2116 *Inorg. Chem.* **1982,** *21,* 2116-2117

Effect of Axial Ligands on the Platinum-Platinum Bond in Binuclear α-Pyridonate-Bridged Platinum(III) Complexes. Structures of $[X(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2X](NO_3)_2 \cdot H_2O$, $X = NO_3, NO_2$

Sir:

Several structural and theoretical studies of binuclear rhodium(II) complexes have been carried out in an attempt to understand the nature of the metal-metal and metal-ligand interactions in a d^7-d^7 system.[1-3] The metal-metal bond distances in $Rh^{II}_2(O_2CR)_4L_2$ compounds, which contain a formal Rh-Rh single bond, depend upon the nature of the axial ligand, L. While the details of this interaction have been carefully examined for the Rh(II) case, similar studies have not been conducted on related binuclear platinum(III) complexes since, until recently, only a few well-characterized examples of compounds in this class were known.[4-7]

In the course of our work on *cis*-diammineplatinum(II) complexes of α-pyridone,[6] a convenient synthetic route to binuclear platinum(III) cations was discovered.[7] In particular, a number of α-pyridonate-bridged $[X(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2X]^{2+}$ complexes have been isolated by chemical oxidation of the platinum(II) dimer $[(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2](NO_3)_2 \cdot 2H_2O$ (**1**).[7] In these reactions, different oxidants were used to provide different axial ligands. Here we report the structures of two such complexes, where $X = NO_3$ and NO_2. The results clearly demonstrate the influence of axial ligands on the Pt-Pt internuclear separation, since the two compounds studied are both bridged in a head-to-tail fashion by two α-pyridonate ligands and differ only with respect to their axial ligands.

The nitrate-capped complex, $[(NO_3)(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2(NO_3)](NO_3)_2 \cdot H_2O$ (**2**), was obtained in high yield by oxidizing compound **1** with 3-5 M nitric acid as described previously.[7] The nitrite-capped complex, $[(NO_2)(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2(NO_2)](NO_3)_2 \cdot H_2O$ (**3**), was prepared from compound **1** by using nitrous acid as the oxidant. The synthesis was accomplished by dissolving 20 mg of **1** and 20 mg of sodium nitrite in 10 mL of water and adjusting the pH of the resulting solution to 1 with nitric acid. Air evaporation of the resulting solution provided a 70-80% yield of **3** as yellow crystals.

The results of X-ray structural studies[8] of compounds **2** and **3** are shown in Figure 1. The Pt-Pt bond distance significantly increases by 0.028 (1) Å when nitrate is replaced by nitrite as the axial ligand. This effect, which results from a difference in the donor strength of the axial ligand, is of comparable magnitude to that observed in the case of the dirhodium tetracarboxylates, $[Rh_2(O_2CR)_4L_2]$.[9] The longer Pt-Pt bond found in the $[(NO_2)(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2(NO_2)]^{2+}$ cation is consistent with the greater trans influence of nitrite compared with that of nitrate ligands.[10] The crystal packings of the isomorphous compounds **2** and **3** are nearly identical and therefore unlikely to be responsible for the observed differences in Pt-Pt bond lengths.

