for the NMR spectra. This work was supported by Grant AI 18362 from the National Institute of Allergy and Infectious Diseases. The National Science Foundation (PCM 79-12083) and the Dreyfus Foundation supported the 7 T Nicolet NMR spectrometer, and the National Institutes of Health (RR 00862) supported the Mass Spectrometric Biotechnology Research Resource.

Registry No. 4, 82136-16-1; **5**, 82136-17-2; **6**, 82136-18-3; **7**, 82136-19-4; **8**, 82136-20-7; **9**, 82136-21-8; BOC-Cys(4-MeC$_6$H$_4$CH$_2$)-OH, 61925-77-7; H-Gly-OMe, 616-34-2; MeCO-Gly-OH, 543-24-8; Cys(4-CH$_3$Bzl)-Gly-OCH$_3$, 82136-22-9; BOC-Gln-OC$_6$H$_4$NO$_2$$^{-4}$, 15387-45-8; Asn-NH-CH$_3$, 82136-23-0; Gln-Asn-NH-CH$_3$, 82136-24-1; Boc-Glu-(OBzl), 13574-13-5.

Homo- and Heterodinuclear Platinum and Palladium Complexes with a Single Unsupported Monoatomic Bridging Group. Crystal Structure of the 2,6-Bis[(dimethylamino)methyl]phenylpalladium(II) Derivative $[(Pd\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\})_2(\mu\text{-}Cl)]BF_4$

David M. Grove, Gerard van Koten,* and Henk J. C. Ubbels

Anorganisch Chemisch Laboratorium
J. H. van't Hoff Instituut, University of Amsterdam
1018 WV Amsterdam, The Netherlands

Anthony L. Spek

Laboratorium voor Struktuurchemie, Rijksuniversiteit
3584 CH Utrecht, The Netherlands

Received March 15, 1982

There are few dinuclear complexes of the nickel triad metals in which the metals are only bridged by a single atom. It was only recently, for example, that $[Ph(PEt_3)_2Pt(\mu\text{-}H)Pt(PEt_3)_2H]^+$, containing a single hydride bridge between two Pt(II) centers, was structurally characterized.[1]

We now report the first examples of homo- and heterodinuclear Pd(II) and Pt(II) complexes possessing a single unsupported chloro, bromo, or iodo bridge. The successful synthesis of these complexes (see Scheme I) involves the use of the terdentate anionic ligand $\{o,o'\text{-}(Me_2NCH_2)_2C_6H_3\}$ (N–C–N) which, as a result of its special attachment, produces square-planar $[M(N\text{–}C\text{–}N)(H_2O)]^+$ (M = Pd, Pt) species with a loosely bound H_2O molecule in a site trans to a σ M–C bond. Displacement of this good leaving group (H_2O) by a terminal halide of a neutral $[M'(N\text{–}C\text{–}N)X]$ complex then leads to formation of the new dinuclear species $[(N\text{–}C\text{–}N)M'(\mu\text{-}X)M(N\text{–}C\text{–}N)]^+$, **1**. This Lewis acid–base pairing reaction[2] carried out at room temperature in CH_2Cl_2 affords these air-stable products in virtually quantitative yield upon evaporation of the solvent.[3] The proposal for **1** of a dinuclear ionic formulation was based on IR,[4] NMR (vide infra), and analytical data and is in accord with the observation that the complexes are readily soluble in polar solvents (e.g., CH_2Cl_2).

