)]), and the corresponding ionic species $[1\text{-}(PtL)\text{-}4\text{-}(PdL)\{C_6(CH_2NMe_2)_4\text{-}2,3,5,6\}](X_2)$ (L = MeCN; **9**, X = OSO_2CF_3 = OTf; **10**, X = BPh_4) proceeds via the monosilane $[1\text{-}(Me_3Si)\{C_6H(CH_2NMe_2)_4\text{-}2,3,5,6\}]$, **3**,[14] obtained directly from **1**.[6] In the first step **3** is lithiated with *n*-BuLi to afford the organolithium species $[1\text{-}(Me_3Si)\text{-}4\text{-}(Li)(C_2N_4)]_2$, which has not been isolated. This organolithium species should have a dimeric structure in the solid state (see Figure 3) and in solution since its related nonsilylated analogue $[1\text{-}(H)\text{-}4\text{-}(Li)(C_2N_4)]_2$ and other organolithium species derived from NCN ligands have been shown to form dimers both in solution and in the solid state.[7,8b] Reaction of the lithium reagent $[1\text{-}(Me_3Si)\text{-}4\text{-}(Li)(C_2N_4)]_2$ with $[PtCl_2(SEt_2)_2]$ in THF gave the heterobimetallic Si/Pt C_2N_4 complex, $[1\text{-}(Me_3Si)\text{-}4\text{-}(PtCl)(C_2N_4)]$, **7**, which was isolated in moderate yield. In this reaction no products resulting from electrophilic C−Si bond platination were found; the reaction mixture contained only the platinum complex **7** and unreacted starting material. The NMR spectroscopic and elemental microanalysis data of **7** are in agreement with the bimetallic structure proposed (Scheme 1).

Treatment of the Pt/Si complex **7** with a solution of $[Pd(OAc)_2]$ in a 1:1 mixture of CH_2Cl_2 and MeOH results in complete and selective cleavage of the C−Si bond *para* to the Pt−C bond, and subsequent addition of LiCl affords the heterobimetallic Pt/Pd C_2N_4 complex, $[1\text{-}(PdCl)\text{-}4\text{-}(PtCl)(C_2N_4)]$, **8**, which was isolated as a white solid in high yield. Heterobimetallic Pt/Pd complex **8** has, like its Pd/Pd analogue **4**, poor solubility in both polar and nonpolar solvents and was converted to heterobimetallic ionic bistriflate complex **9** by treatment with 2 equiv of AgOTf in MeCN as described above for **4**. The NMR spectroscopic and elemental analysis data of **9** are in agreement with the heterobimetallic structure illustrated in Scheme 1.

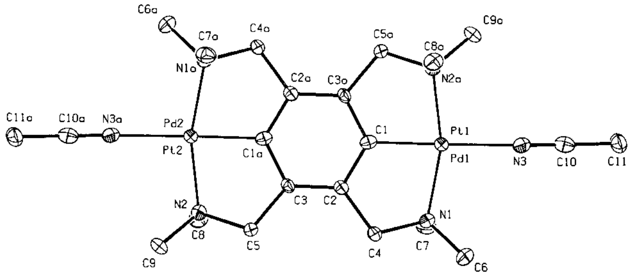
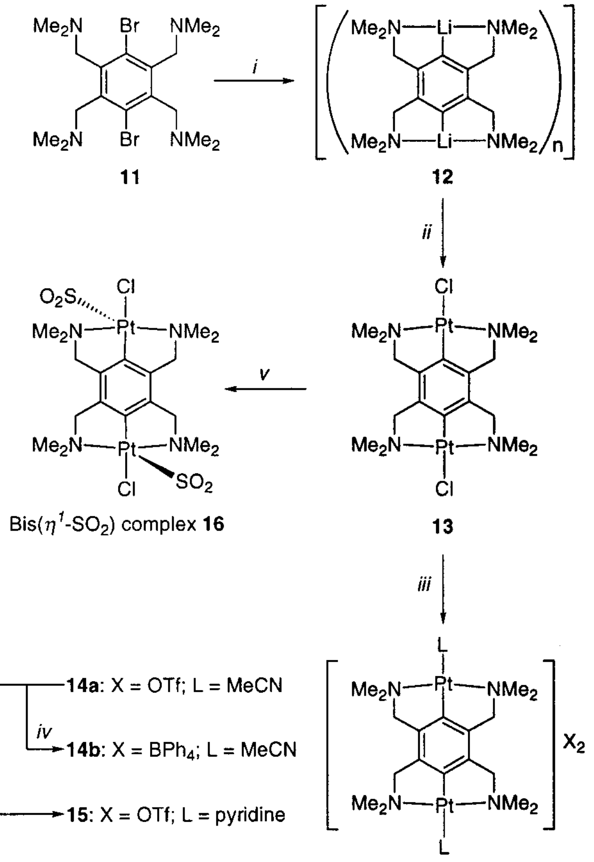


Figure 4. ORTEP drawing (50% probability atomic displacement ellipsoids) of $[1\text{-}\{Pd(MeCN)\}\text{-}4\text{-}\{Pt(MeCN)\}\text{-}\{C_6(CH_2NMe_2)_4\text{-}2,3,5,6\}]^{2+}$, the dication of **10**. Hydrogen atoms, the anions (BPh_4^-), and cocrystallized solvent molecules (MeCN) have been omitted for clarity.

Scheme 2. Synthesis and Derivatization of Homobimetallic Complexes 12−16[a]



[a] Conditions: (*i*) *n*-BuLi (2 equiv), Et_2O, −78 → 0 °C; (*ii*) $[PtCl_2(SEt_2)_2]$, THF, room temp; (*iii*) AgOTf, MeCN, room temp; (*iv*) $NaBPh_4$, MeCN, room temp; (*v*) SO_2(g), CH_2Cl_2, room temp; (*vi*) pyridine, MeCN, room temp.

A MeCN solution of the Pt/Pd bistriflate complex **9**, when treated with $NaBPh_4$ dissolved in MeCN, leads to precipitation of the analogous bistetraphenylborate species **10**. Recrystallization of **10** from hot MeCN afforded crystals that were suitable for an X-ray analysis. The X-ray molecular geometry found for the heterobimetallic dication of **10**, shown in Figure 4, is discussed later.

In Scheme 2 are summarized the synthetic pathways to various neutral and ionic bisplatinum(II) complexes of C_2N_4, **13**−**16**, that make use of $C_6Br_2(CH_2NMe_2)_4$-2,3,5,6, **11**, as the organic ligand precursor. The synthesis and characterization of this aryl dibromide is described elsewhere.[14]

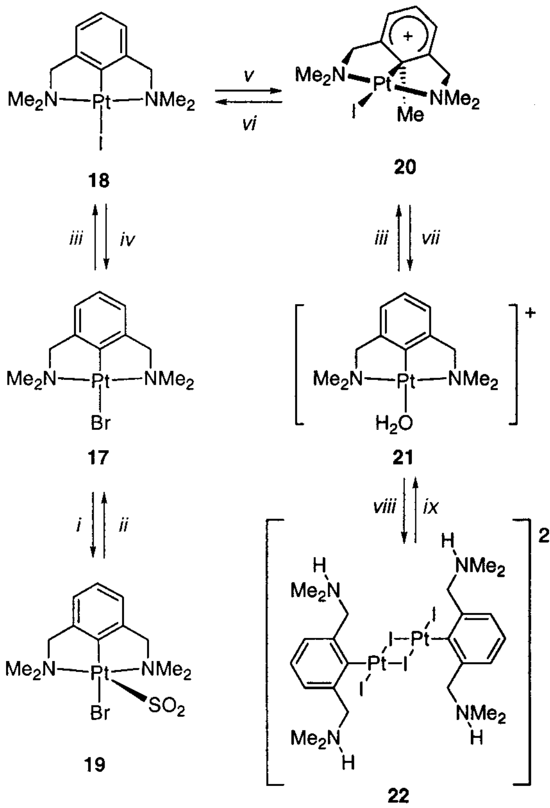
Addition of 2 molar equiv of *n*-BuLi to a suspension of aryl dibromide **11** in Et_2O at low temperature, followed by warming to room temperature, resulted in the formation of a white precipitate of the polymeric organodilithium species [1,4-$Li_2(C_2N_4)$], **12**.[14] We believe that this organodilithium species is polymeric since the related monolithium species derived from NCN ligands, i.e. "NCN−Li" (Figure 3), form dimers both in solution and in the solid state. One could expect that if two of these "NCN−Li" units are present in one molecule, such compounds form linear rodlike polymeric structures via self-assembly (Figure 3).

The reaction of a THF solution of $[PtCl_2(SEt_2)_2]$ with a suspension of the dilithio species **12** afforded a white precipitate of the bis(chloroplatinum) complex [1,4-$(PtCl)_2\{C_6(CH_2NMe_2)_4$-2,3,5,6}], **13**, which was isolated as a white solid in 93% yield. Complex **13** has poor solubility characteristics in common organic solvents and is even less soluble than its bispalladium analogue **4**.

The bisplatinum complex **13** was converted quantitatively into the corresponding ionic MeCN complex [1,4-{Pt(MeCN)}$_2\{C_6(CH_2NMe_2)_4$-2,3,5,6}]$(OTf)_2$, **14a**, by titrating a suspension of **13** in MeCN with a solution of AgOTf in MeCN as described above for Pd/Pd complex **5a**. Acetonitrile complex **14a** is slightly soluble in neat MeCN but becomes significantly more soluble upon addition of a small amount ($\leq 10\%$) of water. Addition of a solution of $NaBPh_4$ in MeCN to a solution of **14a** in MeCN affords the corresponding ionic complex **14b**. Subsequent recrystallization of the poorly soluble **14b** from boiling MeCN gave suitable crystals for an X-ray structure determination. The X-ray molecular geometry found for **14b** is discussed later. The spectroscopic and elemental microanalysis data obtained for complexes **14a**,**b** are in agreement with the proposed structures illustrated in Scheme 2.

In bisplatinum complex **14a** the MeCN ligands can be easily exchanged for pyridine, as was already shown to be the case for the analogous ionic bispalladium(II) complex **5a**. Addition of excess pyridine to a solution of **14a** in MeCN results in the formation of the new bispyridine analogue [1,4-{Pt(py)}$_2(C_2N_4)$]$(OTf)_2$, **15** (Scheme 2), which has been isolated as pale yellow crystals in high yield after appropriate workup (see Experimental Section). This reaction was used as a model reaction for the synthesis of an organoplatinum(II) polymer (Figure 2). In an attempt to prepare the latter, a titration of a solution of **14a** in CD_3CN with pyrazine was performed, as described above for the related bis-Pd(II) complex **5a**. This reaction was followed by ^1H NMR of the resulting solution. ^1H NMR spectra of **14a** showed that upon addition of pyrazine the resonances of the CH_2NMe_2 groups of the C_2N_4 ligand become slightly broadened when the point of equivalence in this titration is reached. Isolation of the bimetallic bispyrazine complex [1,4-{Pt(pyz)}$_2(C_2N_4)$]$(OTf)_2$ in pure form could, however, not be established. The ^1H NMR spectrum of the latter solution clearly pointed to the presence of [1,4-{Pt(pyz)}$_2(C_2N_4)$]$(OTf)_2$ together with free pyrazine, but the appearance of coordinated and noncoordinated pyrazine as one singlet indicates the presence of fast exchange at the metal center, as described above for the palladium(II) and platinum(II) acetonitrile complexes **5a** and **14a**, respectively.

