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Double Cyclometalation via Carbon−Silicon Bond Cleavage by Palladium(II) Acetate. X-ray Structure of a Cationic 1,4-Dipalladated Benzene Ring and Selective Synthesis of Heterobimetallic 1,4-Phenylene-Bridged Platinum(II)−Palladium(II) Complexes

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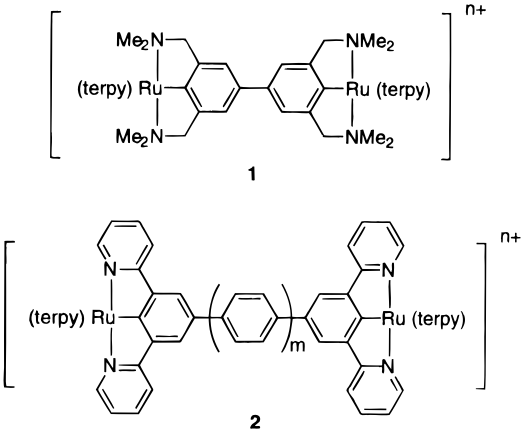
Summary: The disilylated compound 1,4-bis(trimethylsilyl)-2,3,5,6-tetrakis((dimethylamino)methyl)benzene, $(Me_3Si)_2C_2N_4$, **4**, *can be electrophilically palladated selectively at the C−Si bonds to afford the neutral 1,4-bis(palladium) complex $[(AcOPd)_2(C_2N_4)]$, from which the dicationic $[(LPd)_2(C_2N_4)]^{2+}$ (L = MeCN) organometallic species are accessible. The monosilylated species $(Me_3Si)(H)C_2N_4$,* **5**, *can be used for the preparation of the dicationic heterodinuclear platinum(II)−palladium(II) species $[(LPd)(LPt)(C_2N_4)]^{2+}$ (L = MeCN) via a sequence of transmetalation of the organolithium derivative of* **5** *with $[PtCl_2(SEt_2)_2]$, followed by a C−Si bond palladation reaction.*

Much interest exists in homo- and heterobimetallic complexes in which the metal centers are connected via a short carbon chain,[1] and one reason for this is that these systems may function as building blocks for organometallic polymers. However, one of the most intriguing aspects of such bimetallic systems is the electronic contact created when a π-conjugated group is used to separate the metal centers. For example, the oligophenylene-bridged bis(ruthenium) complexes **1** and **2** (Figure 1) exhibit very high comproportionation constants, and in **2** it has been found that an increase in distance between the metal centers results in a decrease in electronic communication.[1]

We have explored the synthesis of linear multimetallic systems using π-conjugated bridging ligands containing *N,C,N′* and related coordination motifs. Our basis for this exploration is the anionic ligand $\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}^-$, which has been shown to be capable of adopting several different coordination modes. The investigation of organometallic complexes of this ligand has enabled us to study mechanistic aspects and reaction intermediates of metal-mediated and -catalyzed reactions.[2]



1

2

Figure 1. Structures of bis(ruthenium) complexes **1** and **2** with a high degree of electronic communication (terpy = 2,2′;2′′,6′-terpyridine; *n* = 2, 3, 4,; *m* = 0, 1, 2).

Our approach here is to prepare the shortest possible aromatic spacer containing two *N,C,N′*-coordination moieties. This is the 1,4-monophenylene bridge, $[C_6(CH_2NMe_2)_4\text{-}2,3,5,6]^{2-}$ (a dianionic ligand derived from $C_6H_2(CH_2NMe_2)_4$-1,2,4,5, **3**; see Scheme 1),[3] that could be anticipated to provide bimetallic complexes in which there would be a higher intermetallic electronic contact than in either **1** or **2**. Moreover, this chosen system contains tertiary amine groups that provide chelating intramolecular coordination to the metal centers, and as a result electron delocalization will be concentrated in the 1,4-phenylenediyl system.