To firmly establish the presence of only a single halo atom bridge, we have completed a single-crystal X-ray structure determination on one representative member, **1a** (M = M′ = Pd, X = Cl).[5]

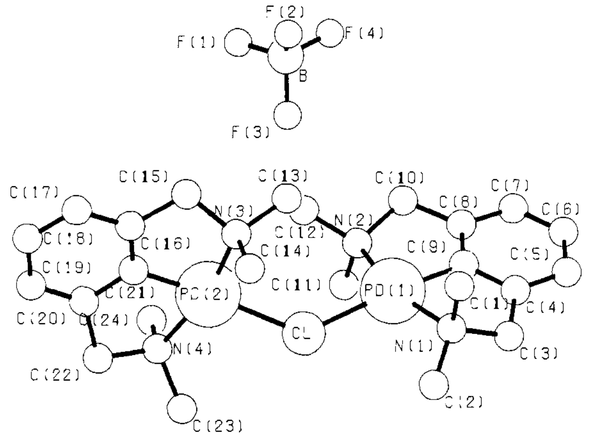
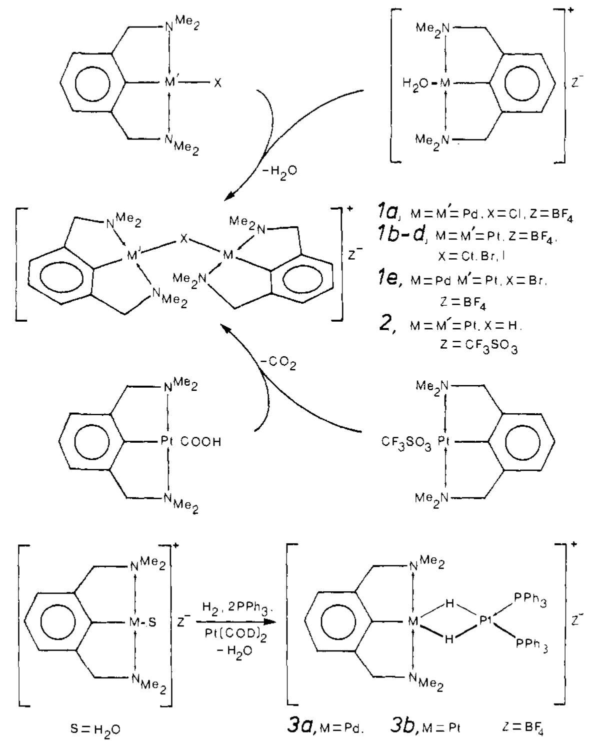


Figure 1. PLUTO drawing along with the adopted numbering scheme. Important distances (Å) are Pd(1)–Cl(1) = 2.463 (1), Pd(1)–N(1) = 2.105 (3), Pd(1)–N(2) = 2.100 (4), Pd(1)–C(9) = 1.929 (4), Pd(2)–Cl(1) = 2.458 (1), Pd(2)–N(3) = 2.094 (3), Pd(2)–N(4) = 2.104 (3), and Pd(2)–C(21) = 1.909 (4). Some relevant angles (°) are Cl(1)–Pd(1)–N(1) = 97.0 (1), Cl(1)–Pd(1)–N(2) = 100.3 (1), Cl(1)–Pd(1)–C(9) = 174.5 (1), N(1)–Pd(1)–N(2) = 162.6 (1), Cl(1)–Pd(2)–N(3) = 97.9 (1), Cl(1)–Pd(2)–N(4) = 97.6 (1), Cl(1)–Pd(2)–C(21) = 174.3 (1), and N(3)–Pd(2)–N(4) = 164.3 (1).

Scheme I



The cation (see Figure 1) as anticipated consists of two *trans-N,N′,C*-$[Pd[C_6H_3(CH_2NMe_2)_2]]$ units sharing a single bridging chlorine atom. Both Pd(II) centers have a slightly distorted square-planar coordination sphere (e.g., N(1)–Pd(1)–

---

(1) Bracher, G.; Grove, D. M.; Venanzi, L. M.; Bachechi, F.; Mura, P.; Zambonelli, L. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 778–779; *Angew. Chem.* **1978**, *90*, 826–827.

(2) For background information see: "Hard and Soft Acids and Bases"; Pearson, R. G., Ed.; Dowden, Hutchinson and Ross: Stroudsburg, PA, 1973.