Scheme 3. Reactivity of Mononuclear Platinum Complexes of NCN. Reversible C−C Bond Formation (with MeX; X = Br, I, OTf), Reversible Binding of SO_2, and Formation of the Diiodide-Bridged Dimeric Complex 22 by Reaction of the Solvento Complex 21 with R−I (R = Et, Allyl, Benzyl)[a]



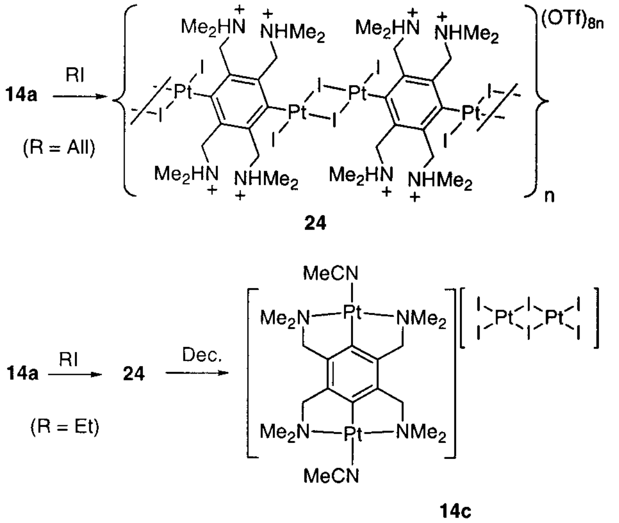
[a] Conditions: (*i*) SO_2, CH_2Cl_2; (*ii*) N_2, CH_2Cl_2 or vacuum; (*iii*) MeI, acetone/H_2O; (*iv*) MeBr, acetone/H_2O; (*v*) MeOTf, acetone/H_2O; (*vi*) NaI, acetone/H_2O; (*vii*) acetone/H_2O; (*viii*) R−I, acetone/H_2O (R = Et, Bn, allyl), −ROH; (*ix*) iPr_2NEt, acetone.

One general characteristic of both the neutral and ionic complexes described above is that they are air and moisture stable both in the solid state and in solution (MeCN) at ambient temperature.

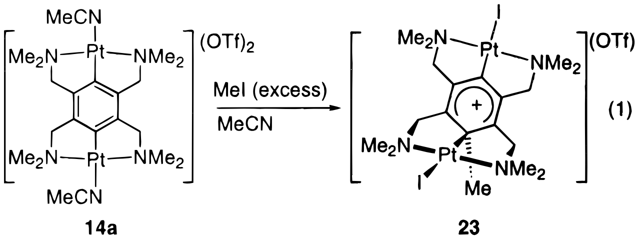
Reactivity of Bisplatinum C_2N_4 Complexes 13 and 14a. In the case of phenylene-bridged bimetallic systems such as **13** or **14** it can be anticipated that the metal centers express their reactivity cooperatively. To study this aspect we first examined cyclic voltammetry of the dicationic triflate complexes **5a** (Pd/Pd), **9** (Pd/Pt), and **14a** (Pt/Pt) to see whether bis(M^{4+}) complexes of C_2N_4 would be readily available. Unfortunately, the cyclic voltammograms of all three complexes in dry acetonitrile showed irreversible oxidations (at ca. 1.3 V, vs SCE).

The chemical reactivity of Pt(II)/Pt(II) complexes **13** and **14** was examined with SO_2 and iodoalkanes, and these results are summarized in Schemes 2 and 4 and

Scheme 4. Proposed Structure and Decomposition Pathway of the Organometallic Polymer 24 and the Formation of the Anionic $[Pt_2I_6]^{2-}$ Units of 14c



in eq 1. Corresponding reactions with neutral mono-



(1)

nuclear complexes [(NCN)PtX] (X = Br (**17**), I (**18**) and ionic complex $[(NCN)Pt(H_2O)](OTf)$ **21**; NCN = $[C_6H_3(CH_2NMe_2)_2\text{-}2,6]^-$; see Scheme 3) have been reported earlier and provided unique isolable arenium species[12] and η^1-SO_2 adducts,[13a,c] and it would be extremely interesting to see whether in the new bimetallic complexes described above the same reactions occur and aspects of cooperativity could be discovered.

When gaseous SO_2 was bubbled through a suspension of bisplatinum complex **13** in CH_2Cl_2, an orange reaction mixture was obtained and all of the poorly soluble starting material dissolved. Slow diffusion of Et_2O into this solution resulted in the formation of large orange crystals of the bis-SO_2 adduct complex $[\{PtCl(\eta^1\text{-}SO_2)\}_2(C_2N_4)]$, **16**, which has been characterized by an X-ray crystallographic analysis. The molecular structure shows η^1-SO_2 bonding to both platinum centers, which is shown in Figure 5 (vide infra). Complex **16** can also be prepared by exposing a sample of solid **13** to an SO_2 atmosphere for several minutes. Unlike Pt/Pt complex **13**, its bis-SO_2 adduct **16** is readily soluble in chlorinated organic solvents, and this has allowed solution NMR spectroscopic investigations of this latter species. The NMR spectroscopic data obtained for bimetallic Pt/Pt C_2N_4 complex **16** are similar to those obtained for the related mononuclear complex $[PtCl(\eta^1\text{-}SO_2)(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$, **19**,[13a] which is discussed later. Solid samples of orange **16** kept under vacuum for 0.5 h at 50 °C, or in air for 24 h, lose their color, and the white solid formed has been identified as **13**; that is, SO_2 binding to the bisplatinum(II) complex **13** is reversible.

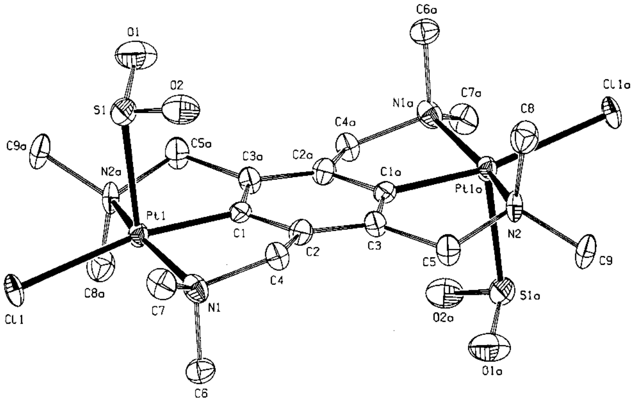


Figure 5. ORTEP drawing (50% probability atomic displacement ellipsoids) of the homodinuclear 1,4-phenylene-bridged bisplatinum complex, $[1,4\text{-}\{PtCl(\eta^1\text{-}SO_2)\}_2\{C_6(CH_2NMe_2)_4\text{-}2,3,5,6\}]$, **16**. Hydrogen atoms and a cocrystallized solvent molecule (CH_2Cl_2) have been omitted for clarity.

Note that complex **19** loses its SO_2 when placed in a vacuum for 5 min at room temperature. UV/vis measurements (SO_2-saturated CH_2Cl_2 solution) show that the distinctive orange-red color of SO_2 adduct **16** comes from a combination of an absorption at 434 nm ($\epsilon = 5357\ M^{-1}\ cm^{-1}$) and a much stronger band at 348 nm ($\epsilon = 20\ 517\ M^{-1}\ cm^{-1}$).

In earlier studies it was shown that the mononuclear platinum NCN complexes [(NCN)PtX] (X = Cl; **17**, X = Br; **18**, X = I) also form orange SO_2 adducts both in the solid state and in solution, and therefore, one can conclude that the effect of the second metal center in bisplatinum complex **16** in this type of adduct-forming reaction is not great. This independence in the reactivity of the two platinum centers of bimetallic **13** is emphasized by comparison of the UV/vis data of its SO_2 adduct **16** with those of the SO_2 adduct of, for example, [(NCN)PtCl]. The latter complex provides an absorption at 411 nm ($\epsilon = 2566\ M^{-1}\ cm^{-1}$) and another at 352 nm ($\epsilon \approx 5000\ M^{-1}\ cm^{-1}$). These values are similar to those found for **16**, and this suggests that the relevant orbitals involved in the MLCT on the individual metal centers are not intimately connected. Interestingly, the ϵ value of the 434 nm absorption of complex **16** is, based on the ϵ value of the 411 nm band of complex $[(NCN)PtCl(\eta^1\text{-}SO_2)]$, significantly higher than expected for two independently operating metal centers; that is, there is some indication for intermetal cooperativity.

The reaction of a colorless solution of ionic triflate complex **14a** in MeCN with an excess of iodomethane (eq 1), as well as the reaction of a white suspension of **14a** in pure iodomethane, gradually resulted in the slow formation of a deep red reaction mixture over a period of 2 weeks. After an appropriate workup, in which the red product was separated from starting material, the diplatinated arenium species $[1,4\text{-}\{PtI\}_2\{C_6Me\text{-}1\text{-}(CH_2NMe_2)_4\text{-}2,3,5,6\}](OTf)$, **23**, was obtained in moderate yield (27%). Recrystallization of **23**, by slow addition of Et_2O (slow distillation by vapor diffusion) to a dark red CH_2Cl_2 solution, afforded analytically pure dark red crystals that were suitable for an X-ray crystallographic study. The molecular geometry of **23**, illustrated in Figure 6, is discussed below.

Attempted ^1H and ^{13}C NMR measurements of solutions of **23** in either CD_3CN, CD_2Cl_2, or $CDCl_3$ yielded,

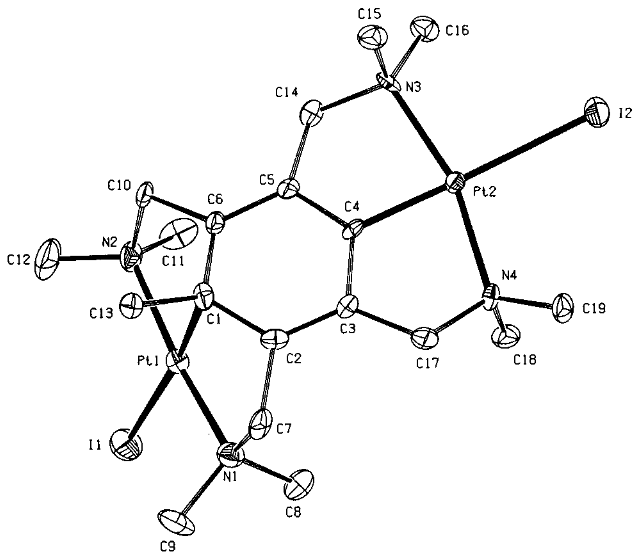


Figure 6. ORTEP drawing (50% probability atomic displacement ellipsoids) of a novel cationic C−Pt σ-bonded bisplatinum(II) arenium ion complex, $[1,4\text{-}\{PtI\}_2\{C_6Me\text{-}1\text{-}(CH_2NMe_2)_4\text{-}2,3,5,6\}]^+$, the cation of **23**. Hydrogen atoms and the anion ($OSO_2CF_3^-$) have been omitted for clarity.

due to the low solubility of the complex, rather poor spectra that contained resonances similar to those of the mononuclear complexes **18** and **20**, together with resonances of other platinated species. Moreover, the reversibility of the C−C bond formation reaction to form monometallic complex **20** was shown by its reaction with water/acetone, producing **21**.[12b] Therefore we conclude that in the absence of MeI complex **23** in solution at low concentration undergoes decomposition reactions probably involving the loss of MeI.