It is clear that our goal of preparing heterobimetallic complexes is not straightforward and is likely to involve the selective introduction of two different metal centers in two separate synthetic sequences. We now report the successful selective syntheses of 1,4-phenylene (=C_2N_4) bridged bis(palladium(II)) complexes **6**−**8**, as well as of heterodinuclear platinum(II)−palladium(II) complexes **10**−**12**. The applied strategies involve combinations of transmetalation[4] and newly developed C−Si bond palladation reactions.[5] This approach was found to be necessary since direct cyclometalation routes, which have been reported for the preparation of monometallic[6a,b]

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(3) A sulfur-containing analog of **3**, i.e. $C_6H_2(CH_2SPh)_4$)-1,2,4,5, has been cyclometalated to afford a monophenylene-bridged bis(palladium) complex: Loeb, S. J.; Shimizu, G. K. H. *J. Chem. Soc., Chem. Commun.* **1993**, 1395.

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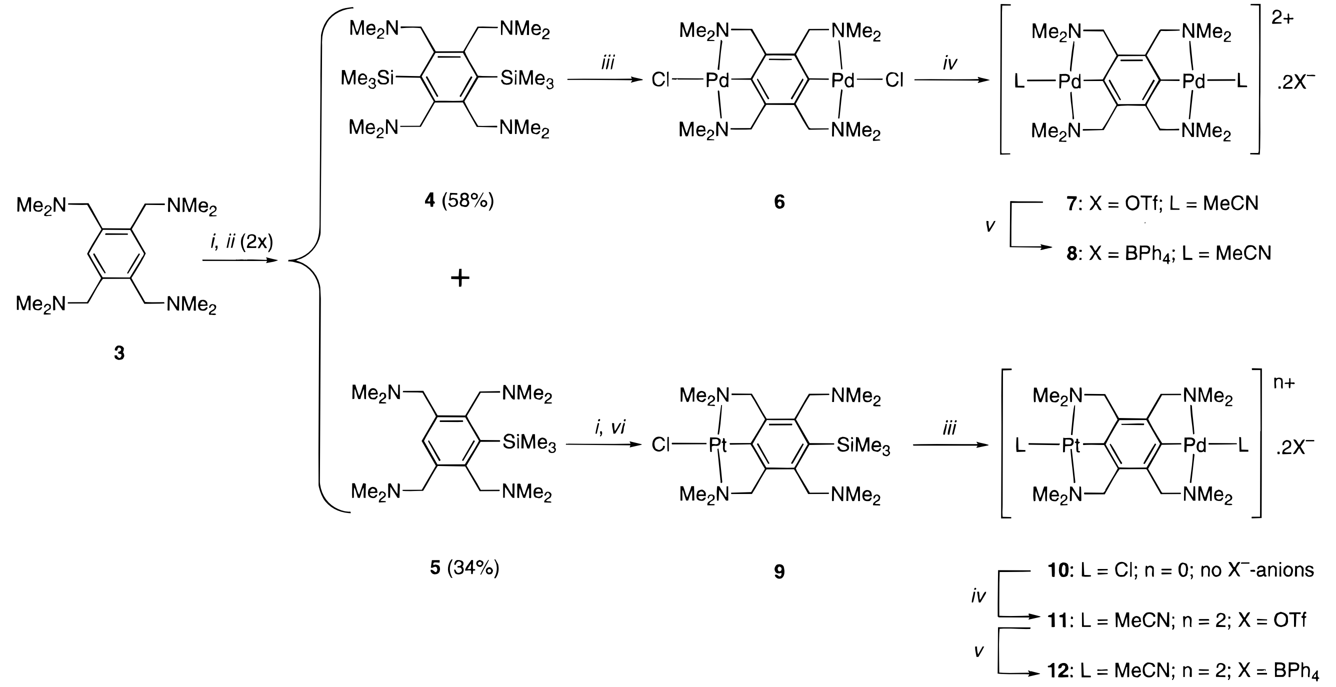
Scheme 1. Synthesis and Subsequent Metalation Reactions of 4 and 5 Yielding Neutral and Cationic Dipalladium(II) and Heterobimetallic Platinum(II)−Palladium(II) Complexes 6−8 and 10−12[a]



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

and bimetallic arylpalladium compounds,[3,6c] are not yet available for tetraamine **3**.