(3) Although a dinuclear species is not isolated when [Ni(N–C–N)X] is included in this reaction scheme, the resultant formation of $[Ni(N\text{–}C\text{–}N)H_2O]^+$ strongly suggests the presence of such a Ni(II)-containing complex as the reactive intermediate.

(4) ν_{BF} 1080 cm^{-1}, no identifiable ν_{MX} or $\nu_{M'X}$.

(5) Pale yellow X-ray analysis crystals of **1a**, $C_{24}H_{38}ClN_4Pd_2\cdot BF_4$, were monoclinic space group $P2_1/c$ with a = 11.163 (1) Å, b = 21.347 (2) Å, c = 12.246 (4) Å, β = 91.48 (2)°, Z = 4, d_{calcd} = 1.634 g/cm^3. The intensity data were measured on a Nonius-Enraf CAD4 diffractometer (Zr-filtered Mo Kα radiation) with θ–2θ scans. A total of 6691 unique reflections were measured for $\theta < 27.5°$ of which 5077 were considered observed [$I < 2.5\sigma(I)$]. The structure was solved by standard Patterson and Fourier techniques and refined by blocked full-matrix least-squares methods. In the final refinement hydrogen atoms were refined in a riding mode with a rotation parameter for the rigid methyl groups. There is some disorder in the BF_4 anion and the ligand on Pd(2) (two equivalent, mirror plane related puckering possibilities), both of which have the same occupation parameters (84:16). Final refinement converged at R_F = 0.042 and R_{wF} = 0.048. Figure 1 and the data apply to the 84% molecule.

N(2), 162.6 (1)°; C(9)–Pd(1)–Cl, 174.5 (1)°, and the two virtually equivalent coordination planes are orientated almost perpendicular to each other (88.5 (2)°).[6] The Pd(1)–Cl–Pd(2) angle of 134.8 (1)° is a dominant structural feature, which taken with the two fairly long Pd–Cl distances (2.463 (1) and 2.458 (1) Å) gives rise to a Pd–Pd separation (4.544 (2) Å) that is much greater than that found in complexes where there is a distinct M–M bond.[7] The large deviation of this angle from that expected for a tetrahedral halide atom (two bonds, two long pairs; cf. isoelectronic $[(C_5H_5)(CO)_2Fe(\mu\text{-}I)Fe(CO)_2(C_5H_5)]$, ∠Fe–I–Fe = 110.8 (1)°)[8] is presumably steric in origin.

The solution ^1H NMR data of **1a** [60 MHz; CD_2Cl_2; δ CH_2 4.03, CH_3 2.95] evidences retention of both the Lewis acid–base interaction and coordination of the N donor ligands on the NMR time scale.[9] Since in the solid-state structure there are not only inequivalent CH_2NMe_2 groupings but also diastereotopic CH_2 and Me groups, the NMR solution observation of only single CH_2 and CH_3 signals means that there is a fluxional process, most likely a rotation about the metal–halogen axes, that renders the CH_2NMe_2 environments equivalent. The ^1H NMR data for the other dinuclear species **1b–e** are similar. There is also NMR evidence for a further fluxional process[10] involving a fast reversible dissociation of the dinuclear units initiated by traces of water (a weak coordinating ligand).

Complexes **1a–e** are, as far as we are aware, the first structurally characterized species in which a single halide bridge atom binds two nickel triad metal centers without the support of bidentate phosphine or arsine ligands as found in, for example, A-frame complexes.[11]

To investigate the versatility of the $[M(N\text{–}C\text{–}N)]^+$ system to act as a Lewis acid, we have extended our interest to hydride-containing species (see scheme). From the reaction of $[Pt(N\text{–}C\text{–}N)(CF_3SO_3)]$ and $[Pt(N\text{–}C\text{–}N)(COOH)]$[12] in benzene at 50 °C was isolated the monohydrogen bridge complex $[(N\text{–}C\text{–}N)Pt(\mu\text{-}H)Pt(N\text{–}C\text{–}N)]^+$, **2**,[13] in almost quantitative yield [^1H NMR (CD_2Cl_2) δ −4.54 (Pt,H,Pt), J(Pt,H) = 576 Hz]. This is the first complex containing N donor ligands that has a structural relationship to the unique dihydride $[Ph(PEt_3)_2Pt(\mu\text{-}H)Pt(PEt_3)_2H]^+$,[1] which also contains a three-center two-electron M–H–M bridge bond.