In earlier studies it was shown that the reaction of $[(NCN)Pt(H_2O)](OTf)$, **21**, with iodomethane afforded, instead of the expected oxidative addition product $[Pt^{IV}(Me)I(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)](OTf)$, a unique arenium complex **20**, with a σ-bonded platinum substituent (Scheme 3). Like complex **23** this species had poor solubility characteristics. In both the mono- and bimetallic complexes **20** and **23** the methyl group of the reacted iodomethane has become bonded, via a 1,2-sigmatropic Me-shift,[12e] to the C atom of the aryl ring that is σ-bonded to the platinum center. Interestingly, however, the rate of the reaction of excess iodomethane with the bisplatinum complex Pt/Pt complex **14a** to form arenium species **23** is much slower than the corresponding rate for formation of mononuclear arenium species **20** from the ionic NCN platinum complex **21**. The latter reaction is complete within 24 h, whereas the reaction of bimetallic **14a** with MeI is still not complete after two weeks. This suggests that there is a strong substituent effect of one of the platinum centers in complex **14a** on the reactivity of the other metal center; that is, there is intermetal cooperativity that deactivates the platinum centers for oxidative addition of iodomethane, which is presumed to be the first step in the formation of an arenium complex such as **14a** or **20**.[12]

To further investigate the chemical behavior of bimetallic complex **14a**, it was reacted with other iodoalkanes R−I (R = ethyl, allyl). When a solution of **14a** in aqueous MeCN was treated with allyl iodide (Scheme 4), a slow reaction occurred, resulting in the precipitation of a white solid after 48 h. This solid was not soluble in common organic solvents, and only elemental microanalysis could be used to identify this probably organometallic species $[1,4\text{-}\{PtI(\mu\text{-}I)_2\}_2(C_6\{CH_2N(H)\text{-}Me_2\}_4\text{-}2,3,5,6\})](OTf)_2$, **24**. We think that this material has an iodo-bridged polymeric structure, shown schematically in Scheme 4, based on earlier related studies on the reactivity of the mononuclear NCN platinum complex **21** with allyl iodide, to afford iodo-bridged bimetallic complex **22** (Scheme 3).[3c] When a solution of **14a** in aqueous MeCN was treated with iodoethane, as expected an extremely slow reaction occurred, and after a period of two months there was the expected white precipitate, along with the formation of black crystals of the tetrametallic complex $[1,4\text{-}\{Pt(MeCN)\}_2\text{-}(C_6\{CH_2NMe_2\}_4\text{-}2,3,5,6)][Pt_2I_6]$, **14c**. Both species were not soluble, but the black crystals formed in this slow reaction were suitable for an X-ray crystallographic analysis. The molecular geometry of **14c** shows it to be an ionic species with a diplatinated dication (as was found for ionic complex **14b**) together with the complex counteranion $[Pt_2I_6]^{2-}$ (the structure of the latter is given as Supporting Information). This counterion shows the structural resemblance of this ionic species to the iodo-bridged bimetallic complex **22** derived from NCN platinum complex **21** (cf. Scheme 3).[3c]

Presumably, also in the reaction of **14a** with iodoalkanes, similar species with the iodo-bridged structural elements are formed. Most probably, the crystals of **14c** that had been formed in the reaction of **14a** with iodoethane are products of a decomposition reaction of the presumed polymeric primary product of this reaction, **24**, by C_{aryl}−Pt bond hydrolysis of the latter species. One possible hydrolysis reaction might involve hydroiodic acid, which can be formed by reaction of the iodoalkane with water.

Spectroscopic Aspects of the New Bimetallic Complexes. The new dinuclear palladium and platinum organometallic complexes of the C_2N_4 ligand were characterized by ^1H and ^{13}C NMR spectroscopy where possible. As mentioned earlier, certain species—but particularly the *neutral* platinum and palladium complexes of C_2N_4—have very poor solubility characteristics, and data quality even for ^1H NMR spectra was sometimes low. For complexes containing platinum, the presence of the ^{195}Pt nucleus ($I = {}^1/_2$, 33.8% natural abundance) often provides satellites with characteristic coupling constant data, and these are a valuable aid to structural characterization. A selection of relevant spectroscopic data is summarized in Table 1.

In the ^1H NMR spectra of both $[1,4\text{-}(PdCl)_2(C_2N_4)]$, **4** ($CDCl_3$, very poor signal-to-noise ratio), and $[1,4\text{-}(PdMeCN)_2(C_2N_4)](OTf)_2$, **5a** ($CD_3CN$), there are no aromatic proton resonances and just two singlet resonances corresponding to the four equivalent methylene and methyl groups of the CH_2NMe_2 substituents. In both cases these resonances are at lower field than those of the free ligand precursor 1,2,4,5-tetrakis[(dimethylamino)methyl]benzene, **1**, and this is indicative for coordination of these N-donor groups to palladium. Similar downfield shifts are also encountered in the mononuclear palladium(II) complexes of NCN.[15]

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[15] Grove, D. M.; van Koten, G.; Louwen, J. N.; Noltes, J. G.; Spek, A. L.; Ubbels, H. J. C. *J. Am. Chem. Soc.* **1982**, *104*, 6609.

Table 1. Selected ^1H and ^{13}C NMR Data of the Ligand Precursors 1 and 4 and of the 1,4-phenylene Bridged Bimetallic Complexes 5a, 6, 7, 9, 11, 14a, 15, and 16 (L_1 = MeCN, L_2 = Pyridine)

	^1H chemical shifts (δ)[a]		^{13}C chemical shifts (δ)[a]			
compound	CH_2	NMe_2	C_{ipso}	C_{ortho}	CH_2	NMe_2
$(C_2N_4)H_2$, **1**[b,c]	3.41	2.14	136.3	132.4	61.0	45.5
$(C_2N_4)Br_2$, **11**[b,c]	3.97	2.27	139.4	131.9	59.7	45.4
$[(C_2N_4)(PdCl)_2]$, **4**[b,c]	3.80	2.94				
$[(C_2N_4)\{Pd(L_1)\}_2](OTf)_2$, **5a**[b,d]	3.87	2.80	153.1	139.4	72.9	53.4
$[(C_2N_4)\{Pd(L_2)\}_2](OTf)_2$, **6**[b,d]	3.94	2.69				
$[(C_2N_4)\{SiMe_3\}\{PtCl\}]$, **7**[b,c]	4.11 (45.3)	3.04 (35.9)	147.0 (1000)	139.1 (44)	77.7 (60)	54.4 (13)
	3.37	2.01	133.5	141.7 (75)	62.6	44.6
$[(C_2N_4)\{Pd(L)\}\{Pt(L)\}](OTf)_2$, **9**[b,d]	4.08 (46.5)	2.96 (39.0)	152.7 (995)	138.9 (82)	75.7 (64)	55.1 (16)
	3.86	2.80	141.2	138.8 (43)	72.8 (11)[e]	53.4
$[(C_2N_4)\{Pt(L_1)\}_2](OTf)_2$, **14a**[b,d]	3.99 (46.4)	2.99 (38.8)	140.8 (995)	138.3 (83 and 42)	75.8 (65)	55.2 (16)
$[(C_2N_4)\{Pt(L_2)\}_2](OTf)_2$, **15**[b,d]	4.08 (47.7)	2.76 (39.5)				
$[(C_2N_4)\{PtCl(\eta^1\text{-}SO_2)\}_2]$, **16**[b,c]	4.13 (39.7)	3.22 (31.7)	145.2	135.3	74.5	54.1 (26)

[a] Coupling constants $^nJ_{Pt-H}$ and $^nJ_{Pt-C}$ (Hz) are given in parentheses. [b] $C_2N_4 = [C_6(CH_2NMe_2)_4\text{-}2,3,5,6]^{2-}$. [c] In $CDCl_3$ at 298 K. [d] In CD_3CN + 10% D_2O at 298 K. [e] $^4J_{Pt-C}$ = 11 Hz.

We were unable to obtain a ^{13}C NMR spectrum of **4**, but that of **5a** (CD_3CN) contains two resonances for the aromatic ring carbon atoms and two resonances for the CH_2NMe_2 N-donor groups. These limited spectroscopic data for **4** and **5a** show that in solution these are highly symmetrical species with fully equivalent metal centers and three mutually perpendicular mirror planes running through the center of the 1,4-bimetalated aromatic ring. This overall geometry has been confirmed by the solid-state structure obtained for the bimetalated tetraphenylborate complex **5b** (vide infra).

For complex **7** the heterobimetallic structure and the presence of a single platinum center are clearly expressed in the NMR spectroscopic data. For example, the ^1H NMR ($CDCl_3$) spectrum of **7** shows singlet resonances at 4.11 ($^3J_{Pt-H}$ = 45.3 Hz) and 3.37 ppm for the CH_2 groups and at 3.04 ($^3J_{Pt-H}$ = 35.9 Hz) and 2.01 ppm for the NMe_2 groups. The resonances with ^{195}Pt satellites represent the CH_2NMe_2 N-donor groups that are coordinated to the Pt center, and their positions are in agreement with those found for related chloroplatinum complexes derived from NCN.[16] The proton resonance for the $SiMe_3$ group is at 0.31 ppm. The ^{13}C NMR ($CDCl_3$) spectrum of **7** shows four resonances in the aromatic region, consistent with a 1,4-heterodisubstituted phenylene ligand, as well as four resonances for two different CH_2NMe_2 groups and a single $SiMe_3$ resonance in the aliphatic region.

For the ionic Pd/Pt complex **9** the NMR data clearly show, as for complex **7**, the heterobimetallic nature of this species. In the ^1H NMR (CD_3CN + 10% D_2O) spectrum of complex **9** there are resonances for two inequivalent *N,C,N′*-coordination moieties. One set of CH_2NMe_2 signals has ^{195}Pt satellites with coupling constants consistent with N-donor atom coordination to the platinum(II) center.[17] The other set shows no ^{195}Pt satellites and has resonance positions consistent with N-coordination of the CH_2NMe_2 groups to a palladium(II) center.[15] The ^{13}C NMR (CD_3CN + 10% D_2O) spectrum of complex **9** unambigiously reveals the presence of one platinum(II) center and one palladium(II) center in the same molecule and excludes the possibility that **9** is a 1:1 mixture of a bispalladium and a bisplatinum species. There are two separate resonances for the aromatic carbon atoms bearing the CH_2NMe_2 groups, and each has only one set of ^{195}Pt satellites. In a symmetrically doubly platinated aryl ring such as found in **14** the carbon atoms bearing the CH_2NMe_2 groups would give rise to a single resonance with two sets of satellites, i.e., $^2J_{Pt-C}$ and $^3J_{Pt-C}$ (vide infra).

The ^1H and ^{13}C NMR (CD_3CN + 10% D_2O) spectra of complex **14a** give data that allow definitive identification of a symmetrically doubly platinated species. The ^1H NMR spectrum is simple, with two resonances for the CH_2NMe_2 groups, each of which shows a single set of platinum satellites. Similarly, the ^{13}C NMR spectrum shows only two aromatic carbon resonances and two resonances from the four equivalent CH_2NMe_2 groups, with chemical shift data and $^{13}C-^{195}Pt$ coupling constants that are similar to those of related mononuclear NCN species.[17] However, in the ^{13}C NMR spectrum of **14a** several resonances exhibit double sets of ^{195}Pt satellites, and the second-order nature of the CH_2 group satellite lines even allows an estimation of the long-range $^5J_{Pt-Pt}$ (ca. 5 Hz) through spin simulation techniques.[18]

The bimetallic complex **13** proved too insoluble for NMR spectroscopic investigations, but its bis-SO_2 adduct, complex **16**, is readily soluble in $CDCl_3$. On the basis of the solid-state X-ray data for the mono- and bimetallic SO_2 adducts **19** (Scheme 3) and **16** (Figure 5), respectively, one would expect solution NMR data to reflect the asymmetry represented by the square pyramidal geometry of the platinum centers. Such a five-coordinate metal environment would give rise to several resonances resulting from diastereotopic protons of the CH_2 and the NMe_2 groups. However, the ^1H NMR ($CDCl_3$ + SO_2) spectrum of a solution of **16** shows only two singlet resonances for the CH_2NMe_2 groups, and each of these has ^{195}Pt satellites; that is, all four CH_2NMe_2 groups are equivalent and coordinated to platinum on the NMR time scale. Thus, bimetallic bis-SO_2 adduct **16** appears to have a high degree of molecular symmetry, like that of the bimetallic complexes **4** and **13**. In the ^{13}C NMR spectrum of **16** the situation is similar and there are just two singlet aromatic carbon resonances and two aliphatic resonances (both showing coupling to ^{195}Pt) for the CH_2-

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[16] Terheijden, J.; van Koten, G.; Muller, F.; Grove, D. M.; Vrieze, K.; Nielsen, E.; Stam, C. H. *J. Organomet. Chem.* **1986**, *315*, 401.

[17] Schmülling, M.; Grove, D. M.; van Koten, G.; van Eldik, R.; Veldman, N.; Spek, A. L. *Organometallics* **1996**, *15*, 1384.

[18] Budzelaar, P. H. M. *gNMR*; Cherwell Scientific Publishing Limited: Oxford, U.K.