Starting from **3**,[7] the route to bis(palladium) complexes proceeds via the disilylated compound **4**, whereas the route to heterobimetallic species proceeds via monosilylated compound **5**. Compounds **4** and **5** have been prepared as a mixture from two successive monolithiation/silylation cycles employing **3** as a substrate with *n*-BuLi and Me_3SiOTf (OTf = trifluoromethanesulfonate) as the reagents; subsequent column chromatographic separation affords pure **4** and **5**, which have been fully characterized (NMR, elemental microanalysis, X-ray of **4**).[8]

Compound **4** reacts with $Pd(OAc)_2$ in a direct C−Si bond cleavage reaction to afford, after addition of LiCl, the bis(palladium(II)) complex $[(PdCl)_2C_2N_4]$, **6**, as a white solid in 78% yield (Scheme 1). Complex **6** has poor solubility characteristics and was converted into the ionic derivative **7** using silver triflate and precipitated as its tetraphenylborate salt **8**.[9] Recrystallization of **8** from hot acetonitrile gave crystals that were suitable for X-ray analysis, and the molecular geometry of **8** is shown in Figure 2.[10] The Pd−phenylene−Pd unit is planar with a Pd⋯Pd distance of 6.5474(9) Å across the central metalated ring. Coordination of the *ortho*-amine arms to the palladium centers affords C_2 symmetry related pairs of puckered five-membered rings, in which the N-donor atoms are lifted 19.9(3) and −21.2(3)° out of the plane of the bimetalated ring (C(2)−C(3)−C(5)−N(2) = −160.1(3)° and C(3)−C(2)−C(4)−

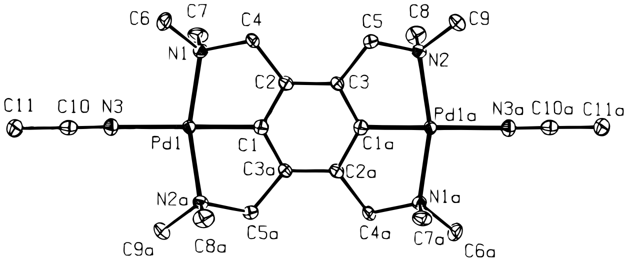


Figure 2. ORTEP drawing (50% probability level) of the dication of **8**. Hydrogen atoms, tetraphenylborate anions, and acetonitrile solvate molecules are omitted for clarity.

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(9) ^1H NMR data for **7** (CD_3CN, 200 MHz): δ 3.87 (s, 8 H, CH_2), 2.80 (s, 24 H, NMe_2). ^{13}C NMR data for **7** (CD_3CN, 50 MHz): δ 153.1, 139.4 (Ar), 72.9 (CH_2), 53.4 (NMe_2).

(10) Crystal data for **8**, $[C_{22}H_{38}N_6Pd_2][C_{24}H_{20}B]_2[C_2H_3N]_2$: M_r = 1320, colorless, crystal (0.08 × 0.10 × 0.60 mm), triclinic, space group $P\bar{1}$ (No. 2) with a = 10.2037(12) Å, b = 11.4148(11) Å, c = 15.368(2) Å, α = 86.982(10)°, β = 81.848(11)°, γ = 68.900(9)°, V = 1653.1(3) Å^3, Z = 1, D_x = 1.326 g cm^{-1}, $F(000)$ = 686, μ(Mo Kα) = 5.9 cm^{-1}, 10 530 reflections measured, 7572 independent, R_{int} = 0.077 (1.3° < θ < 27.5°, ω scan, T = 150 K, Mo Kα radiation, graphite monochromator, λ = 0.710 73 Å) on an Enraf-Nonius CAD4-T diffractometer on rotating anode. The structure was solved by automated Patterson methods (DIRDIF92). Refinement on F^2 was carried out by full-matrix least-squares techniques (SHELXL-93); no observance criterion was applied during refinement. Refinement converged at a final w$R2$ value of 0.1010, $R1$ = 0.0437 (for 6109 reflections with $F_o > 4\sigma(F_o)$), and S = 1.02, for 394 parameters. H atoms were placed on calculated positions riding on their carrier atom. A final difference Fourier showed no residual density outside −0.69 and 0.79 e Å^{-3}.

N(1) = 158.8(3)°). Spectroscopic and elemental microanalysis data for **6**−**8** are consistent with the bimetallic structures depicted in Scheme 1, and all the species have square planar metal coordination as established for **8** in the solid state.

