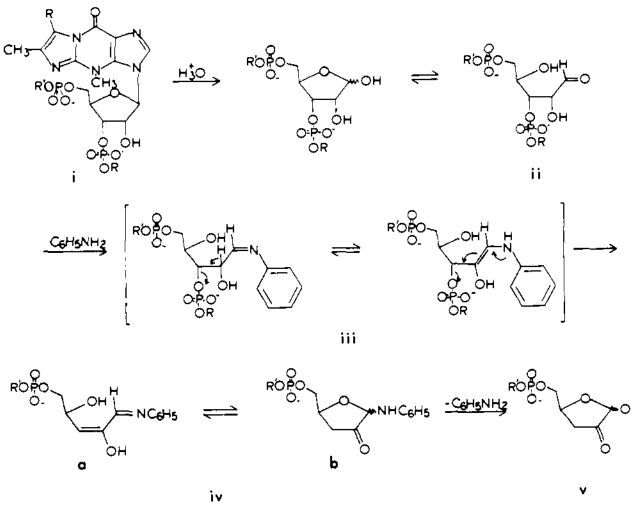
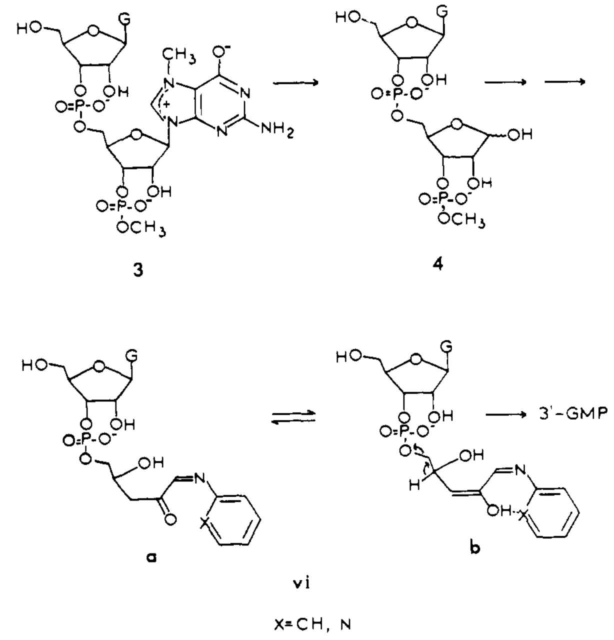
Scheme I



Scheme II



The chemical transformations described herein provide a basis for the modification of intact RNA's and for the characterization and manipulation of species following alteration, e.g., by mutagens. In the present case the alterations afforded a highly unusual tRNA species (**2**) having only six nucleotides in the anticodon loop. This tRNA is of considerable interest for biochemical studies, e.g., of the structural features in tRNA^{Phe} that permit interaction with[22] and conformational activation of[23] its cognate aminoacyl-tRNA synthetase. Diminution in the size of the anticodon loop was found to have a dramatic effect on certain biochemical properties of tRNA^{Phe}.[24]

Acknowledgment. We thank Professor Glenn McGarvey for a helpful discussion during the course of this work. This investigation was supported by PHS Research Grant GM27815.

Registry No. Nucleoside Y, 55196-46-8.

---

[22] (a) Woese, C. R.; Dugre, D. H.; Dugre, S. A.; Kondo, M.; Saxinger, W. C. *Cold Spring Harbor Symp. Quant. Biol.* **1966**, *31*, 723. (b) Alford, B.; Hecht, S. M. *J. Biol. Chem.* **1978**, *253*, 4844.

[23] Renaud, M.; Basha, H.; Remy, P.; Ebel, J.-P. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 1606.

[24] Nishikawa, K.; Hecht, S. M., in preparation.