Table 2. Selected Bond Distances (Å) and Bond and Dihedral Angles (deg) of Ionic Complexes $[1\text{-}\{M(MeCN)\}\text{-}4\text{-}\{M'(MeCN)\}\{C_6(CH_2NMe_2)_4\text{-}2,3,5,6\}](X)_2$ (5b, M = M′ = Pd, X = BPh_4; 10, M = Pd, M′ = Pt, X = BPh_4; 14b, M = M′ = Pt, X = BPh_4; 14c, M = M′ = Pt, X = $[Pt_2I_6]$; esd's in Parentheses)[a]

	5b	10	14b	14c
Bond Distances				
M−C(1)	1.915(3)	1.910(5)	1.917(4)	1.906(16)
M−N(1)	2.098(2)	2.092(4)	2.089(3)	2.078(14)
M−N(2)A	2.104(3)	2.089(4)	2.078(3)	2.107(17)
M−N(3)	2.126(3)	2.109(4)	2.089(4)	2.122(16)
C(1)−C(2)	1.398(5)	1.393(7)	1.406(6)	1.39(2)
C(1)−C(3)A	1.396(4)	1.402(7)	1.395(6)	1.41(2)
C(2)−C(3)	1.396(4)	1.392(7)	1.393(6)	1.40(2)
M(1)···M(2)	6.5474(9)	6.5446(7)	6.5596(5)	6.5567(13)
Bond Angles				
N(1)−M−N(2)A	163.04(11)	163.58(17)	163.86(13)	162.8(6)
N(1)−M−N(3)	98.35(12)	98.12(17)	97.83(14)	98.8(6)
N(2)A−M−N(3)	98.60(11)	98.30(17)	98.30(14)	98.5(6)
C(1)−M−N(1)	81.72(12)	82.0(2)	82.25(6)	80.8(6)
C(1)−M−N(2)A	81.33(12)	81.53(19)	81.62(16)	82.0(7)
C(1)−M−N(3)	176.05(13)	176.5(2)	176.49(17)	179.3(7)
C(1)−C(2)−C(3)	117.5(3)	118.1(4)	117.9(4)	118.1(14)
C(2)−C(1)−C(3)A	123.4(3)	123.0(4)	123.1(4)	122.6(15)
C(2)−C(3)−C(1)A	119.1(3)	118.9(4)	119.0(4)	119.3(14)
Dihedral Angles				
M−C(1)−C(2)−C(3)	−177.7(2)	−176.9(4)	−177.6(3)	179.3(12)
M−C(1)−C(3)A−C(2)A	177.7(2)	176.9(4)	177.6(3)	−179.3(12)
C(1)−C(2)−C(3)−C(1)A	0.9(5)	0.5(8)	−0.2(6)	2(2)
C(2)−C(1)−C(3)A−C(2)A	1.0(5)	0.5(8)	−0.2(7)	2(2)
C(3)A−C(1)−C(2)−C(3)	−1.0(5)	−0.5(8)	0.2(7)	−2(2)
C(1)−C(2)−C(4)−N(1)	−23.9(4)	−24.7(6)	−23.9(6)	−27.0(19)
C(3)−C(2)−C(4)−N(1)	158.8(3)	158.0(5)	158.7(4)	159.3(16)
C(1)A−C(3)−C(5)−N(2)	24.8(4)	25.1(6)	25.2(5)	26.9(19)
C(2)−C(3)−C(5)−N(2)	−160.1(3)	−161.2(5)	−161.3(4)	−156.0(16)

[a] Suffix A stands for a crystallographic inversion operation ([2−*x*, −*y*, −*z*] for **5b** and **14b**; [2−*x*, 1−*y*, −*z*] for **10**; [1−*x*, −*y*, 1−*z*] for **14c**).

NMe_2 groups. The same ^1H and ^{13}C NMR patterns were also found when solutions of **16** in $CDCl_3$ were measured at low temperature. These ^1H and ^{13}C NMR data indicate that in solutions of bis-SO_2 adduct **16** in the presence of excess SO_2 there is either a fast exchange between coordinated and noncoordinated SO_2 at both metal centers or a species present in which two molecules of SO_2 are symmetrically *trans*-bonded to each of the platinum centers. In this context it should also be noted that in solution nickel(II) complexes of ligands such as NCN show reversible binding of SO_2 that was identified by IR photoacoustic techniques.[13b] The SO_2 adducts of platinum complexes [(NCN)PtX] (X = halide, e.g., **17** and **18**) and related multimetallic systems are known to exhibit NMR behavior like that of **16**.[13a,c] More detailed NMR and mechanistic studies of such SO_2 adducts are still in progress; low-temperature ^1H NMR spectra show resonances from nondiastereotopic CH_2NMe_2 groups, and measurements with variable SO_2 concentrations show only changes in chemical shifts with no additional CH_2NMe_2 resonances and no decoalescence behavior.[13d]

Solid-State Structures of Bimetallic Complexes 5b, 10, 14b, 14c, 16, and 23. To obtain more structural information on the newly prepared complexes in the solid state, X-ray crystallographic studies of a number of representative species have been performed. Table 2 contains selected geometrical parameters for the ionic complexes $[1,4\text{-}\{Pd(MeCN)\}_2(C_2N_4)](BPh_4)_2$, **5b**, $[1\text{-}\{Pd(MeCN)\}\text{-}4\text{-}\{Pt(MeCN)\}(C_2N_4)](BPh_4)_2$, **10**, $[1,4\text{-}\{Pt(MeCN)\}_2(C_2N_4)](BPh_4)_2$, **14b**, and $[1,4\text{-}\{Pt(MeCN)\}_2(C_2N_4)][Pt_2I_6]$, **14c**, all of which contain a dication, based on a bismetalated C_2N_4 ligand. The molecular geometry of the dication of the heterobimetallic Pd/Pt complex **10** (see Supporting Information) is representative of that of the complex dications of **5b** and **14**. For the list of crystallographic data for complexes **5b**, **10**, and **14b**, see Table 4. These data for **14c** are included in Table 5.

In all of these dicationic complexes the structures show a central dianionic C_2N_4 ligand bridging between two platinum group metal centers. This ligand is 1,4-bismetalated, and it functions as a bis *N,C,N′*-terdentate coordinating system. Each metal center has a square planar ligand array resulting from this terdentate coordination together with ligation from a single molecule of acetonitrile. As a result, these cations are rodlike species having virtually linear $L{-}M{-}(C_2N_4){-}M{-}L$ arrangements (L = MeCN) with the metal coordination planes and the 1,4-phenylene aromatic skeleton all being close to coplanar. Coordination of two *ortho*-amine arms to each metal center affords C_2 symmetry related pairs of puckered five-membered chelate rings in which the N-donor atoms are approximately mutually *trans* and are lifted out of the plane of the bimetalated phenylene ring system. The resulting N−M−N angle is in the range 162−164°, and C−M−N (M = Pd, Pt) bite angles are typically 80−83°.

The molecular geometry of the bispalladated complex dication of $[1,4\text{-}\{Pd(MeCN)\}_2(C_2N_4)](BPh_4)_2$, **5b**, has been reported earlier[6] and shows a Pd···Pd distance of 6.5474(9) Å across the central dimetalated ring. The aromatic ring of the bridging C_2N_4 ligand is located on a crystallographic inversion center and is slightly distorted, with C−C−C bond angles of 117.5(3)−123.4(3)° and internal dihedral angles up to 1.0(5)°. The two metal centers are virtually in the plane of the aromatic ring, as is shown by the dihedral angles Pd(1)−C(1)−C(2)−C(3) and Pd(1)−C(1)−C(3)A−C(2)A of −177.7(2)° and 177.7(2)°, respectively. In the puckered five-membered chelate rings, the N-donor atoms are lifted out of the plane of the bimetalated ring with dihedral angles C(2)−C(3)−C(5)−N(2) and C(3)−C(2)−C(4)−N(1) of −160.1(3)° and 158.8(3)°.

The molecular geometry of the heterobimetallic Pt/Pd complex $[1\text{-}\{Pt(MeCN)\}\text{-}4\text{-}\{Pd(MeCN)\}(C_2N_4)](BPh_4)_2$, **10**, depicted in Figure 4, shows an average set of structural parameters, due to the disorder in packing of the cationic bimetallic units of **10**, caused by the location of the molecule at a crystallographic inversion center. X-ray structure refinement calculations revealed an approximately equal ratio of platinum and palladium in the unique cationic unit. The overall structure of **10** is like that of **5b**, and the intramolecular Pd···Pt (average) distance is 6.5446(7) Å.

The molecular geometry of the dication of the bisplatinum borate complex $[1,4\text{-}\{Pt(MeCN)\}_2(C_2N_4)](BPh_4)_2$, **14b**, has a Pt···Pt distance across the aromatic ring of 6.5596(5) Å; to the best of our knowledge this is the first crystallographically characterized 1,4-diplatinated phenylene ring system (see Supporting Information). The two square planar Pt^{II} moieties in this complex are related by a crystallographic inversion center and have coordination spheres that are similar to that of the mononuclear triflate complex $[(NCN)Pt(H_2O)](OTf)$, **21**

Table 3. Selected Bond Distances (Å) and Bond and Dihedral Angles (deg) of [1,4-{PtCl(η^1-SO_2)}$_2${$C_6(CH_2NMe_2)_4$-2,3,5,6}], 16, and of Ionic Complex [1,4-(PtI)$_2${$C_6Me(CH_2NMe_2)_4$-2,3,5,6}](OSO_2CF_3), 23 (esd's in Parentheses)[a]

bond distance		bond angle		dihedral angle	
			16		
Pt(1)−Cl(1)	2.4510(19)	C(1)−Pt(1)−Cl(1)	167.57(16)	C(1)−Pt(1)−S(1)−O(1)	−58.2(2)
Pt(1)−C(1)	1.924(6)	C(1)−Pt(1)−N(1)	82.5(2)	C(1)−Pt(1)−S(1)−O(2)	61.9(3)
Pt(1)−N(1)	2.088(5)	C(1)−Pt(1)−N(2)A	83.0(2)	Cl(1)−Pt(1)−S(1)−O(1)	121.52(19)
Pt(1)−N(2)A	2.098(5)	C(1)−Pt(1)−S(1)	92.45(16)	Cl(1)−Pt(1)−S(1)−O(2)	−118.4(2)
Pt(1)−S(1)	2.480(2)	N(1)−Pt(1)−N(2)A	160.80(19)	C(3)A−C(1)−C(2)−C(3)	2.5(8)
C(1)−C(2)	1.399(9)	N(1)−Pt(1)−S(1)	96.99(15)	C(1)−C(2)−C(3)−C(1)A	−2.3(7)
C(2)−C(3)	1.399(8)	N(1)−Pt(1)−Cl(1)	96.22(13)	C(2)−C(1)−C(3)A−C(2)A	−2.5(8)
C(3)−C(1)A	1.414(7)	N(2)A−Pt(1)−Cl(1)	95.30(12)	C(1)−C(2)−C(4)−N(1)	−27.6(6)
C(2)−C(4)	1.496(8)	N(2)A−Pt(1)−S(1)	96.08(15)	C(3)−C(2)−C(4)−N(1)	157.3(5)
C(3)−C(5)	1.506(8)	Cl(1)−Pt(1)−S(1)	99.97(6)	C(1)A−C(3)−C(5)−N(2)	−26.0(7)
C(4)−N(1)	1.545(7)	Pt(1)−S(1)−O(1)	104.5(3)	C(2)−C(3)−C(5)−N(2)	159.3(5)
C(5)−N(2)	1.519(7)	Pt(1)−S(1)−O(2)	105.73(19)		
S(1)−O(1)	1.450(5)	O(1)−S(1)−O(2)	113.5(3)		
S(1)−O(2)	1.451(5)	C(1)−C(2)−C(3)	118.7(5)		
		C(2)−C(3)−C(1)A	117.8(5)		
Pt(1)···Pt(2)	6.570(4)	C(2)−C(1)−C(3)A	123.5(5)		
			23		
Pt(1)−C(1)	2.159(13)	C(1)−Pt(1)−I(1)	171.6(3)	C(5)−C(6)−C(10)−N(2)	106.8(14)
Pt(2)−C(4)	1.910(12)	C(1)−Pt(1)−N(1)	85.5(4)	C(1)−C(6)−C(10)−N(2)	−65.6(12)
Pt(1)−N(1)	2.098(11)	C(1)−Pt(1)−N(2)	86.1(4)	C(3)−C(2)−C(7)−N(1)	−107.4(12)
Pt(1)−N(2)	2.118(10)	N(1)−Pt(1)−N(2)	171.4(4)	C(1)−C(2)−C(7)−N(1)	64.2(12)
Pt(2)−N(3)	2.105(10)	C(4)−Pt(2)−I(2)	175.3(4)	C(3)−C(2)−C(1)−C(13)	−139.2(13)
Pt(2)−N(4)	2.075(11)	C(4)−Pt(2)−N(3)	81.6(5)	C(5)−C(6)−C(1)−C(13)	139.5(12)
Pt(1)−I(1)	2.6219(11)	C(4)−Pt(2)−N(4)	82.4(4)	C(3)−C(2)−C(1)−Pt(1)	111.2(11)
Pt(2)−I(2)	2.6918(11)	N(3)−Pt(2)−N(4)	163.7(4)	C(5)−C(6)−C(1)−Pt(1)	−111.6(11)
C(1)−C(2)	1.445(15)	C(1)−C(2)−C(3)	121.9(12)	C(6)−C(5)−C(14)−N(3)	158.2(12)
C(2)−C(3)	1.371(17)	C(2)−C(3)−C(4)	118.4(10)	C(4)−C(5)−C(14)−N(3)	−27.4(14)
C(3)−C(4)	1.414(18)	C(3)−C(4)−C(5)	121.9(11)	C(2)−C(3)−C(17)−N(4)	161.8(12)
C(4)−C(5)	1.395(15)	C(4)−C(5)−C(6)	119.5(11)	C(4)−C(3)−C(17)−N(4)	−23.4(15)
C(5)−C(6)	1.369(17)	C(5)−C(6)−C(1)	120.8(10)	C(2)−C(3)−C(4)−Pt(2)	179.9(11)
C(6)−C(1)	1.465(17)	C(6)−C(1)−C(2)	115.3(10)	C(6)−C(5)−C(4)−Pt(2)	179.7(8)
C(1)−C(13)	1.512(16)	Pt(1)−C(1)−C(13)	104.6(8)	C(5)−C(6)−C(1)−C(2)	−15.5(17)
Pt(1)···Pt(2)	5.7870(8)			C(6)−C(1)−C(2)−C(3)	15.4(17)