Starting from monosilylated compound **5**, the multistep pathway to heterobimetallic complexes **10**−**12** involves lithiation with *n*-BuLi to afford the corresponding organolithium reagent $[(Me_3Si)(Li)(C_2N_4)]$. Transmetalation of the latter with $[PtCl_2(SEt_2)_2]$ in THF provides the Pt(II) complex $[(Me_3Si)(PtCl)(C_2N_4)]$, **9**, in moderate yield (Scheme 1). Complex **9** affords elemental microanalysis and spectroscopic data (^{1}H and ^{13}C NMR) consistent with the proposed structure shown in Scheme 1.[11] Treatment of **9** with a solution of $Pd(OAc)_2$ in a 1:1 mixture of CH_2Cl_2/MeOH, followed by addition of LiCl, results in selective cleavage of the C−Si bond mutually *trans* to the platinum(II) center, affording heterobimetallic platinum(II)−palladium(II) complex $[(PdCl)\text{-}1\text{-}(PtCl)\text{-}4\text{-}\{C_6(CH_2NMe_2)_4\text{-}2,3,5,6\}]$, **10**, quantitatively. Complex **10** has poor solubility characteristics (like **6**) and was converted to ionic complexes $[(LPd)(LPt)(C_2N_4)]^{2+}(X^-)_2$ (L = MeCN; **11**, X = OTf; **12**, X = BPh_4) which have been characterized by standard spectroscopic and microanalytic methods.[11]

The heterobimetallic ionic triflate complex **11** is prepared by treatment of **10** with AgOTf in acetonitrile and shows ^{1}H NMR resonances (CD_3CN solution) of two inequivalent *N,C,N′*-coordination moieties, with one set of CH_2NMe_2 signals having ^{195}Pt satellites; i.e., the N-donor atom is coordinated to the platinum(II) center. The other set of CH_2NMe_2 signals shows no ^{195}Pt satellites and has resonance positions consistent with coordination of these groups to a palladium(II) center. The ^{13}C NMR spectrum of bimetallic complex **11** (CD_3CN) reveals features indicative of the presence of one platinum(II) center and one palladium(II) center in the same molecule; 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 symmetrical doubly platinated aryl ring 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 $^3J_{Pt-C}$.[11] The analogous tetraphenylborate species **12** was prepared by precipitation from a solution of **11** treated with $NaBPh_4$. Elemental microanalysis (**12**) and spectroscopic data (**11**) are in agreement with the proposed structures (Scheme 1).

The novel neutral and ionic bimetallic compounds are air and moisture stable, and an interesting aspect of the ionic triflate complexes **7** (Pd/Pd) and **11** (Pd/Pt) lies in the potential offered by the lability of the MeCN ligands for further development of new organometallic materials. Preliminary experiments show that on the ^{1}H NMR time scale the coordinated CH_3CN is labile and exchanges rapidly with the solvent (CD_3CN) and that addition of pyridine results in the formation of a dicationic complex in which both metal centers are coordinated by pyridine. These experiments illustrate the real possibility of using cationic monophenylene bridged homo- and heterobimetallic complexes **7** and **11** as building blocks for air- and moisture-stable (directional) organometallic polymers[12] when additional bridging ligands such as 4,4′-bipyridine or pyrazine are used. This approach is currently being studied as species such as **7** and **11** have potential for electronic M−M′ communication and could possibly be employed as structural elements in new materials or bimetallic catalyst systems.

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Supporting Information Available: Tables of X-ray parameters, all positional parameters, thermal parameters, bond lengths, and bond angles for **8** (8 pages). Ordering information is given on any current masthead page. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre; see the Notice to Authors, issue no. 1.

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[11] ^{1}H NMR data of **9** ($CDCl_3$, 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 data of **9** ($CDCl_3$, 75 MHz): δ 147.0 (*C*−Pt, $^1J_{Pt-C}$ = 1000 Hz), 141.7 ($^3J_{Pt-C}$ = 75 Hz), 139.1 ($^2J_{Pt-C}$ = 44 Hz), 133.5 (C_{aryl}−$SiMe_3$), 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 ($SiMe_3$). ^{1}H NMR data of **11** (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 data of **11** (CD_3CN + 10% D_2O, 50 MHz): δ 152.7 (C−Pd), 141.2 (C−Pt; $^1J_{Pt-C}$ not observed), 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 (NMe_2).

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