A Mixed-Metal Nitrido Carbonyl Cluster Compound. Synthesis and X-ray Structure of the $[PtRh_{10}N(\mu\text{-}CO)_{10}(CO)_{11}]^{3-}$ Anion

Secondo Martinengo*

Centro del C.N.R. per la Sintesi
e la Struttura dei Composti dei Metalli di Transizione
nei Bassi Stati di Ossidazione
Via G. Venezian 21, 20133-Milano, Italy

Gianfranco Ciani* and Angelo Sironi

Istituto di Chimica Generale
ed Inorganica dell'Università
Via G. Venezian 21, 20133-Milano, Italy

Received July 30, 1981

Two of the newly growing fields in the chemistry of carbonyl cluster compounds concern the studies of novel mixed-metal species and clusters containing new types of interstitial atoms. We have recently reported the synthesis and structure of the first cluster compounds containing interstitial nitrogen atoms, namely, the $[M_6N(CO)_{15}]^-$ anions (M = Co and Rh)[1] and we wish to describe here the characterization of the first example of a mixed-metal cluster compound containing an interstitial nitrogen atom, the anion $[PtRh_{10}N(CO)_{21}]^{3-}$. This species exhibits many interesting features because (i) it is an unusual example of an 11-metal cluster compound, (ii) it is a new step in the chemistry of mixed platinum–rhodium clusters which were up to now limited to five[2] or six[3] metal species, (iii) it is the compound with the highest metal-to-interstitial atom ratio presently known, and (iv) it is a good example for comparison of the bonding properties of interstitial nitrides vs. carbides[4] in large metal atom clusters.

The $[PtRh_{10}N(CO)_{21}]^{3-}$ anion has been first obtained as a byproduct in the synthesis of $[Rh_6N(CO)_{15}]^-$ from K_3RhCl_6 containing traces of platinum salts. It is now prepared by reaction of $[Rh_6N(CO)_{15}]^-$ with $[PtRh_4(CO)_{14}]^{2-}$:[2]

$$[Rh_6N(CO)_{15}]^- + [PtRh_4(CO)_{14}]^{2-} \xrightarrow[N_2,\ \text{reflux}]{\text{acetone}} [PtRh_{10}N(CO)_{21}]^{3-} + \text{other products}$$

The reaction is slow and, due to the concomitant decomposition of the starting anions,[5] gives a mixture of products from which the mixed-metal anion has to be separated by fractional precipitation of the potassium salts.[6] The corresponding cesium and bulky organic cation salts can be obtained by metathesis in water and aqueous alcohols, respectively.

The IR spectrum of the $[N(CH_3)_4]^+$ salt in CH_3CN solution shows bands at 1988 vs, 1952 m, 1812 m, 1800 sh, and 1770 sh cm^{-1}.

The nitrogen nature of the interstitial atom is proved by the synthetic reaction itself and further by the reaction of the

---

[1] Martinengo, S.; Ciani, G.; Sironi, A.; Heaton, B. T.; Mason, J. *J. Am. Chem. Soc.* **1979**, *101*, 7095.

[2] Fumagalli, A.; Martinengo, S.; Chini, P.; Albinati, A.; Bruckner, S. XIII Congresso Nazionale di Chimica Inorganica, Camerino, Italy, 1980; Abstracts A 11.

[3] Fumagalli, A.; Martinengo, S.; Chini, P.; Albinati, A.; Bruckner, S.; Heaton, B. T. *J. Chem. Soc., Chem. Commun.* **1978**, 195.

[4] Albano, V. G.; Martinengo, S. *Nachr. Chem. Tech. Lab.* **1980**, *28*, 654.

[5] It is very probable that the real Pt furnishing species is the $[PtRh_4(CO)_{12}]^{2-}$ anion, which is quickly formed from the $[PtRh_4(CO)_{14}]^{2-}$ anion by loss of CO[2] and which is more stable under our reaction conditions. The $[Rh_6N(CO)_{15}]^-$ anion also undergoes slow thermal decomposition to give new nitrido species.[11]

[6] In a typical synthesis $(PPN)_2[PtRh_4(CO)_{14}]$ (0.29 g) and $K[Rh_6N(CO)_{15}]$ (0.15 g) are refluxed in acetone (20 mL) under nitrogen until the IR band of the bridging COs at 1873 cm^{-1} of the $[Rh_6N(CO)_{15}]^-$ anion disappears (~25 h). The mixture of products is then transformed into the sodium salts by addition of $NaB(C_6H_5)_4$ (0.24 g), evaporation to dryness in vacuum, and extraction with water (10 mL). The excess $NaB(C_6H_5)_4$ is eliminated by addition of 3% aqueous KCl (10 mL); the solution is filtered, briefly pumped in vacuum to eliminate residual traces of acetone, and treated with solid KCl up to an 8% KCl concentration. The potassium salt precipitates as a powder which is filtered, washed first with 6.5% aqueous KCl (3 mL) and then with saturated aqueous KBr, and finally vacuum dried; yield 10–20%. The dark violet solutions of the anion are quickly oxidized in air.

