J. Am. Chem. Soc. **1991**, *113*, 5129–5130

Acknowledgment. C.B. thanks the EEC for contract SC1.0027.C. The Laboratoire de Chimie Théorique is associated with the CNRS (URA 506) and is a member of ICMO and IPCM. C.C. thanks the CNRS for a BDI fellowship. This work was supported by an NSF/CNRS grant for international U.S./France scientific collaboration (K.G.C. and O.E.).

Supplementary Material Available: Positional and thermal parameters for (triphos)RhCl(C$_4$H$_4$) and [(triphos)Ir(C$_6$H$_6$)]-BPh$_4$·THF (6 pages). Ordering information is given on any current masthead page.

Nucleobase Complexes with Metal–Metal Dative Bonds: Mixed Pt,Pd Compounds with Bridging 1-Methylcytosinato Ligands and Unprecedented Short Pt(II)–Pd(II) Contacts

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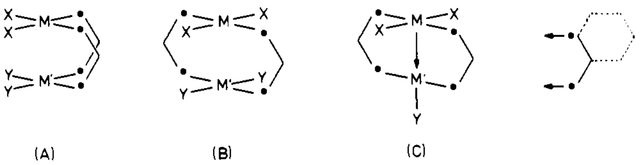
Received March 28, 1991

Metal–metal dative bond formation in complexes containing d^8 metal ions is relatively rare in organometallic and coordination chemistry[2] considering the large number of examples with weaker metal–metal "interactions" via the d$_{z^2}$ orbital(s) of the d^8 metal(s). We report here on the facile formation of three mixed Pt,Pd complexes containing two bridging anionic 1-methylcytosine (1-MeC$^-$) nucleobases and on their structures which display unprecedented short Pt–Pd distances.

Dinuclear complexes of the types *cis*-[X$_2$M(L)$_2$M'Y$_2$]$^{n+}$, containing the d^8 metal ions M = M' = Pt(II) or Pd(II), or M = Pt(II) and M' = Pd(II), and two 1,2-difunctional ligands L,[3-6] as well as additional X and Y ligands (typically NH$_3$, amines, or halogens), virtually always are built up such that the metal coordination planes face each other (A in Chart I). Intracomplex M–M' distances are usually around 2.8–3 Å. In the case of M = M' = Pt(II), oxidation of the two metals is facilitated, either to mixed-valence-state compounds[7] or to diplatinum(III) species.[8]

Chart I



From model building it is obvious that a similar arrangement is impossible for the corresponding trans complexes due to severe steric hindrance between X and Y ligands (B). Only with nonheterocyclic bridging ligands having a larger bite distance are compounds of type B formed.[9]

As has recently been shown by us,[10] *trans*-[(NH$_3$)$_2$Pd(1-MeC-*N3*)$_2$]$^{2+}$,[11] when reacted with *trans*-[(NH$_3$)$_2$Pd(H$_2$O)$_2$]$^{2+}$, escapes the steric clash between X = Y = NH$_3$ ligands in a hypothetical *trans*-[(NH$_3$)$_2$Pd(1-MeC$^-$-*N3*,*N4*)$_2$Pd(NH$_3$)$_2$]$^{2+}$ by isomerization to the corresponding cis complex (head–tail). We have now observed another pattern by which steric hindrance between X and Y ligands is prevented, yet the trans geometry of both metals is maintained: When *trans*-[(NH$_3$)$_2$Pt(1-MeC-*N3*)$_2$](NO$_3$)$_2$ (**1**)[12] is reacted with *trans*-[(NH$_3$)$_2$Pd(H$_2$O)$_2$]$^{2+}$[13] in H$_2$O,[14] *trans*-[(NH$_3$)$_2$Pt(1-MeC$^-$-*N3*,*N4*)$_2$Pd(NH$_3$)](NO$_3$)$_2$·3H$_2$O (**2**) is formed in high yield. The structure[15] of **2** (C in Chart I and Figure 1) reveals an essentially square-planar coordination geometry of Pd and a square-pyramidal one for Pt with Pd in the apical position. Pd and Pt coordination planes are virtually at right angles (88.4 (2)°). The two metals are bridged by two almost parallel (dihedral angle 9.1 (1)°) 1-methylcytosinato anions, trans with respect to Pt, in a head–head arrangement. Pd is surrounded by two deprotonated amino groups of 1-MeC$^-$, an NH$_3$, and a Pt. The second NH$_3$, which originally was bound to Pd, has been lost during the reaction. The metal–metal distance

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(1) (a) Universität Dortmund. (b) Università di Trieste.