[a] Suffix A denotes symmetry operation (−*x*, −*y*, −*z*).

(see Scheme 2), as regards both bond distances and bond angles.[17] Between the C-bonded phenylene ring and the N-coordinated MeCN molecule there is a C_{ipso}−Pt(1)−N(3) bond angle of 176.49(17)°. In this complex the distortion from a square planar arrangement is the result of N−Pt−C_{ipso} bite angles of 82.25(16)° and 81.62(16)° for C(1)−Pt(1)−N(1) and C(1)−Pt(1)−N(2)A, respectively, and a N−Pt−N bond angle of 163.86(13)°. The two unique five-membered chelate rings exhibit clear puckering of a C_2-axis type (through C(1), as indicated by the asymmetry parameter $\Delta C_2[C_1] = 4.2(5)°$ and 6.9(5)°). The C_{ipso}−Pt bond of 1.917(4) Å and the Pt−N bonds of 2.089(3) and 2.078(3) Å are at the shorter end of the ranges for Pt−C_{aryl} bond distances (1.901−2.010 Å) and Pt−N bond distances (2.070−2.316 Å) in related Pt^{II} complexes of NCN.

The molecular geometry of the tetrametallic platinum complex [1,4-{Pt(MeCN)}$_2${$C_6(CH_2NMe_2)_4$-2,3,5,6}][Pt_2I_6], **14c**, has a dication that shows great similarity in structural parameters to that of complex **14b** with an almost identical Pt···Pt distance of 6.5567(13) Å. The planar dianionic $[Pt_2I_6]^{2-}$ unit of **14c** contains two inversion-center-related square planar platinum(II) centers, each of which bears two terminal iodide ligands. These centers are linked by two bridging iodine atoms. Pt−I bond distances range from 2.5995(14)° to 2.6011(15) Å and I−Pt−I bond angles vary from 84.21(5)° to 92.46(5)°, with those involving the bridge being the smallest; the Pt−I−Pt′ angle is 95.79(5)°. Other structurally characterized complexes having the $[Pt_2I_6]^{2-}$ unit as the counteranion include ones with a tetraalkylammonium cation[19a] and a chelated potassium cation.[19b]

In Table 3 are listed selected geometrical parameters for the neutral bis-SO_2 complex [1,4-{PtCl(η^1-SO_2)}$_2${$C_6(CH_2NMe_2)_4$-2,3,5,6}], **16**, and the unique monocationic arenium complex [1,4-{PtI}$_2${C_6Me-1-$(CH_2NMe_2)_4$-2,3,5,6}](OTf), **23**. For the list of crystallographic data for these complexes, see Table 5.

Bimetallic platinum complexes **16** and **23** are the products of reactivity studies involving the essentially planar bimetallic neutral species **13** and ionic bistriflate complex **14a**, respectively.

The molecular geometry of the bisplatinum complex [1,4-{PtCl(η^1-SO_2)}$_2$(C_2N_4)], **16**, which is depicted in Figure 5, shows two equivalent platinum(II) centers, each of which has a square pyramidal coordination array and which are symmetry related by a crystallographic center of inversion. Like the ionic bimetallic complexes described above, there is a planar 1,4-bimetalated phenylene-bridging ligand that affords terdentate *N,C,N′*-bonding to both platinum centers. The coordination sphere of each metal is completed by a single chloro ligand *trans* to C_{ipso} and a single SO_2 molecule η^1-S bonded in the apical position. The Pt−phenylene−Pt unit shows an intramolecular Pt···Pt distance of 6.570(4) Å across the central dimetalated

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(19) (a) Rogers, R. D.; Isci, H.; Mason, W. R. *J. Crystallogr. Spectrosc. Res.* **1984**, *14*, 383. (b) Martin-Gil, J.; Martin-Gil, F. J.; Pérez-Méndez, M.; Fayos, J. *Z. Kristallogr.* **1985**, *173*, 179.

Table 4. Crystallographic Data for Complexes 5b, 10, and 14b

	5b	**10**	**14b**
Crystal Data			
formula	$C_{74}H_{84}B_2N_8Pd_2$	$C_{74}H_{84}B_2N_8PdPt$	$C_{74}H_{84}B_2N_8Pt_2$
mol wt	1320.00	1408.66	1497.32
cryst system	triclinic	triclinic	triclinic
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	10.2037(12)	10.1994(7)	10.2239(7)
b, Å	11.4148(11)	11.3919(10)	11.3859(8)
c, Å	15.368(2)	15.3405(9)	15.3358(8)
α, deg	86.982(10)	87.031(6)	87.067(5)
β, deg	81.848(11)	81.707(5)	81.643(5)
γ, deg	68.900(9)	68.881(5)	68.878(5)
V, Å^3	1653.1(4)	1645.3(2)	1647.59(19)
D_{calc}, g cm^{-3}	1.326	1.422	1.509
Z	1	1	1
F(000)	686	718	750
μ [Mo Kα], cm^{-1}	5.9	24.5	42.9
cryst size, mm	0.08 × 0.10 × 0.60	0.1 × 0.2 × 0.5	0.05 × 0.12 × 0.40
cryst color	colorless	colorless	colorless
Data Collection			
θ_{min}, θ_{max}, deg	1.34, 27.5	1.34, 27.5	1.34, 27.5
SET4 θ_{min}, θ_{max}, deg	10.11, 14.01 [25 refl.]	10.41, 14.09 [25 refl.]	11.73, 13.96 [24 refl.]
$\Delta\omega$, deg	$0.50 + 0.35 \tan \theta$	$0.65 + 0.35 \tan \theta$	$0.59 + 0.35 \tan \theta$
hor., ver. aperture, mm	$3.00 + 1.50 \tan \theta$, 4.00	$2.73 + 1.37 \tan \theta$, 4.00	$3.00 + 1.50 \tan \theta$, 4.00
X-ray exposure time, h	23	13	14
linear instability, %	8	1	2
reference reflns	2 −3 −2, 3 −2 −2, 2 0 −2	−2 0 2, −1 2 3, 2 4 2	−2 −4 −2, −2 −2 −3, 2 −3 −2
data set	−13:12, −14:9, −19:19	−12:13, −9:14, −19:19	−13:12, −14:9, −19:19
no. of total data	10 530	9102	10 090
no. of total unique data	7572 [$R_{\mathrm{int}} = 0.0772$]	7550 [$R_{\mathrm{int}} = 0.0531$]	7549 [$R_{\mathrm{int}} = 0.0313$]
no. of observed data	7572 [$I > -3\sigma(I)$]	7548 [$I > -3\sigma(I)$]	7549 [$I > -3\sigma(I)$]
transmission range		0.683, 0.973 [ABSP]	0.581, 0.680 [ABSORB]
Refinement			
no. of refined params	394	394	394
final R1[a]	0.0437 [6109$I > 2\sigma(I)$]	0.0460 [6036$I > 2\sigma(I)$]	0.0355 [6377$I > 2\sigma(I)$]
final wR2[b]	0.1010	0.1073	0.0718
goodness of fit	1.018	1.011	1.021
w^{-1} [c]	$\sigma^2(F^2) + (0.0295P)^2 + 1.16P$	$\sigma^2(F^2) + (0.0543P)^2$	$\sigma^2(F^2) + (0.0292P)^2$
$(\Delta/\sigma)_{\mathrm{av}}$, $(\Delta/\sigma)_{\mathrm{max}}$	0.001, 0.014	0.000, 0.002	0.000, 0.001
min. and max. residual density, e Å^{-3}	−0.69, 0.79	−1.72, 1.52 [near Pd/Pt]	−1.35, 1.69 [near Pt]

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$. [c] $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

ring, and the aromatic ring has only slight distortions from planarity (all ring carbon atoms lie within 0.009 Å from the least-squares plane through this ring). The two metal centers lie almost in the plane of the aromatic ring, but as is shown by the dihedral angles Pt(1)−C(1)−C(2)−C(3) and Pt(1)−C(1)−C(3)A−C(2)A of −172.3(4)° and 172.4(4)°, respectively, as well as other geometrical parameters, these metal centers are positioned a little above the basal plane of the pyramid. Coordination of two *ortho*-amine substituents to each platinum center affords pairs of puckered five-membered rings, which are local mirror-plane related, and a N(1)−Pt(1)−N(2)A bond angle of 160.80(19)°. As a result of the symmetry present, the SO_2 ligands occupying the apical position of the square pyramidal ligand arrays are bonded in an *anti*-fashion with respect to the central phenylene ring. There is a Pt(1)−S(1) bond distance of 2.480(2) Å that is significantly shorter than that of 2.613(7) Å found in the related mononuclear NCN platinum complex [(NC-N)PtBr(η^1-SO_2)], **19**.[13a] Furthermore, whereas in **19** the SO_2 molecule is oriented with one S−O bond parallel to the Pt−Br bond, in bisplatinum complex **16** both S−O bonds of SO_2 point away from its adjacent chloride atom, affording dihedral angles C(1)−Pt(1)−S(1)−O(1) and C(1)−Pt(1)−S(1)−O(2) of −58.2(2)° and 61.9(3)°, respectively. Accordingly, the S−O bonds in bimetallic **16** are nearly equal in length (1.450(5) and 1.451(5) Å), whereas those in monometallic **19** are distinctly different (1.47(1) and 1.42(2) Å).