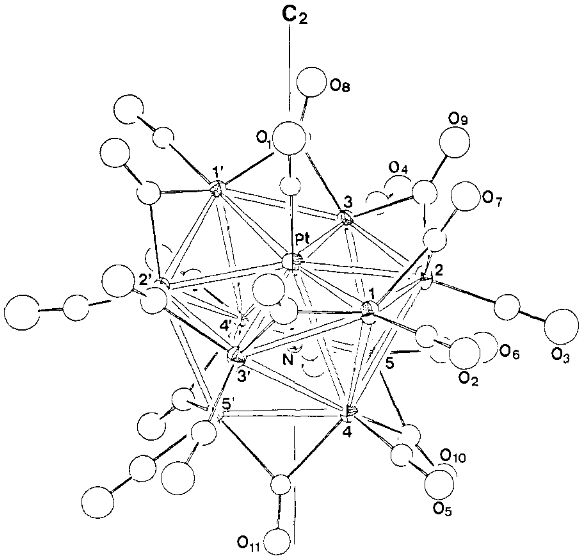


Figure 1. View of the anion $[PtRh_{10}N(CO)_{21}]^{3-}$. The rhodium atoms are indicated by their sequence numbers and the carbonyl ligands by their oxygen atoms.

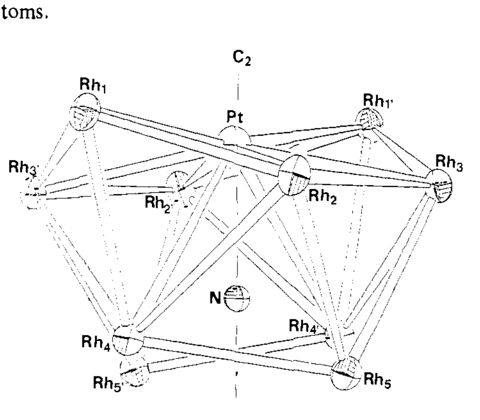


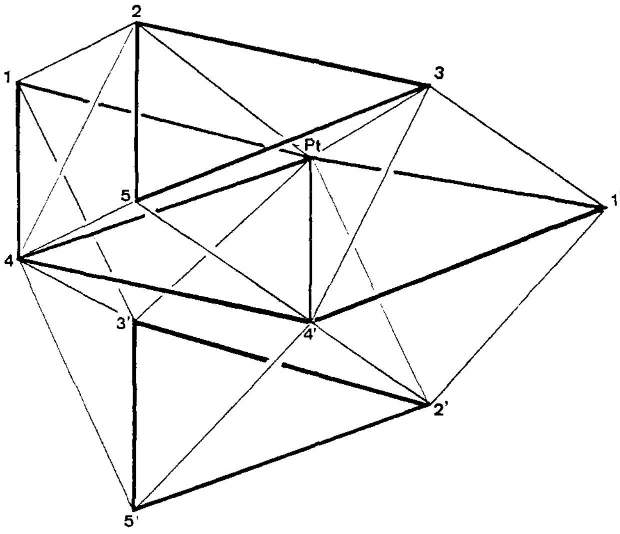
Figure 2. View of the $PtRh_{10}N$ moiety. The metal–metal bond distances are as follows: Pt–Rh(1), 2.752 (2); Pt–Rh(2), 2.700 (1); Pt–Rh(3), 2.681 (1); Pt–Rh(4), 3.180 (2); Rh(1)–Rh(2), 2.755 (2); Rh(1)–Rh(3′), 2.728 (2); Rh(1)–Rh(4), 2.912 (2); Rh(2)–Rh(3), 2.797 (2); Rh(2)–Rh(4), 2.984 (2); Rh(2)–Rh(5), 2.816 (2); Rh(3)–Rh(4′), 3.088 (2); Rh(3)–Rh(5), 2.828 (2); Rh(4)–Rh(5), 2.789 (2); Rh(4)–Rh(5′), 2.755 (2) Å.