(2) See, e.g.: (a) Frew, A. A.; Muir-Manojlovic, L.; Muir, K. W. *J. Chem. Soc., Chem. Commun.* **1980**, 624. (b) Brown, M. P.; Cooper, S. J.; Frew, A. A.; Muir-Manojlovic, L.; Muir, K. W.; Puddephatt, R. J.; Seddon, K. R.; Thomson, M. A. *Inorg. Chem.* **1981**, *20*, 1500. (c) van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K.; Spek, A. L. *Inorg. Chem.* **1982**, *21*, 2014. (d) Arsenault, G. J.; Anderson, C. M.; Puddephatt, R. J. *Organometallics* **1988**, *7*, 2094. (e) McDonald, R.; Cowie, M. *Inorg. Chem.* **1990**, *29*, 1564. (f) Uson, R.; Forniés, J.; Tomás, M.; Casas, J. M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 748. (g) Balch, A. L.; Rowley, S. P. *J. Am. Chem. Soc.* **1990**, *112*, 6139.

(3) For Pt,Pt, see, e.g.: (a) Micklitz, W.; Renn, O.; Schöllhorn, H.; Thewalt, U.; Lippert, B. *Inorg. Chem.* **1990**, *29*, 1836 and references cited. (b) O'Halloran, T. V.; Lippard, S. J. *Inorg. Chem.* **1989**, *28*, 1289 and references cited. (c) Matsumoto, K.; Miyamae, H.; Moriyama, H. *Inorg. Chem.* **1989**, *28*, 2959 and references cited. (d) Laurent, J.-P.; Lepage, P.; Dahan, F. *J. Am. Chem. Soc.* **1982**, *104*, 7335. (e) Umakoshi, K.; Kinoshita, I.; Fukui-Yasube, Y.; Matsumoto, K.; Ooi, S.; Nakai, H.; Shiro, M. *J. Chem. Soc., Dalton Trans.* **1989**, 815.

(4) For Pd,Pd, see, e.g.: (a) Micklitz, W.; Sheldrick, W. S.; Lippert, B. *Inorg. Chem.* **1990**, *29*, 211. (b) Matsumoto, K.; Moriyama, H.; Suzuki, K. *Inorg. Chem.* **1990**, *29*, 2096. (c) Umakoshi, K.; Kinoshita, I.; Ooi, S. *Inorg. Chim. Acta* **1987**, *127*, L41.

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(6) References 3–5 do not include examples with two nonheterocyclic bridging ligands.

(7) See, e.g.: (a) Barton, J. K.; Rabinowitz, H. N.; Szalda, D. J.; Lippard, S. J. *J. Am. Chem. Soc.* **1977**, *99*, 2827. (b) Matsumoto, K.; Fuwa, K. *J. Am. Chem. Soc.* **1982**, *104*, 897. (c) Renn, O.; Albinati, A.; Lippert, B. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 84.

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(11) Abbreviations used: 1-MeC-*N3* = neutral 1-methylcytosine, C$_5$H$_7$N$_3$O, with metal at N3; 1-MeC$^-$-*N3*,*N4* = 1-methylcytosinate anion with metals binding via N3 and the deprotonated amine group; 1-MeU = 1-methyluracilate anion, C$_5$H$_5$N$_2$O$_2$.

(12) Lippert, B.; Lock, C. J. L.; Speranzini, R. A. *Inorg. Chem.* **1981**, *20*, 808.

(13) Prepared in situ from *trans*-(NH$_3$)$_2$PdCl$_2$ and 2Ag$^+$ in H$_2$O.

(14) Preparation of **2**: *trans*-[(NH$_3$)$_2$Pd(H$_2$O)$_2$]X$_2$ (X = NO$_3^-$ or ClO$_4^-$) and **1** were mixed in a 1:1 ratio in H$_2$O, the pH was adjusted to 8, and the sample was kept for 18 h at 22 °C. On slow evaporation at 4 °C, mixtures of **1** and **2** were obtained initially. Red plates of pure **2** were isolated only toward the end of the crystallization procedure, in ca. 5% yield, although ^{1}H NMR spectroscopy clearly indicates a yield of at least 60% under the conditions of the experiment. Satisfactory elemental analysis (C, H, N) was obtained for the ClO$_4$ salt trihydrate, NO$_3$ salt directly used for the X-ray analysis.