It is also possible to synthesize dihydride-bridged complexes $[N\text{–}C\text{–}N)M(\mu\text{-}H)_2Pt(PPh_3)_2]^+$ (M = Pd (**3a**), Pt (**3b**)) by using a procedure in which a reactive hydride is generated in situ from the reaction of Pt(0) phosphine species and gaseous H_2. From spectroscopic data [^1H NMR (acetone-d_6) δ (**3a**) −3.84 (μ-H)$_2$, J(Pt,H) = 818 Hz); (**3b**) −1.86 (μ-H)$_2$, $J(Pt_A,H)$ = 707 Hz, $J(Pt_B,H)$ = 385 Hz],[14] these complexes are anticipated to have a geometry in which there is both a four- and a five-coordinate center, a situation also existing in the related tertiary phosphine species $[(PR_3)_2Pt(\mu\text{-}H)_2Pt(PR_3)_2H]BF_4$ (R = Ph, Cy, Et).[15]

The present results emphasize that for mononuclear complexes of the nickel triad Lewis acid–base pairing, via either a halide or hydride ligand, is readily attained, and therefore it may play an important role in the reaction mechanisms of ligand substitution and exchange. It is worth noting that the terdentate ligand (N–C–N) has enabled the isolation of [(N–C–N)Pt(μ-RNCHNR)-AgX] species[16] containing a direct Ag–Pt interaction, and further research in this laboratory is being directed to a better understanding of this ligand's role in stabilizing heteronuclear complexes.

Acknowledgment. Professor K. Vrieze and Professor L. M. Venanzi are thanked for helpful discussions. This investigation was supported in part by the Netherlands Foundation for Chemical Research (SON), with financial aid from the Netherlands Organization for Pure Research (ZWO) (A.L.S.)

Registry No. 1a, 82112-75-2; **1b**, 82112-77-4; **1c**, 82112-79-6; **1d**, 82112-81-0; **1e**, 82112-83-2; **2**, 82112-85-4; **3a**, 82112-87-6; **3b**, 82112-89-8; $Pt(NCN)(CF_3SO_3)$, 82112-90-1; Pt(NCN)(COOH), 82112-91-2; $[Pt(NCN)(H_2O)]BF_4$, 82112-93-4; $[Pt(NCN)(H_2O)]BF_4$, 82112-95-6; Pt(NCN)Cl, 82112-96-7; Pt(NCN)Br, 67507-09-9; Pt(NCN)I, 82112-97-8; Pd(NCN)Cl, 82112-98-9; $Pt(COD)_2$, 12130-66-4.

Supplementary Material Available: Tables of positional and thermal parameters for $[(Pd\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\})_2(\mu\text{-}Cl)]BF_4$ and of bond distances and bond angles (5 pages). Ordering information is given on any current masthead page.

---

[6] Calculated from the least-squares planes of the carbon atoms of the two phenyl moieties.

[7] In $[Pd_2(Ph_2PCH_2PPh_2)_2Br_2]$ the M–M separation is only 2.699 (5) Å: Holloway, R. G.; Penfold, B. R.; Colton, R.; McCormick, M. *J. Chem. Soc., Chem. Commun.* **1976**, 485–486.

[8] Cotton, F. A.; Frenz, B. A.; White, A. J. *J. Organomet. Chem.* **1973**, *60*, 147–152.

[9] N donor coordination to palladium centers is established from ^1H NMR shift data, but for platinum species this is subtantiated by the presence of ^{195}Pt couplings with the CH_2NMe_2 signals.