$[PtRh_{10}N(CO)_{21}]^{3-}$ anion with CO, which gives slow demolition to a mixture of products among which the $[Rh_6N(CO)_{15}]^-$ anion has been recognized.

Crystals of the mixed salt $[PtRh_{10}N(CO)_{21}](Cs)[N(CH_3)_4]_2$ which are well suited for X-ray analysis[7] were obtained together with the less suitable ones of the tris-tetramethylammonium salt by slow diffusion of $[N(CH_3)_4]Cl$ dissolved in CH_3OH/2-propanol into a methanolic solution of the cesium salt.

The anion is illustrated in Figure 1. It lies on a twofold crystallographic axis passing through the Pt atom and the interstitial nitrogen atom. The overall idealized symmetry of the anion is C_{2v}. The metal atom cluster is shown in Figure 2. It exhibits a novel geometry which could be described as a two-layer arrangement, i.e., a folded hexagon of rhodium atoms [Rh(1,2,3,1′,2′,3′)], centered by the platinum atom, superimposed along the C_2 axis direction on a folded square of rhodium atoms, [Rh(4,5,4′,5′)]. Of the 21 carbonyl groups 11 are bound terminally, one per metal atom, and 10 are double bridged on the Rh–Rh edges of the folded hexagonal and square layers. Alternatively the cluster geometry can be derived from a fragment of a hexagonal close-packed array of metals consisting of three layers (3/5/3) as shown in Scheme I. The interstitial N atom causes a distortion of this compact fragment and, in particular, the breaking of the 4-4′ edge.

Scheme I



The metal–metal bond interactions are scattered (see Figure 2). The platinum atom, which has the highest number of metal–metal connections, exhibits six Pt–Rh bonds, with the rhodium atoms of the folded hexagon, at a mean distance of 2.711 Å. These are somewhat shorter than the corresponding interactions in $[PtRh_5(CO)_{15}]^-$ (mean 2.790 Å).[3] Of the other four Pt–Rh contacts two [with Rh(4) and Rh(4′)] are significantly longer [3.180 (2) Å] and the remaining two [with Rh(5) and Rh(5′)] are much too long [3.492 (2) Å] to be considered as bonded. The Rh–Rh bond lengths range from 2.728 (2) to 3.088 (2) Å, the longer ones being the interlayer connections between the folded hexagon and the folded square.

The interstitial nitride atom occupies an unusual type of cavity in which it is connected to five metal atoms. It contains a short bond to the Pt atom [1.92 (2) Å] and longer bonds to the four Rh atoms [Rh(4) = Rh(4′) = 2.05 (1) Å and Rh(5) = Rh(5′) = 2.12 (1) Å].

The metal–carbon and carbon–oxygen interactions of the terminal carbonyls are as follows: Pt–C and C–O are 1.88 (3) and 1.12 (4) Å, and Rh–C and C–O are 1.85 and 1.16 Å (mean values). The Rh–C and C–O mean bond lengths for the bridging CO groups are 2.01 and 1.18 Å, respectively.

The anion possesses 150 valence electrons, corresponding to 75 cluster valence molecular orbitals. The hcp cluster illustrated in the above scheme should have 73 cluster molecular orbitals.[8] The increment of two MOs is clearly a consequence of the presence of the interstitial N atom which causes an enlargement distortion with lowering of compactness.