(15) Crystallography: (**2**) C$_{10}$H$_{21}$N$_{11}$O$_8$PdPt·3H$_2$O, space group $P\bar{1}$, a = 7.207 (2) Å, b = 11.692 (3) Å, c = 15.457 (4) Å, α = 108.89 (1)°, β = 101.13 (1)°, γ = 92.79 (1)°, V = 1200.4 (5) Å^3, D_{calcd} = 2.15 g cm^{-3}, D_{measd} = 2.16 g cm^{-3}, Z = 2, R = 0.037, R_w = 0.043, for 4379 unique reflections. (3) C$_{10}$H$_{18}$N$_9$O$_5$PdPtCl·H$_2$O, space group $P\bar{1}$, a = 9.116 (4) Å, b = 10.508 (6) Å, c = 11.370 (6) Å, α = 115.33 (2)°, β = 90.00 (3)°, γ = 92.62 (3)°, V = 983.1 (9) Å^3, D_{calcd} = 2.36 g cm^{-3}, D_{measd} = 2.32 g cm^{-3}, Z = 2, R = 0.038, R_w = 0.048, for 4960 unique reflections. (4) C$_{15}$H$_{23}$N$_{11}$O$_7$PdPt·3H$_2$O, space group $P\bar{1}$, a = 9.956 (5) Å, b = 10.619 (6) Å, c = 14.460 (4) Å, α = 68.66 (4)°, β = 85.88 (3)°, γ = 67.10 (4)°, V = 1307 (1) Å^3, D_{calcd} = 2.09 g cm^{-3}, D_{measd} = 2.10 g cm^{-3}, Z = 2, R = 0.39, R_w = 0.047, for 5023 unique reflections. Diffraction data were collected by using a CAD-4 Enraf-Nonius single-crystal diffractometer with Mo Kα radiation (λ = 0.7107 Å). All the structures were solved by conventional Patterson and Fourier methods and refined by full-matrix anisotropic least-squares methods. The contributions of the hydrogen atoms (kept at calculated positions) were included in the final refinements.

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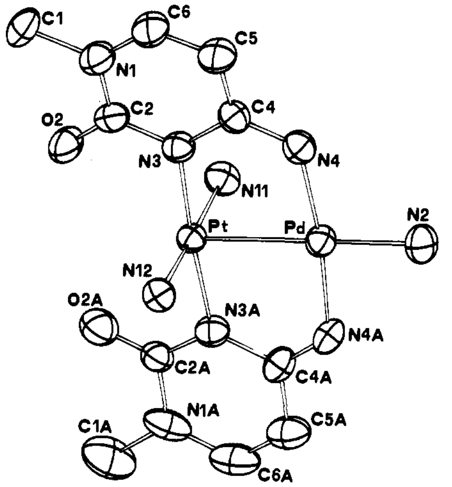

Figure 1. ORTEP drawing of the cation of *trans*-$[(NH_3)_2Pt(C_5H_6N_3O)_2Pd(NH_3)](NO_3)_2 \cdot 3H_2O$ (**2**). Selected structural data are as follows: Pt–N3, 2.011 (4) Å, Pt–N3A, 2.024 (4) Å; Pt–N11, 2.038 (5) Å; Pt–N12, 2.037 (5) Å; Pd–N4, 2.005 (5) Å; Pd–N4A, 2.014 (5) Å; Pt–Pd, 2.511 (1) Å; Pd–N2, 2.001 (5) Å; Pd–Pt–N3, 87.4 (1)°; Pd–Pt–N3A, 88.1 (1)°; Pt–Pd–N4, 87.2 (1)°; Pt–Pd–N4A, 86.1 (1)°; Pt–Pd–N2, 178.5 (2)°. The cation of *trans*-$[(NH_3)_2Pt(C_5H_6N_3O)_2PdCl]NO_3 \cdot H_2O$ (**3**) is very similar to that of **2** and therefore not shown. The ammonia ligand N2 is replaced by Cl, with Pd–Cl and Pt–Pd distances of 2.313 (1) and 2.518 (1) Å, respectively.

within the cation is 2.511 (1) Å and is best described by a Pt(II) → Pd(II) dative bond formalism rather than a Pt(III)–Pd(I) bond. The normal bond length Pd–(NH_3) (2.001 (5) Å) strongly opposes this alternative description.

Two closely related compounds, *trans*-$[(NH_3)_2Pt(1\text{-MeC}^-\text{-}N3,N4)_2PdCl](NO_3) \cdot H_2O$ (**3**) and *trans*-$[(NH_3)_2Pt(1\text{-MeC}^-\text{-}N3,N4)_2Pd(1\text{-MeU-}N3)](NO_3) \cdot 3H_2O$ (**4**), were obtained upon reaction of **1** with K_2PdCl_4[16] and by reacting **3** with 1-methyluracil (1-MeUH),[17] respectively. X-ray structures[15] of **3** and **4** show closely similar $(NH_3)_2Pt(1\text{-MeC}^-)_2Pd$ entities, e.g., Pt–Pd distances of 2.518 (1) Å (**3**) and 2.515 (1) Å (**4**) and dihedral angles of 81.6 (2)° $[PdN_2Cl/PtN_4$ (**3**)] and 87.3 (2)° $[PdN_3/PtN_4$ (**4**)]. The Pd–Cl bond length of 2.313 (1) Å in **3** appears to support the Pt(II) → Pd(II) formalism. Only the cation of **4** is depicted in Figure 2. 1-MeU acts as a monodentate ligand through N3, and its molecular plane is almost perpendicular to the Pd coordination plane (75.1 (2)°).