The X-ray crystal structure analysis of the bimetallic species $[1,4\text{-}\{PtI\}_2\{C_6Me\text{-}1\text{-}(CH_2NMe_2)_4\text{-}2,3,5,6\}](OTf)$, **23**, shows a diplatinated complex monocation and a separate triflate anion. The molecular geometry of the monocation is depicted in Figure 6, and this shows it to be built up of two Pt^{II} centers, two terminal I^- ligands, and a monoanionic bridging system that has arisen from the formal addition of Me^+ to a terminal carbon atom of a C_2N_4 dianion. The central bridging system is thus a 1,4-bimetalated arenium ion ring that is coordinated in a different manner to two nonequivalent platinum centers. This bridging ligand, in which the positive charge is distributed within the C_6 ring in a manner found in Wheland intermediates of electrophilic aromatic substitution reactions, is formally an arenium ion system.[12] At one end an sp^3 carbon atom, C(1), is bonded to a platinum(II) center, Pt(1), and a methyl group (e.g., C(13)), whereas at the other end there is an sp^2 carbon atom, C(4), that is only bonded to a platinum(II) iodide moiety. The latter square planar platinum center, Pt(2), has *N,C,N′*-coordination from the bridging ligand that is like that found in complexes **14** and **16** and in related mononuclear platinum(II) complexes of NCN,[17] and as a result, the metal coordination plane coincides with that of the arenium ring. The atom

Table 5. Crystallographic Data for Complexes 14c, 16, and 23

	14c	**16**	**23**
Crystal Data			
formula	$C_{22}H_{38}I_6N_6Pt_4$	$C_{19}H_{34}Cl_4N_4O_4Pt_2S_4$	$C_{20}H_{35}F_3I_2N_4O_3Pt_2S$
mol wt	1928.33	978.61	1112.55
cryst system	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$ (No. 2)	$C2/c$ (No. 15)	$P2_1$/c (No. 14)
a, Å	8.5406(11)	12.306(7)	15.9773(8)
b, Å	9.4944(8)	20.756(8)	10.6538(4)
c, Å	11.8601(10)	12.2393(15)	19.0865(13)
α, deg	86.583(7)		
β, deg	80.599(9)	112.50(3)	117.623(4)
γ, deg	86.100(8)		
V, Å^3	945.5(2)	2888(2)	2878.6(3)
D_{calc}, g cm^{-3}	3.387	2.251	2.567
Z	1	4	4
F(000)	842	1856	2048
μ [Mo Kα], cm^{-1}	196.7	102.2	119.7
cryst size, mm	0.03 × 0.12 × 0.50	0.1 × 0.2 × 0.8	0.05 × 0.10 × 0.35
cryst color	orange-brown	red	reddish-brown
Data Collection			
θ_{min}, θ_{max}, deg	1.75, 27.5	1.80, 27.5	1.21, 27.5
SET4 θ_{min}, θ_{max}, deg	10.07, 15.64 [25 refl.]	11.41, 13.95 [25 refl.]	10.57, 13.89 [25 refl.]
$\Delta\omega$, deg	$0.71 + 0.35 \tan\theta$	$0.68 + 0.35 \tan\theta$	$0.50 + 0.35 \tan\theta$
hor., ver. aperture, mm	$3.00 + 1.50 \tan\theta$, 4.00	$2.31 + 1.15 \tan\theta$, 4.00	$3.00 + 1.50 \tan\theta$, 4.00
X-ray exposure time, h	8	22	9
linear instability, %	2	6	1
reference reflns	2 3 1, 3 2 −3, 3 −2 −2	−3 1 5, 4 0 2, −1 9 2	−2 −2 7, 4 2 1, 3 3 −1
data set	−7:11, −12:12, −15:15	−15:14, −26:26, −10:15	−19:20, 0:13, −19:24
no. of total data	4964	8917	7150
no. of total unique data	4333 [$R_{int} = 0.0574$]	3320 [$R_{int} = 0.0577$]	6580 [$R_{int} = 0.0515$]
no. of observed data	3903 [$I > 0$]	3320 [$I > -3\sigma(I)$]	6579 [$I > -3\sigma(I)$]
transmission range	0.382, 1.000 [DIFABS]	0.233, 0.695 [DIFABS]	0.317, 1.000 [DIFABS]
Refinement			
no. of refined params	177	163	325
final R1[a]	0.0604 [2878$I > 2\sigma(I)$]	0.0303 [2857$I > 2\sigma(I)$]	0.0516 [4829$I > 2\sigma(I)$]
final wR2[b]	0.1338	0.0782	0.1146
goodness of fit	1.004	1.039	1.040
w^{-1} [c]	$\sigma^2(F^2) + (0.0576P)^2$	$\sigma^2(F^2) + (0.0403P)^2 + 16.18$	$\sigma^2(F^2) + (0.0437P)^2 + 8.66P$
$(\Delta/\sigma)_{av}$, $(\Delta/\sigma)_{max}$	0.000, 0.000	0.000, 0.000	0.000, 0.001
min. and max. residual density, e Å^{-3}	−1.88, 1.96 [near Pt, I]	−1.94, 1.38 [near Pt, solvent]	−1.44, 1.66 [near Pt, I]

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$. [c] $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

Pt(1), bonded to the sp^3 carbon atom, has also a square planar environment from terdentate *N,C,N′*-coordination and a terminal iodine atom, but in contrast to the other platinum center, its coordination plane does not coincide with that of the bridging ligand and affords a dihedral angle of 66.4(5)°. As a result of the Wheland type structure of the central bimetalated ring in the bisplatinum complex **23**, the C_6 ring shows severe distortions. These distortions can be clearly seen in the variation in C−C bond lengths from 1.369(17) to 1.465(17) Å and in the bond angles, which are in the range 115.3(10)−121.9(12)°. In addition, there are dihedral angles in this particular ring that range from −15.5(17)° to 15.4(17)°.

As a result of the different ligand environments of the two platinum centers, their geometrical parameters relating to the ligating atoms show significant differences. For example, the C−Pt bonds C(1)−Pt(1) and C(4)−Pt(2) are 2.159(13) and 1.910(12) Å, respectively, and the terminal Pt−I bonds Pt(1)−I(1) and Pt(2)−I(2) are 2.6219(11) and 2.6918(11) Å, respectively; that is, bonds involving Pt(1) are significantly longer than those involving Pt(2). Similarly, there are also notable bond angle differences within the platinum-containing *N,C,N′*-coordination motifs. For example, the N−Pt−N bond angles for Pt(1) and Pt(2) are 171.4(4)° and 163.7(4)°, respectively, and the corresponding C−Pt−I bond angles are 171.6(3)° and 175.3(4)°.

Discussion

In general, the reactivity of the new dinuclear complexes differs significantly from that of the related mononuclear palladium(II) and platinum(II) complexes of the NCN ligand. For example, the reaction of bimetallic Pt/Pt complex **14a** with iodomethane, which results in a stable diplatinated arenium ion complex, is much slower than that of the related mononuclear NCN-platinum complex **21**.[12] This reduction in reaction rate for **14a** may be the result of the organometallic *para*-substituent, which is attached to the aryl−platinum moiety that is involved in the formation of the arenium ion species. This is one of several indications for a cooperative effect between the platinum centers in **14a**.

The formation of the SO_2 adduct **16** is similar to that observed earlier for the related mononuclear platinum NCN complex **19**.[13a] However, in the case of the bimetallic Pt/Pt complex **16** described in this paper, the SO_2 molecules are more strongly bonded than the single SO_2 molecule in **19**. This is reflected in both the difference in Pt−S bond distances in the solid-state structures of **16** and **19** and the experimental observation that **19** loses its SO_2 (and color) more readily than **16** when placed in a vacuum. Furthermore, the UV/vis bands responsible for the color of bisplatinum complex **16** have ϵ values that are much higher than those of the monoplatinum complex **19**. These observations are also indicative of cooperativity between the metal centers in Pt/Pt complex **16**.

The good air and moisture stability of the novel neutral and ionic bimetallic complexes **4**–**15** (except **12**) makes these species interesting starting materials for the development of new multimetallic and polymetallic materials as well as in bimetallic catalyst systems. For example, the lability of the MeCN ligands of the dicationic monophenylene-bridged triflate complexes **5a** (Pd/Pd) and **14a** (Pt/Pt) in the presence of ligands such as pyridine offers a potential method for linking the bimetallic cationic units together. Extending these experiments to the use of α,ω-bifunctional (bridging) ligands such as pyrazine should provide a route to air- and moisture-stable, linear (directional) organometallic polymers in which complexes such as **5**, **9**, and **14** could function as the building blocks.[5,20] In addition, it could be anticipated that the use of tri- or tetrafunctional ligands (such as, for example, tris- or tetrakis(4-pyridyl)-methane or 1,3,5-tris[4-pyridyl)ethynyl]benzene[21]) may lead to the formation of branched organometallic polymers using the procedures described above. This approach is currently being studied further, since bimetallic species such as those discussed in this paper do show some cooperativity between the metal centers (electronic M–M′ communication).

Conclusion

In this paper we have shown that dinuclear organometallic complexes of palladium(II) and platinum(II) with the versatile C_2N_4 aryltetramine ligand are easily accessible. The synthetic strategies involve C–Si bond activation, aromatic ortholithiation, lithium–halogen exchange, and transmetalation reactions. The products of these reactions form an interesting new class of homo- and heterobimetallic complexes, in which the metal centers are separated by a 1,4-phenylene bridge. Furthermore, the C_2N_4 ligand applied in this paper can also be used to prepare homo- and heterodinuclear organometallic complexes of other transition metals, using the synthetic routes to monometallic complexes of the NCN ligand, which have been described thoroughly.[3a,b] Interestingly, the ligand precursor $C_6Br_2(CH_2NMe_2)_4$-2,3,5,6 may also be used for the synthesis of bimetallic complexes via procedures that involve oxidative addition of low-valent metal complexes, such as nickel(0) species.[2a–c] The ligand exchange behavior of the biscationic acetonitrile complexes described here, in combination with the use of α,ω-bifunctional ligands, offers interesting future potential for such materials as building blocks for new multimetallic materials through self-assembly.

Studies of various bisplatinum complexes of C_2N_4 show that these species have chemical reactivity similar to that of mononuclear platinum complexes of the NCN ligand. However, the metal–metal cooperativity generates distinctive characteristic properties that lead to unusual site-selective reactions and new bonding arrangements.

Experimental Section

General Procedures. All experiments were conducted in a dry nitrogen 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, ^{13}C, and ^{31}P NMR spectra were recorded at 298 K on a Bruker AC200 or AC300 spectrometer. UV/vis spectra were recorded on a Varian Cary 1. The starting materials $[PtCl_2(SEt_2)_2]$,[22] $C_6H_2(CH_2NMe_2)_4$-1,2,4,5, **1**,[7] [1-(Me_3Si)-4-(R)-$\{C_6(CH_2NMe_2)_4$-2,3,5,6$\}$] (**2**, R = Me_3Si; **3**, R = H),[14] and $C_6Br_2(CH_2NMe_2)_4$-2,3,5,6, **11**,[14] were prepared according to literature procedures; $[Pd(OAc)_2]$ and $PtCl_2$ were obtained from Degussa.

Synthesis of [2,3,5,6-Tetrakis{(dimethylamino)methyl}-phenylene-1,4-bis{chloropalladium(II)}] (4). A solution of $[Pd(OAc)_2]$ (1.21 g, 5.4 mmol) in MeOH (30 mL) was added in one portion to a stirred suspension of the bistrimethylsilyl compound **2** (0.89 g, 2 mmol) in MeOH (30 mL) at room temperature. The reaction mixture was stirred for 18 h at room temperature and then filtered through Celite to remove some colloidal palladium. The filtrate was then added in one portion to a solution of LiCl (0.64 g, 15 mmol) in MeOH (30 mL), and the resulting mixture was stirred for 15 min, during which time a white precipitate had formed. The precipitated product was collected by centrifugation, washed with MeOH (3 × 50 mL) and Et_2O (2 × 50 mL), and dried in vacuo to afford the bispalladium(II) complex **4** as a white solid. Yield: 0.72 g (78%), mp > 200 °C. ^1H NMR ($CDCl_3$, 200 MHz): δ 3.80 (s, 8 H, NCH_2), 2.94 (s, 24 H, NMe_2).