A comparison of $[PtRh_{10}N(CO)_{21}]^{3-}$ with the structural data of a number of carbido carbonyl cluster compounds[4] leads to the following conclusions: while in small metal clusters the nitrides and carbides show analogous behavior, as indicated by the similarity of the $[M_6N(CO)_{15}]^{-1}$ and $[M_6C(CO)_{15}]^{2-}$[9] anions (M = Co, Rh), in larger clusters differences are possible. Interstitial carbides generally occupy trigonal prismatic, octahedral, or square antiprismatic cavities, with coordinations to the metals of 6 or 8.[4] Moreover, in species with a high metal-to-interstitial atom ratio, carbides can lie in cavities which do not lower the compactness of the metal atom fragment, as in the $[Os_{10}C(CO)_{24}]^{2-}$ anion.[10] The present results, on the other hand, show a tendency

---

(7) Crystal data: The salt $[PtRh_{10}N(CO)_{21}](Cs)[N(CH_3)_4]_2$, $M = 2107.6$, crystallizes in the monoclinic space group $C2/c$ (No. 15) with cell constants $a = 10.992$ (4) Å, $b = 19.347$ (8) Å, $c = 21.900$ (8) Å, $\beta = 94.41$ (4)°, $Z = 4$. The structure has been solved by Patterson and Fourier methods and refined by block-matrix least squares on the basis of 2845 independent significant counter data. Anisotropic thermal factors were assigned to the Pt, Rh, and Cs atoms, while the other atoms were refined isotropically. The refinements are in progress, the current R value being 5.9%.

(8) Ciani, G.; Sironi, A. *J. Organomet. Chem.* **1980**, *197*, 233.

(9) Albano, V. G.; Sansoni, M.; Chini, P.; Martinengo, S. *J. Chem. Soc., Dalton Trans.* **1973**, 651.

of interstitial nitrides to a lower coordination (5) and their preference for unusual and less regular cavities. Thus the chemistry of large nitrido clusters might reveal a novel variety of geometries, stabilized by these interstitial atoms. Further work on large species of this class is in progress,[11] and preliminary structural results seem to confirm our suggestions.

Acknowledgment. We thank the Italian C.N.R. for financial support.

Supplementary Material Available: A listing of positional and thermal parameters and of interatomic distances and angles (13 pages). Ordering information is given on any current masthead page.

---

(10) Jackson, P. F.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Chem. Commun.* **1980**, 224.

(11) Martinengo, S.; Ciani, G.; Sironi, A., unpublished results.

Geometric and Electronic Structure of $C_2H_6^{2+}$ (Dimer of Methyl Cation)

George A. Olah

Hydrocarbon Research Institute and
Department of Chemistry
University of Southern California
Los Angeles, California 90007

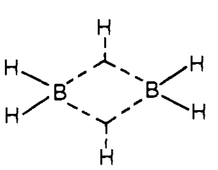
Massimo Simonetta*

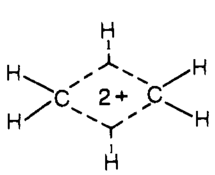
Institute of Physical Chemistry and C.N.R. Center
University of Milan, 20133 Milan, Italy

Received August 3, 1981

Diborane has two fewer valence electrons than ethane, but it took a long time before the non-ethane-like bridged structure for B_2H_6 was established. Neither the discarded ethane-like nor the bridged structure can be represented satisfactorily by a single Lewis structure. Such molecules are termed "electron deficient". The nature of the multicenter bonding in B_2H_6 was first described by Longuet-Higgins. Basically, four electrons hold the two boron atoms and the two bridging hydrogens together (the remaining four B–H bonds can be described by conventional 2c–2e bonds). B_2H_6 can be thus regarded as possessing two three-center–two electron bonds.

When considering the relationship of diborane, an electron-deficient boron compound, with its possible carbocationic analogue, the corresponding compound would be $C_2H_6^{2+}$, the dimer of the methyl cation, i.e., $(CH_3^+)_2$.





There was no evidence so far for $(CH_3^+)_2$ even in the gas phase in mass spectrometric studies (i.e.). Charge–charge repulsion seems mainly responsible for the inability to observe $(CH_3^+)_2$.

In a theoretical study Peyerimhoff and Buenker[1] investigated by SCF–MO and CI calculations ammonia borane ($NH_3{\cdot}BH_3$) and positive ions of ethane, including $C_2H_6^{2+}$. Their calculations found the open-shell configuration of $(CH_3^+)_2$ the more stable in the D_{3d} geometry.