[10] Mixing [Pt(N–C–N)Br] with $[Pt(N\text{–}C\text{–}N)(H_2O)]BF_4$ in CH_2Cl_2 at room temperature in ratios other than 1:1 gives rise to only *one* CH_2NMe_2 ^1H NMR resonance pattern (with ^{195}Pt satellites).

[11] The geometric constraints of bridging bidentate ligands can have a significant influence on the geometry of A-frame complexes. The structure of $[Pd_2(Ph_2PCH_2PPh_2)_2(\mu\text{-}I)(CH_3)I]BF_4$ shows a Pd–I–Pd angle of 67.0 (1) Å: Olmstead, M. M.; Farr, J. P.; Balch, A. L. *Inorg. Chim. Acta* **1981**, *52*, 47–54.

[12] Synthesized from $[Pt(N\text{–}C\text{–}N)(H_2O)]BF_4$ and NaCOOH in H_2O at room temperature (^1H NMR (benzene-d_6) δ 9.78 (COOH, J(Pt,H) = 52 Hz).

[13] The synthesis of a terminal Pt–H bond by thermal elimination of CO_2 from a Pt(COOH) group has been documented. See for example: Catellani, M.; Halpern, J. *Inorg. Chem.* **1980**, *19*, 566–568.

[14] Pt_A is bound to the two PPh_3 groups. The ^{195}Pt satellites arising from Pt_B are significantly broadened owing to incomplete collapse of spin–spin coupling of ^{195}Pt to the ^{14}N donor atoms.

[15] Bracher, G.; Grove, D. M.; Pregosin, P. S.; Venanzi, L. M. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 155–156; *Angew. Chem.* **1979**, *91*, 169–170.

[16] Van der Ploeg, A. F. M. J.; van Koten, G.; Vrieze, K. *Inorg. Chem.* **1982**, *21*, 2026.

Multiplet Selection in Crowded ^1H NMR Spectra via Double Quantum Coherence

P. J. Hore, E. R. P. Zuiderweg, K. Nicolay, K. Dijkstra, and R. Kaptein*

Department of Physical Chemistry
University of Groningen
9747 AG Groningen, The Netherlands

Received March 25, 1982

We propose a new method for tackling a perennial problem in NMR spectroscopy, that of spectral overcrowding. It allows one to detect specific multiplet resonances in circumstances where they would be partially or totally obscured by line overlap in a conventional ^1H NMR spectrum. All that is required is prior knowledge of the approximate chemical shifts and J couplings of the protons of interest.

Our approach was inspired by recent experiments[1,2] for observing ^{13}C–^{13}C spin–spin coupling in natural-abundance ^{13}C NMR spectra. The method, known as INADEQUATE,[2–4] relies on the momentary creation of double quantum coherence between coupled ^{13}C nuclei to suppress the strong signals from molecules with an isolated ^{13}C. INADEQUATE was later extended into a two-dimensional Fourier transform experiment[5,6] for correlating

---

[1] Bax, A.; Freeman, R.; Kempsell, S. P. *J. Am. Chem. Soc.* **1980**, *102*, 4849.

[2] Bax, A. Doctoral Thesis, Technische Hogeschool Delft, The Netherlands, 1981.

[3] Richarz, R.; Ammann, W.; Wirthlin, T. *J. Magn. Reson.* **1981**, *45*, 270.

[4] Sørensen, O. W.; Freeman, R.; Frenkiel, T.; Mareci, T. H.; Schuck, R. *J. Magn. Reson.* **1982**, *46*, 180.

[5] Bax, A.; Freeman, R.; Frenkiel, T. A. *J. Am. Chem. Soc.* **1981**, *103*, 2102.

[6] Bax, A.; Freeman, R.; Frenkiel, T. A.; Levitt, M. H. *J. Magn. Reson.* **1981**, *43*, 478.

[7] Aue, W. P.; Bartholdi, E.; Ernst, R. R. *J. Chem. Phys.* **1976**, *64*, 2229.

[8] Equation 3 and the cosine part of eq 2 are also valid for strong coupling.[7]