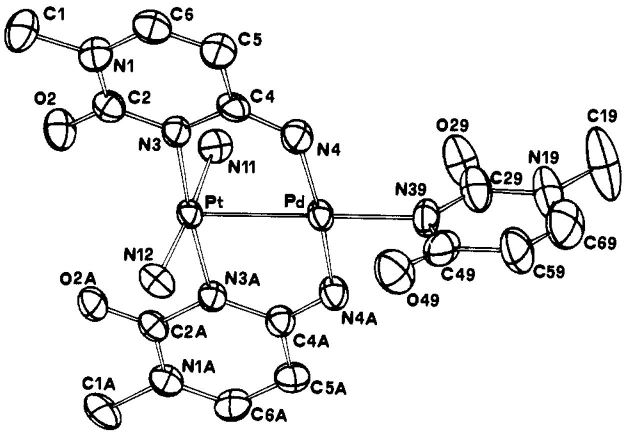

Figure 2. ORTEP drawing of the cation of *trans*-$[(NH_3)_2Pt(C_5H_6N_3O)_2Pd(C_5H_5N_2O_2)]NO_3 \cdot 3H_2O$ (**4**). Salient structural features are as follows: Pt–N3, 2.020 (4) Å; Pt–N3A, 2.020 (4) Å; Pt–N11, 2.021 (5) Å; Pt–N12, 2.036 (5) Å; Pd–N4, 1.985 (4) Å; Pd–N4A, 1.994 (4) Å; Pt–Pd, 2.515 (4) Å; Pd–N39, 2.056 (4) Å; Pd–Pt–N3, 88.0 (1)°; Pd–Pt–N3A, 86.8 (1)°; Pt–Pd–N4, 86.5 (1)°; Pt–Pd–N4A, 87.1 (1)°; Pt–Pd–N39, 178.3 (2)°.

The compounds described herein are of interest for several reasons: First, they reveal a binding pattern dramatically different from that seen in dinuclear metal nucleobase complexes derived from *cis*-$(NH_3)_2Pt^{II}$. This refers in particular to the donor-acceptor bond between Pt and Pd as opposed to weak "interactions" in the latter case. Second, the shortness of the Pt–Pd bond is unprecedented. It is shorter than the shortest Pt–Pt bond in related diplatinum(III) compounds[18] and much shorter than the Pt → Pt dative bond (2.769 (1) Å) in $[Pt_2(CH_3)_3(dppm)_2]PF_6$.[2a,b] Third, metalation of the exocyclic amino group of a cytosine nucleobase in the pH range 6–9, as observed in our compounds, is very rare.[19] Fourth, the binding pattern seems to explain why analogues of the mixed-valence-state "platinum pyrimidine blues"[19] have never been obtained from *trans*-$(NH_3)_2Pt^{II}$.

Acknowledgment. This work has been supported by the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and Murst, Rome, Italy.

Supplementary Material Available: Tables of complete crystallographic data, atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and hydrogen atom coordinates for **2–4** (18 pages); tables of observed and calculated structure factors for **2–4** (60 pages). Ordering information is given on any current masthead page.

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(16) **3** was prepared in a similar way as **2** from **1** and K_2PdCl_4 (pH 6–9). Dark greenish-yellow crystals of **3** were isolated in >60% yield. Satisfactory elemental analysis was obtained for C, H, N, Cl. ^1H NMR (D_2O) shifts (ppm): H6, 7.010, d (7.6 Hz); H5, 5.569, d; CH_3, 3.300, s.

(17) Reaction of **3** with 1.25 equiv of 1-methyluracil at pH 8–9 and slow evaporation gave brownish-red crystals of **4** in good yield (>90% according to ^1H NMR). Satisfactory elemental analysis was obtained for C, H, N. ^1H NMR (D_2O) shifts (ppm): 1-MeC$^-$ H6, 6.981, d (7.6 Hz); H5, 5.495, d; CH_3, 3.288; 1-MeU H6, 7.544, d (7.4 Hz); H5, 5.707, d; CH_3, 3.400.

(18) The shortest Pt–Pt single bond in a pyrimidine nucleobase complex is 2.543 (1) Å. Cf.: Lippert, B.; Schöllhorn, H.; Thewalt, U. *Inorg. Chem.* **1986**, *25*, 407.

(19) Lippert, B. *Prog. Inorg. Chem.* **1989**, *37*, 1 and references cited.