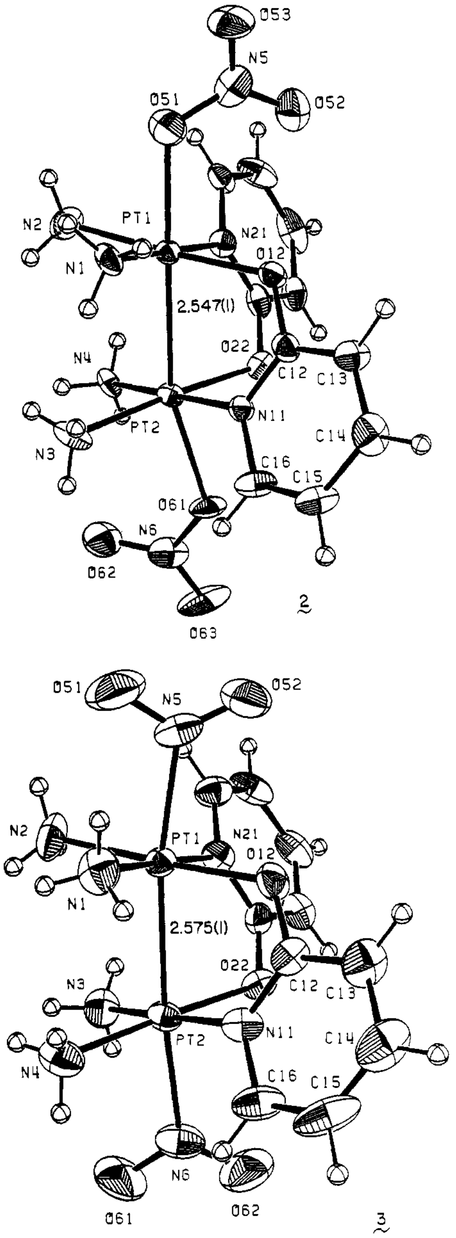


Figure 1. ORTEP drawings of the structures of the binuclear Pt(III) cations $[X(NH_3)_2Pt(C_5H_4NO)_2Pt(NH_3)_2X]^{2+}$, where $X = NO_3$ (**2**) and NO_2 (**3**), showing the 40% probability thermal ellipsoids and the Pt-Pt distances (in Å). For clarity, hydrogen atoms are depicted as spheres with *B* set at 1 Å^2. Average Pt-ligand distances: for **2**, $Pt\text{-}NH_3 = 2.06$ Å, Pt-N = 2.04 Å, Pt-O = 2.01 Å, $Pt\text{-}ONO_2 = 2.17$ Å; for **3**, $Pt\text{-}NH_3 = 2.06$ Å, Pt-N = 2.06 Å, Pt-O = 2.01 Å, $Pt\text{-}NO_2 = 2.18$ Å. Standard deviations are ≤0.01 Å.

The mutual trans influence in metal-metal and metal-ligand bonding in **2** and **3** is illustrated by their elongated platinum-to-axial-ligand distances. The axial Pt-O distance in compound **2** is 0.16 Å longer than that normally found when

---

[1] Norman, J. G.; Kolari, H. J. *J. Am. Chem. Soc.* **1978**, *100*, 791.

[2] Christoph, G. G.; Halpern, J.; Khare, G. P.; Koh, Y. B.; Romanowski, C. *Inorg. Chem.* **1981**, *20*, 3029.

[3] Bursten, B. E.; Cotton, F. A. *Inorg. Chem.* **1981**, *20*, 3042.

[4] Schagen, J. D.; Overbeek, A. R.; Schenk, H. *Inorg. Chem.* **1978**, *17*, 1938.

[5] Muraveiskaya, G. S.; Kukina, G. A.; Orlova, V. S.; Evstaf'eva, O. N.; Porai-Koshits, M. A. *Dokl. Akad. Nauk SSSR* **1976**, *226*, 596.

[6] Hollis, L. S.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 1230 and references cited therein.

[7] Hollis, L. S.; Lippard, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 6761.

[8] Crystal data: Compound **2** crystallizes in the monoclinic system, space group *C*2/*c*, with the following cell parameters: $a = 32.447$ (7), $b = 9.404$ (1), $c = 18.199$ (6) Å; $\beta = 123.78$ (2)°; $\rho_{obsd} = 2.64$ (2) g/cm^3, $\rho_{calcd} = 2.63$ g/cm^3; $Z = 8$. The structure was solved by standard Patterson and Fourier methods using 2506 unique reflections collected out to $2\theta = 55°$ on a Nonius CAD-4F diffractometer with Mo Kα ($\lambda = 0.7017$ Å) radiation. Refinement of the absorption corrected data has converged to a value of 0.034 for the discrepancy index $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$. Compound **3** also crystallizes in the monoclinic system, space group *C*2/*c*, with the following cell parameters: $a = 32.184$ (5), $b = 8.712$ (2), $c = 18.500$ (4) Å; $\beta = 124.20$ (1)°; $\rho_{obsd} = 2.72$ (2) g/cm^3, $\rho_{calcd} = 2.73$ g/cm^3; $Z = 8$. The structure was solved as above by using 2806 unique reflections, and refinement has converged at $R_1 = 0.039$.