Synthesis of [2,3,5,6-Tetrakis{(dimethylamino)methyl}-phenylene-1,4-bis(acetonitrilepalladium(II))] Bis(trifluoromethanesulfonate) (5a). A suspension of bispalladium-(II) complex **4** (0.60 g, 1 mmol) in MeCN (25 mL) was titrated with a solution containing a slight excess of AgOTf (0.54 g, 2.1 mmol) in MeCN (25 mL) at room temperature. During this titration AgCl precipitated as a white solid, and the endpoint was identified by the coagulation of the precipitate. The AgCl was removed by centrifugation, and the supernatant filtered through Celite. The filtrate was then concentrated to ~10 mL and layered with Et_2O (20 mL). Over a period of 24 h this resulted in precipitation of a white microcrystalline solid, which was collected by filtration, washed with Et_2O (2 × 20 mL), and dried in vacuo. Yield: 0.86 g (96%), mp 184 °C (dec). ^1H NMR (CD_3CN, 200 MHz): δ 3.87 (s, 8 H, NCH_2), 2.80 (s, 24 H, NMe_2). ^{13}C NMR (CD_3CN, 50 MHz): δ 153.1, 139.4 (Ar), 72.9 (NCH_2), 53.4 (NMe_2).

Synthesis of [2,3,5,6-Tetrakis{(dimethylamino)methyl}-phenylene-1,4-bis(acetonitrilepalladium(II))] Bis(tetraphenylborate) (5b). A filtered solution of $NaBPh_4$ (0.85 g, 2.5 mmol) in MeCN (15 mL) was added in one portion to a stirred solution of the bistriflate complex **5a** (0.70 g, 0.78 mmol) in MeCN (15 mL) at room temperature, and the reaction mixture was left undisturbed for 1 h. After this time the product, which precipitated as a white solid, was collected by

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[20] (a) Hagihara, N.; Sonogashira, K.; Takahashi, S. *Adv. Polym. Sci.* **1981**, *41*, 149. (b) Shears, J. E. *Metal-Containing Polymer Systems*; Carraher, C. E., Jr., Pittmann, C. U., Jr., Eds.; Plenum: New York, 1985. (c) Khan, M. S.; Kakkar, A. K.; Ingham, S. L.; Raithby, P. R.; Lewis, J.; Spencer, B.; Wittmann, F.; Friend, R. H. *J. Organomet. Chem.* **1994**, *472*, 247. (d) Anderson, H. L.; Martin, S. J.; Bradley, D. D. C. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 655.

[21] Stang, P. J.; Olenyuk, B.; Muddiman, D. C.; Smith, R. D. *Organometallics* **1997**, *16*, 3094.

[22] $[PtCl_2(SEt_2)_2]$ was prepared in a 1:1 *cis/trans* mixture by the reaction of a suspension of $PtCl_2$ (5.32 g, 20 mmol) in benzene (50 mL) with excess Et_2S (8.6 mL, 80 mmol). When all solids dissolved the clear yellow reaction mixture was evaporated to dryness, washed with pentane (4 × 50 mL), and dried in vacuo; yield 8.0–8.5 g (90–95%): Albrecht, M.; van Koten, G. Private communication.

filtration and subsequently recrystallized by cooling a hot saturated solution in MeCN. The colorless crystals of **5b** that formed were collected by filtration, washed with cold MeCN (10 mL) and Et_2O (50 mL), and then dried in vacuo. Yield: 0.89 g (92%), mp > 200 °C. ^{1}H NMR (CD_3CN, 200 MHz): δ 7.32−7.24 (m, 16 H, Ar), 7.05−6.95 (m, 16 H, Ar), 6.90−6.80 (m, 8 H, Ar), 3.83 (s, 8 H, NCH_2), 2.79 (s, 24 H, NMe_2). Anal. Calcd for [$C_{70}H_{78}B_2N_6Pd_2$]: C, 67.92; H, 6.35; N, 6.79. Found: C, 67.72; H, 6.30; N, 6.85.

Synthesis of [2,3,5,6-Tetrakis{(dimethylamino)methyl}-phenylene-1,4-bis(pyridinepalladium(II))] Bis(trifluoromethanesulfonate) (6). A stirred colorless solution of the bisacetonitrile complex **5a** (55 mg, 61 μmol) in MeCN (2 mL) was treated with pyridine (0.2 mL, excess) at room temperature. The color of the reaction mixture turned to pale yellow instantaniously. The reaction mixture was stirred at room temperature for 5 min, after which time Et_2O (3 mL) was slowly added by vapor diffusion. This resulted in the formation of pale yellow crystals of **6**, which were filtered off, washed with Et_2O (2 × 5 mL), and dried in vacuo. Yield: 39 mg (73%), mp 152 °C (dec). ^{1}H NMR (CD_3CN, 200 MHz): δ 8.77 (d, 4 H, $^3J_{HH}$ = 4.4 Hz, py-H), 7.93 (t, 2 H, $^3J_{HH}$ = 7.6 Hz, py-H), 7.54 (m, 4 H, py-H), 3.94 (s, 8 H, NCH_2), 2.69 (s, 24 H, NMe_2). Anal. Calcd for [$C_{30}H_{34}F_6N_6O_6Pd_2S_2$]: C, 37.32; H, 3.55; N, 8.70. Found: C, 37.25; H, 3.68; N, 8.62.

Synthesis of [2,3,5,6-Tetrakis{(dimethylamino)methyl}-phenylene-1-trimethylsilyl-4-(chloroplatinum(II))] (7). A solution of *n*-BuLi (1.1 mL, 1.6 M solution in hexanes, 1.76 mmol) was added dropwise over 5 min to a solution of the monosilylated aryltetramine **3** (0.62 g, 1.64 mmol) in hexane (30 mL) at room temperature, and the resulting reaction mixture was stirred for 18 h at this temperature. After this time, the volatiles were removed in vacuo, and the residue was then dissolved in Et_2O (15 mL) and added in one portion to a stirred suspension of [$PtCl_2(SEt_2)_2$] in Et_2O (15 mL) at room temperature. The resulting reaction mixture was stirred at room temperature for 2 h, after which the solvent was evaporated. The crude oily product was purified by column chromatography (neutral alumina) using the mixture CH_2Cl_2/EtOAc/Et_3N = 35:60:5 as eluent. The fractions that contained the desired product (identified by TLC) were collected together and concentrated in vacuo. The solid residue was subsequently recrystallized from warm hexane. This resulted in the formation of white crystals of the Pt/Si complex **7**, which were collected by filtration and dried in vacuo. Yield: 0.35 g (35%), mp 78−81 °C (dec). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 4.11 (s, 4 H, $^3J_{Pt-H}$ = 45.3 Hz, NCH_2), 3.37 (s, 4 H, NCH_2), 3.04 (s, 12 H, $^3J_{Pt-H}$ = 35.9 Hz, NMe_2), 2.01 (s, 12 H, NMe_2), 0.31 (s, 9 H, $SiMe_3$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 147.0 (C_{ipso}−Pt, $^1J_{Pt-C}$ = 1000 Hz), 141.7 (C_{meta}, $^3J_{Pt-C}$ = 75 Hz), 139.1 (C_{ortho}, $^2J_{Pt-C}$ = 44 Hz), 133.5, 77.7 (NCH_2, $^2J_{Pt-C}$ = 60 Hz), 62.6 (NCH_2), 54.4 (NMe_2, $^2J_{Pt-C}$ = 13 Hz), 44.6 (NMe_2), 4.2 ($SiMe_3$). Anal. Calcd for [$C_{21}H_{41}ClN_4PtSi$]: C, 41.47; H, 6.79; N, 9.21. Found: C, 41.36; H, 6.75; N, 9.16.

Synthesis of [2,3,5,6-Tetrakis{(dimethylamino)methyl}-phenylene-1-(chloroplatinum(II))-4-(chloropalladium(II))] (8). A solution of [$Pd(OAc)_2$] (19 mg, 85 μmol) in MeOH (5 mL) was added in one portion to a stirred solution of the platinum complex **7** (50 mg, 82 μmol) in CH_2Cl_2 (5 mL) at room temperature. The reaction mixture was stirred for 1 h and then filtered through Celite. The filtrate was added to a stirred solution of LiCl (10 mg, 235 μmol) in MeOH, and the resulting reaction mixture was stirred for 15 min. The precipitated product was collected by centrifugation, washed with MeOH (3 × 15 mL) and Et_2O (2 × 15 mL), and dried in vacuo. Yield: 48 mg (90%), white solid (mp > 200 °C). This product has very poor solubility properties, and conventional ^{1}H and ^{13}C NMR spectroscopic characterization was not successful. It was used without further purification for the preparation of the more soluble and easily characterizable ionic heterobimetallic species **9** and **10**.

Synthesis of [2,3,5,6-Tetrakis{(dimethylamino)methyl}-phenylene-1-(acetonitrileplatinum(II))-4-(acetonitrile-palladium(II))] Bis(trifluoromethanesulfonate) (9). Preparation was as described for **5a**, using the neutral Pt/Pd complex **8** (48 mg, 74 μmol) as starting material. Yield: 68 mg (92%), white solid (mp 141−144 °C). ^{1}H NMR (CD_3CN + 10% D_2O, 200 MHz): δ 4.08 (s, 4 H, $^3J_{Pt-H}$ = 46.5 Hz, NCH_2), 3.86 (s, 4 H, NCH_2), 2.96 (s, 12 H, $^3J_{Pt-H}$ = 39.0 Hz, NMe_2), 2.80 (s, 12 H, NMe_2). ^{13}C NMR (CD_3CN + 10% D_2O, 50 MHz): δ 152.7, 141.2, 138.9 ($^3J_{Pt-C}$ = 82 Hz), 138.8 ($^2J_{Pt-C}$ = 43 Hz), 75.7 (NCH_2, $^2J_{Pt-C}$ = 64 Hz), 72.8 (NCH_2, $^4J_{Pt-C}$ = 11 Hz), 55.1 (NMe_2, $^2J_{Pt-C}$ = 16 Hz), 53.4.

Synthesis of [2,3,5,6-Tetrakis{(dimethylamino)methyl}-phenylene-1-(acetonitrileplatinum(II))-4-(acetonitrile-palladium(II))] Bis(tetraphenylborate) (10). Preparation as described for **5b**, using the Pt/Pd bistriflate complex **9** (40 mg, 41 μmol) as starting material. Yield: 48 mg (89%), colorless crystals, mp 167−169 °C (dec). Anal. Calcd for [$C_{70}H_{78}B_2N_6PdPt$ + $2CH_3CN$]: C, 63.10; H, 6.01; N, 7.95. Found: C, 63.14; H, 5.90; N, 7.78.

Synthesis of [2,3,5,6-Tetrakis{(dimethylamino)methyl}-phenylene-1,4-bis(chloroplatinum(II))] (13). A solution of *n*-BuLi (7.5 mL, 1.6 M solution in hexanes, 12 mmol) was added to a stirred suspension of the aryl dibromide **11** (2.32 g, 5 mmol) in Et_2O (100 mL) at −78 °C. The resulting reaction mixture was stirred for 15 min at −78 °C, then allowed to warm to room temperature and subsequently stirred for an additional 30 min at this temperature. The precipitated organodilithium compound **12** was collected by centrifugation, washed with Et_2O (50 mL), and suspended in THF (50 mL). To this white stirred suspension was added a solution of [$PtCl_2(SEt_2)_2$] (4.91 g, 11 mmol) in THF (100 mL) at room temperature. The reaction mixture was stirred for 30 min, and the product that had precipitated during this time was collected by filtration. The product was washed with MeOH (3 × 50 mL) and Et_2O (2 × 50 mL) and dried in vacuo to afford the bisplatinum(II) complex **13** (3.58 g, 94% based on the dibromide **11**) as a white solid (mp > 200 °C). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.88 (s, 8H, NCH_2, $^3J_{Pt-H}$ not observed), 2.27 (s, 24H, NMe_2, $^3J_{Pt-H}$ not observed due to very poor S/N ratio).