Table I. Energy, Bond Lengths, Bond Angles, and Charges in $C_2H_6^{2+}$ (D_{2h} Symmetry)[a]

	4-31G	6-31**G
energy, a.u.	−78.09449	−78.24919
C–C, Å	1.548	1.536
CH_b, Å	1.288	1.285
CH_t, Å	1.088	1.101
H_bCH_b, deg	106.2	106.6
H_tCH_t, deg	120.2	119.3
q(C), e	−0.403	−0.242
q(H_b), e	+0.461	+0.398
q(H_t), e	+0.471	+0.422

[a] The energy of optimized CH_3^+ (planar, C–H = 1.086 Å) is -39.23621 a.u. at the 6-31**G level.

Table II. Force Constants of $C_2H_6^{2+}$[a]

symmetry	*i,j*	*F*(*i,j*)	description	symmetry	*i,j*	*F*(*i,j*)	description
A_g	1,1	5.630	s–s	B_{1g}	11,11	5.694	s–s
	2,2	2.758	s–s		12,12	1.327	b–b
	3,3	2.917	b–b		11,12	−0.035	s–b
	4,4	1.936	b–b	B_{1u}	13,13	1.809	s–s
	1,2	+0.041	s–s		14,14	0.881	b–b
	1,4	+0.025	s–b		13,14	+0.130	s–b
	2,4	−1.420	s–b	B_{3g}	15,15	0.692	b–b
	3,4	−0.836	b–b	B_{3u}	16,16	5.718	s–s
A_u	5,5	0.289	b–b		17,17	2.386	s–s
					18,18	2.601	b–b
B_{2g}	6,6	1.639	s–s		16,17	−0.010	s–s
	7,7	0.679	b–b		16,18	−0.059	s–b
	6,7	−0.432	s–b		17,18	−0.004	s–b
B_{2u}	8,8	5.760	s–s				
	9,9	1.068	b–b				
	10,10	0.666	b–b				
	8.9	+0.040	s–b				
	8,10	+0.066	s–b				
	9,10	+0.386	b–b				

[a] Symmetry coordinates and force constants defined as in ref 6. Units are mdyn $Å^{-1}$, mdyn, and mdyn Å for stretching (s–s), stretch/bend (s–b), and bending (b–b) force constants, respectively.

Due to our interest in higher coordinate carbon compounds and their relationship to boron analogues, we have restudied the problem of the methyl cation dimer and, in sharp contrast to Peyerimhoff and Buenker, found the bridged, diborane-like structure to be stable.

We performed a geometry optimization of $C_2H_6^{2+}$ by means of MO calculations of the 4-31G type[2] imposing D_{3d} or D_{2h} symmetry. In the former case the system in the closed-shell configuration dissociates without barrier to $2CH_3^+$, while in the latter case we found a minimum for the geometry reported in Table I. Since in isoelectronic diborane boron d orbitals have a significant influence on the electron density,[3] the geometry optimization has been repeated, for the D_{2h} species, using a 6-31**G basis set.[4] These results are also reported in Table I. It can be noticed that while the total energy and charge densities are substantially changed, the geometry is almost unaffected by the inclusion of polarization functions. To obtain further evidence that a true energy minimum had been found we carried on a complete vibrational analysis of ethane dication. The method given by Blom and Altona[5] was shown to perform successfully in the case of diborane[6] using 4-31G wave functions and energies. For this reason and taking account of the results in Table I, force constants have been evaluated at the 4-31G level by the same procedure. They are reported in Table II. Since we could not calibrate scale factors on experimental frequencies, a direct comparison with diborane is not appropriate. It is worth noting, however, that our values are in general somewhat higher than the

---

(1) Peyerimhoff, S. D.; Buenker, R. J. *J. Chem. Phys.* **1968**, *49*, 312–325.

(2) Ditchfield, R.; Here, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724–728.

(3) Bianchi, R.; Morosi, G.; Simonetta, M. *Chem. Phys. Lett.* **1981**, *81*, 406–408.

(4) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213–222.

(5) Blom, C. E.; Altona, C. *Mol. Phys.* **1976**, *31*, 1377–1391.

(6) Blom, C. E.; Muller, A. *J. Chem. Phys.* **1978**, *69*, 3397–3402.

0002-7863/82/1504-0330$01.25/0