[9] Koh, Y. B.; Christoph, G. G. *Inorg. Chem.* **1979**, *18*, 1122.

[10] Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

0020-1669/82/1321-2116$01.25/0

nitrate is coordinated to platinum; for example, Pt–O_{av} = 2.01 Å in *cis*-$Pt(NH_3)_2(NO_3)_2$.[11] A similar increase in the axial Pt–N distance is revealed when the average Pt–NO_2 value of 2.18 (1) Å in compound **3** is compared to Pt–N distances of ~2.02 Å found in mononuclear platinum nitrite complexes.[12] A comparable increase in metal-to-axial-ligand distance is also observed in the dirhodium(II) tetracarboxylate complexes.

The structures of **2** and **3** compare favorably with that of $[(4\text{-}CH_3C_5H_4N)(CH_3)_2Pt(O_2CCF_3)_2Pt(CH_3)_2(4\text{-}CH_3C_5H_4N)]$,[4] which has a Pt–Pt distance of 2.557 (1) Å and canted, twisted Me_2Pt units analogous to the $(NH_3)_2Pt$ units in a variety of *cis*-diammineplatinum complexes.[7] A family of platinum(III) dimers that lacks such sterically interacting ligands includes $K_2[Pt_2(SO_4)_4(H_2O)_2]$,[5] $Na_2[Pt_2(HPO_4)_4(H_2O)_2]$,[13] and $K_2[Pt_2(SO_4)_4(OSMe_2)_2]\cdot 4H_2O$,[13] which have metal–metal bond lengths of 2.466, 2.486 (2), and 2.471 (1) Å, respectively. The shorter metal–metal distances observed for these molecules may be due to the absence of unfavorable nonbonded interactions between parallel platinum coordination planes. Finally, the Pt–Pt distance of 2.575 (1) Å observed for the nitro complex **3** may be compared with the value of 2.584 (1) Å reported for the deprotonated 1-methylcytosine dimer, $[(NO_2)(NH_3)_2Pt(C_5H_6N_3O)_2Pt(NH_3)_2(NO_2)]^{n+}$ (**4**), where *n* was assigned as 1.[14] The near equality of the metal–metal distances in **3** and **4** further underscores the need to reinvestigate the assignment of the Pt(2.5) oxidation state in the deprotonated 1-methylcytosine dimer to determine whether **4** might really be a binuclear Pt(III) complex, a possibility suggested previously.[7] The synthetic route to Pt(III) dimers described here should provide a convenient way to make compound **4**, the preparation of which has been difficult to reproduce.[14]

Acknowledgment. This work was supported by National Institutes of Health Research Grant CA-15826. We thank Engelhard Institutes for a loan of K_2PtCl_4 and Professor F. A. Cotton for preprints of ref 13.

Registry No. **2**, 81277-22-7; **3**, 81277-25-0.

Supplementary Material Available: Atomic positional and thermal parameters for compounds **2** and **3** (3 pages). Ordering information is given on any current masthead page.

---

(11) Lippert, B.; Lock, C. J. L.; Rosenberg, B.; Zvagulis, M. *Inorg. Chem.* **1977**, *16*, 1525.

(12) (a) Kaduk, J. A.; Ibers, J. A. *Inorg. Chem.* **1977**, *16*, 3278. (b) Boer, F. P.; Carter, V. B.; Turley, J. W. *Ibid.* **1971**, *10*, 651.

(13) Cotton, F. A.; Falvello, L. R.; Han, S., submitted for publication.

(14) Faggiani, R.; Lippert, B.; Lock, C. J. L.; Speranzini, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 1111.