Reaction of 13 with SO_2. A 300 mg portion of the bis(chloroplatinum) complex **13** was suspended in CH_2Cl_2 (75 mL) in a 200 mL Schlenk tube, and SO_2 was bubbled through this stirred suspension at room temperature. The color of the reaction mixture immediately turned to deep orange, and when the solution was saturated with SO_2, all solids had dissolved. A saturated solution of SO_2 in Et_2O (75 mL) in a Schlenk tube was then connected through a knee tube to the one containing the metal complex. Slow vapor diffusion of Et_2O into the CH_2Cl_2 solution then afforded dark orange crystals of the Pt/Pt bis(SO_2) adduct **16**, which were suitable for an X-ray analysis when kept in an SO_2 atmosphere. These crystals slowly decolorize in contact with air. ^{1}H NMR (SO_2-saturated $CDCl_3$, 200 MHz): δ 3.99 (s, 8 H, $^3J_{Pt-H}$ = 46.4 Hz, NCH_2), 2.99 (24 H, $^3J_{Pt-H}$ = 38.8 Hz, NMe_2). ^{13}C NMR (SO_2-saturated $CDCl_3$, 50 MHz, 298 K): δ 145.2 (C_{ipso}, $^1J_{Pt-C}$ not observed), 135.3 (C_{ortho}, $^2J_{Pt-C}$ not observed), 74.5 (NCH_2, $^2J_{Pt-C}$ not observed), 54.1 (NMe_2, $^2J_{Pt-C}$ = 26 Hz). UV/vis (CH_2Cl_2): λ_{max} [nm] (ϵ [10^4 M^{-1} cm^{-1}]) = 434 (0.54), 348 (2.05).

Synthesis of [2,3,5,6-Tetrakis{(dimethylamino)methyl}-phenylene-1,4-bis(acetonitrileplatinum(II))] Bis(trifluoromethanesulfonate) (14a). A stirred suspension of the neutral bisplatinum complex **13** (3.58 g, 4.68 mmol) in a mixture of MeCN and water (100 mL, 19:1) was titrated with a solution of AgOTf (2.47 g, 9.6 mmol) in MeCN (25 mL) at room temperature. During this procedure, AgCl precipitated as a white solid. After removal of the AgCl by centrifugation, the supernatant solution was filtered through Celite. The resulting filtrate was then concentrated to ~25 mL and layered with Et_2O (50 mL). The precipitated product was collected by filtration, washed with Et_2O (25 mL), and dried in vacuo. Yield: 4.78 g (95%), white solid (mp 194−196 °C). ^1H NMR (CD_3CN, 200 MHz): δ 3.99 (s, 8 H, $^3J_{Pt-H} = 46.4$ Hz, NCH_2), 2.99 (24 H, $^3J_{Pt-H} = 38.8$ Hz, NMe_2). ^{13}C NMR (CD_3CN, 50 MHz): δ 140.8 (C_{ipso}, $^1J_{Pt-C} = 995$ Hz), 138.3 (C_{ortho}, $^2J_{Pt-C} = 83$ Hz, $^3J_{Pt-C} = 42$ Hz), 75.8 (NCH_2, $^2J_{Pt-C} = 65$ Hz), 55.2 (NMe_2, $^2J_{Pt-C} = 16$ Hz). Anal. Calcd for $[C_{24}H_{38}F_6N_6O_6Pt_2S_2]$: C, 26.82; H, 3.56; N, 7.82. Found: C, 26.66; H, 3.65; N, 7.88.

Synthesis of [2,3,5,6-Tetrakis{(dimethylamino)methyl}-phenylene-1,4-bis(acetonitrileplatinum(II))] Bis(tetraphenylborate) (14b). A filtered solution of $NaBPh_4$ (0.60 g, 1.75 mmol) in MeCN (15 mL) was added to a colorless stirred solution of the Pt/Pt bistriflate complex **14a** (0.59 g, 0.55 mmol) in a mixture of MeCN and water (15 mL, 19:1 v/v) at room temperature. After 1 h the Pt/Pt borate complex **14b** precipitated as a white solid, which was collected by filtration and recrystallized by cooling a saturated hot solution in MeCN. The colorless crystals of **14b** that had formed were collected by filtration, washed with cold MeCN (10 mL) and Et_2O (25 mL), and dried in vacuo. Yield: 0.69 g (89%), mp > 200 °C. Anal. Calcd for $[C_{70}H_{78}B_2N_6Pt_2 + 2CH_3CN]$ C, 59.36; H, 5.65; N, 7.48. Found: C, 59.32; H, 5.51; N, 7.46.

Synthesis of [2,3,5,6-Tetrakis{(dimethylamino)methyl}-phenylene-1,4-bis(pyridineplatinum(II))] Bis(trifluoromethanesulfonate) (15). A stirred colorless solution of the Pt/Pt bisacetonitrile complex **14a** (100 mg, 93 μmol) in MeCN (5 mL) was treated with pyridine (0.5 mL, excess) at room temperature. The reaction mixture remained colorless during the addition step. After being stirred for 5 min at room temperature, the reaction mixture was concentrated to ca. 2.5 mL, and Et_2O (5 mL) was slowly added by vapor diffusion. This resulted in the formation of pale yellow crystals of the Pt/Pt bispyridine complex **15**, which was filtered off, washed with Et_2O (3 × 15 mL), and dried in vacuo. Yield: 87 mg (81%), mp 167 °C (dec). ^1H NMR (CD_3CN, 200 MHz): δ 8.93 (m, 4 H, py-H), 8.05 (m, 2 H, py-H), 7.74 (m, 4 H, py-H), 4.08 (s, 8 H, $^3J_{Pt-H} = 47.7$ Hz, NCH_2), 2.76 (s, 24 H, $^3J_{Pt-H} = 39.5$ Hz, NMe_2). Anal. Calcd for $[C_{30}H_{34}F_6N_6O_6Pt_2S_2]$: C, 31.53; H, 3.00; N, 7.35. Found: C, 31.39; H, 3.15; N, 7.24.

Reaction of Bimetallic Triflate Complexes 5a and 14a with Pyrazine. In a typical NMR experment a solution of **14a** (20 mg, 18.6 μmol) in CD_3CN (0.5 mL) in an NMR tube was treated with a 0.10 mL portions of a solution of pyrazine (5.0 mg, 63 μmol) in CD_3CN (1.00 mL). After each addition of pyrazine (pyz) a ^1H NMR spectrum was recorded of the resulting solution. In the last addition step an excess of pyrazine (20 mg, 250 μmol) was added and a ^1H NMR spectrum was recorded of the resulting solution. The last experiment resulted in complete conversion of **14a** to its bis(pyrazine) derivative $[1,4\text{-}\{Pt(pyz)\}_2(C_2N_4)](OTf)_2$. Isolation of this species in a pure form could, however, not be established. $[1,4\text{-}\{Pd(pyz)\}_2(C_2N_4)](OTf)_2$: ^1H NMR (CD_3CN, 200 MHz) δ 8.64 (s, pyz-H), 3.61 (s, 8 H, NCH_2), 2.68 (s, 24 H, NMe_2). $[1,4\text{-}\{Pt(pyz)\}_2(C_2N_4)](OTf)_2$: ^1H NMR (CD_3CN, 200 MHz) δ 8.72 (s, pyz-H), 3.82 (s, 8 H, $^3J_{Pt-H} = 44.3$ Hz, NCH_2), 2.89 (s, 24 H, $^3J_{Pt-H} = 34.1$ Hz, NMe_2).

Synthesis of [2,3,5,6-Tetrakis{(dimethylamino)methyl}-1,4-bis{iodoplatinum(II)}-1-methylcyclohexa-2,5-dienylcarbocation] Trifluoromethanesulfonate (23). A white suspension of the Pt/Pt bistriflate complex **14a** (100 mg, 93 μmol) in neat methyl iodide (10 mL) was stirred for two weeks at room temperature. The deep red suspension/solution that had formed during this time was evaporated to dryness, and the resulting red oily residue extracted with CH_2Cl_2 (20 mL). The resulting deep red CH_2Cl_2 extract was concentrated to 10 mL and layered with Et_2O (15 mL). The precipitated insoluble, red product was collected by filtration, washed with Et_2O, and dried in vacuo. Yield: 28 mg (27%), red microcrystalline powder. Analytically pure crystals of the Pt/Pt arenium ion complex **23** (mp 114−118 °C) could be obtained by vapor diffusion of Et_2O into a solution of **23** in CH_2Cl_2. Anal. Calcd for $[C_{20}H_{35}F_3I_2N_4O_3Pt_2S]$: C, 21.59; H, 3.17; N, 5.04. Found: C, 21.55; H, 3.19; N, 4.98.

Reaction of 14 with Allyl Iodide. The Pt/Pt bistriflate complex **14a** (100 mg) was dissolved in a mixture of MeCN (15 mL) and H_2O (1 mL), and allyl iodide (1 mL, excess) was added in one portion at room temperature while stirring. The reaction mixture was stirred at room temperature for 48 h, during which time an off-white precipitate formed. The solid was collected by centrifugation, washed with MeCN (2 × 20 mL) and Et_2O (2 × 20 mL), and dried in vacuo to afford the organometallic polymer **24** as an off-white insoluble solid.

Reaction of 14 with Ethyl Iodide. The Pt/Pt bistriflate complex **14a** (100 mg) was dissolved in a mixture of MeCN (15 mL) and H_2O (1 mL), and EtI (1 mL, excess) was added in one portion at room temperature. The reagents were mixed and left undisturbed. After 2 months a white precipitate and black crystals formed, which were separated manually. The white precipitate was identified as **14a** (starting material). The black crystals (mp > 200 °C) of the bisplatinum complex **14c** were suitable for an X-ray analysis. The yield was not determined.

X-ray Structure Determination of 5b, 10, 14b, 14c, 16, and 23. The crystal structure of **5b** has been reported elsewhere.[6] Pertinent numerical data have been included in Table 5 for comparison. Crystals suitable for X-ray diffraction were glued to the tip of a glass fiber and transferred into the cold nitrogen stream on an Enraf-Nonius CAD4-T diffractometer on a rotating anode. Accurate unit-cell parameters and an orientation matrix were determined by least-squares fitting of the setting angles of a set of well-centered reflections (SET4).[23] Reduced-cell calculations did not indicate higher lattice symmetry.[24] Crystal data and details on data collection and refinement are collected in Tables 4 and 5. All data were collected at 150 K in ω-scan mode using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å).

Data were corrected for *Lp* effects and for the observed linear instability of the three periodically measured reference reflections. No absorption correction was applied for complex **5b**. For the other complexes either numerical (ABSORB,[25] based on Gaussian integration) or (semi-)empirical methods (ABSP, based on measured ψ-scans or DIFABS,[26] based on ΔF^2, both implemented in PLATON[27]) were applied.

The structure of **16** was solved by automated direct methods (SHELXS96).[28] The structures of the other complexes were solved by automated Patterson methods and subsequent difference Fourier techniques (SHELXS86[29] for **10** and DIRDIF-92[30] for **5b**, **14b**, **14c**, and **23**).

All structures were refined on F^2 using full-matrix least-squares techniques (SHELXL-93).[31] Hydrogen atoms were included in the refinement on calculated positions, riding on their carrier atoms. Methyl hydrogen atoms were refined in a rigid group, allowing for rotation around the C−C or C−N bonds. The disordered Pt and Pd atoms of complex **10** were

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constrained to the same site with the same atomic displacement parameters. The non-hydrogen atoms of all structures were refined with anisotropic thermal parameters. The hydrogen atoms were refined with a fixed isotropic displacement parameter related to the value of the equivalent isotropic displacement parameter of their carrier atoms.

Neutral atom scattering factors and anomalous dispersion corrections were taken from the International Tables for Crystallography.[32] Geometrical calculations and illustrations were performed with PLATON;[27] all calculations were performed on a DECstation 5000 cluster.

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Supporting Information Available: ORTEP drawings (50% probability atomic displacement ellipsoids) of the dications of complexes **5b**, **14b**, and the $Pt_2I_6^{2-}$ dianion of **14c**. Hydrogen atoms, the anions (BPh_4^-), and cocrystallized solvent molecules (MeCN) have been omitted for clarity. Further details of the structure determinations, including atomic coordinates, bond lengths and angles, and thermal parameters (34 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions. Further details for the structure determination of **5b** are available as Supporting Information to the preliminary report.[6]

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