Department of Chemistry
Columbia University
New York, New York 10027

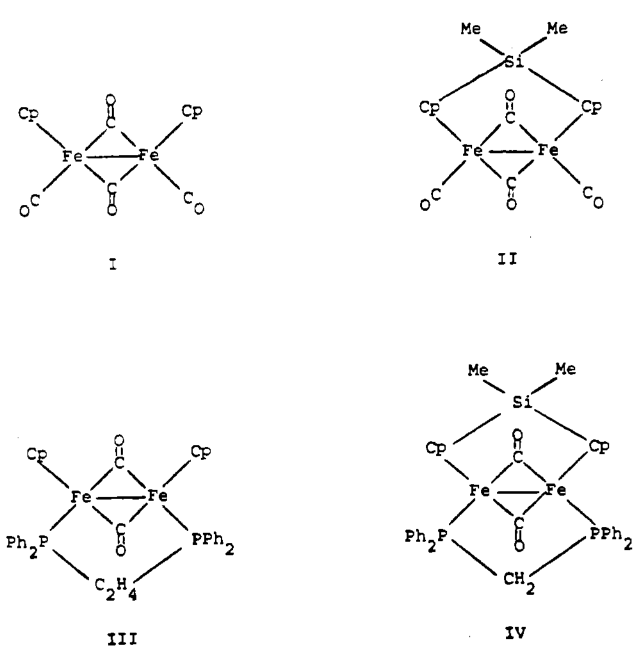
L. Steven Hollis
Stephen J. Lippard*

Received January 4, 1982

Hydridic Reduction of Carbon Monoxide on Various Iron Dimers

Sir:

We have previously reported the reduction of carbon monoxide on $Cp_2Fe_2(CO)_4$ by reaction with $LiAlH_4$ (LAH).[1,2]



I II III IV

Figure 1. Structures of the iron dimers that have been reacted with LAH.

The products were hydrocarbons ranging up to butane and butene.[1,2] The specific role of the terminal and bridging carbonyls could not be assessed in these studies. The recent preparation of the new iron dimers shown in Figure 1 has allowed a determination of the necessity of terminal CO's for reduction chemistry.[3]

Experimental Section. Purification of solvents was effected as previously described.[2] The iron dimers were prepared, purified, and characterized as reported earlier.[3] $Cp_2Fe_2(CO)_4$ (Strem Chemical) and LAH (Alfa) were used as received.

The reduction reactions were accomplished as described previously with 0.25 mmol of iron dimer and 5.0 mmol of LAH in toluene for a specified period of time. Gas chromatographic analysis was performed as in the earlier work.[2] After the reduction was completed, the solution was filtered and the infrared spectrum was recorded.

Results and Discussion. Reaction of $Me_2Si[(\eta^5\text{-}C_5H_4)Fe(Co)_2]_2$ with LAH produced hydrocarbon products very similar to those observed in reduction of CO on $Cp_2Fe_2(CO)_4$,[1,2] and these results are summarized in Tables I and II. The amounts of olefins declined during the course of the reaction just as observed for reduction on $Cp_2Fe_2(CO)_4$. The linking of the cyclopentadienes evidently has very little effect on the CO reduction chemistery. No Me_2SiH_2 was detected by GC analysis, suggesting that the bridging is not disrupted by LAH.

Reactions of $C_2H_4[(Ph)_2PFeCp(CO)]_2$ (III) and $Me_2Si[(\eta^5\text{-}C_5H_4)Fe(CO)]_2L$ (L = bridging $Ph_2PCH_2PPh_2$) (IV) with LAH show essentially no hydrocarbon products. The amounts are 2 orders of magnitude less than seen in reactions of I and II. The amounts of hydrocarbons do not increase with time, and the dimers are recovered after reaction times of 10 days. Apparently, trace impurities are giving rise to the hydrocarbon production and complexes III and IV do not react with LAH.[4] The reactions of these two complexes with LAH are very different from the reaction with $Cp_2Fe_2(CO)_4$.

The feature of primary importance appears to be the presence or absence of terminal carbonyls. Compounds I and

---

(1) Wong, A.; Atwood, J. D. *J. Organomet. Chem.* **1980**, *199*, C90.

(2) Wong, A.; Atwood, J. D. *J. Organomet. Chem.* **1981**, *210*, 395.

(3) Nelson, G. O.; Wright, M. E. *J. Organomet. Chem.* **1981**, *206*, C21 and references therein.

(4) It is very difficult to remove trace quantities of tetranuclear complexes with the bidentate phosphines bridging two iron dimers.

0020-1669/82/1321-2117$01.25/0