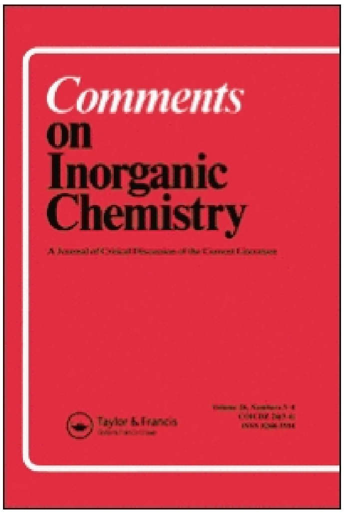

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Odd Oxidation States of Palladium and Platinum

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Odd Oxidation States of Palladium and Platinum

Recent research has uncovered a variety of compounds of palladium or platinum in formal oxidation states I and III. These are generally dimeric with some form of metal–metal interaction and many of them show unique chemical behavior.

Classical coordination chemistry explored extensively the chemistry of platinum, and palladium to a lesser extent, in the oxidation states II (d^8) and IV (d^6). Subsequently compounds of the zero valent (d^{10}) forms of these elements were discovered and their chemistry exploited. However, it is only in the last 10 years or so that compounds of these metals in the I (d^9) and III (d^7) oxidation states have been adequately characterized. Here I review some of the highlights of the observations that have been made in this area.

Monomeric Compounds Most compounds of the odd oxidation states of platinum or palladium exist as binuclear metal–metal bonded species. The occurrence of stable and necessarily paramagnetic complexes with only a single platinum or palladium ion present is rare. It is largely confined to species with specific ligands which stabilize these radical species by delocalization of the odd electron onto the ligand itself. For example, the anionic complexes **1**[1-3] which formally would contain M(III) and have D_{2h} symmetry have been shown to possess a doublet ground state in which the unpaired electron resides in a π^* orbital of either b_{3g} or b_{2g} symmetry.[2]

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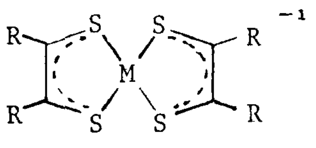
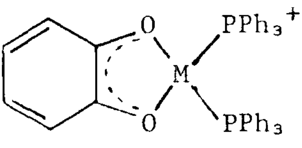


1 R = CN, CF_3, Ph



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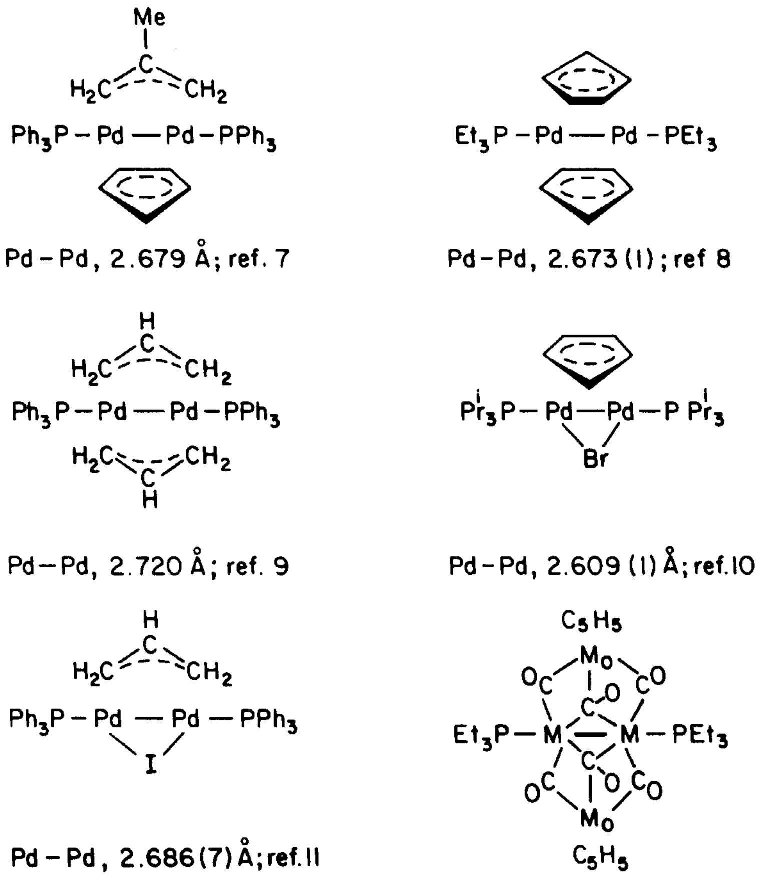
Similarly, in the cationic complexes **2**, which would also formally contain M(III), the electron spin resonance data indicate that the single unpaired electron is largely localized on the semiquinone π system.[4,5] The major emphasis in this area then has revolved around understanding of the ground state electronic structure as well as studies of the oxidation/reduction processes which link these species to their one-electron oxidized/reduced forms. Because of the delocalization of the unpaired electron in these species there are no observations of their dimerization to form metal–metal bonded compounds.

Recently, preliminary results have been reported which suggest that somewhat stable Pd(I) and Pd(III) monomeric compounds can be prepared by electrochemical techniques using what appear to be rather sterically protected metal centers. Quantitative reduction of (π-Ph_5C_5)Pd(1,5-cyclooctadiene)$^+$ at -0.6 V (versus a saturated calomel electrode) generated (π-Ph_5C_5)Pd(1,5-cyclooctadiene) which shows an electron spin resonance spectrum centered at $<g> = 2.0706$ with satellites (with $<a>_{\mathrm{Pd}} = 25$ G) due to coupling to ^{105}Pd ($I = {}^5/_2$, 22.2% natural abundance).[6] (π-Ph_5C_5)Pd (1,5-cyclooctadiene)$^+$ is also reported to undergo a reversible oxidation. The pentaphenyl cyclopentadienide ligand appears to play a crucial role in stabilizing these radical species.

Dimeric M(I) compounds Diamagnetic M(I) complexes invariably exist as bridged, binuclear species. They are remarkable for the variety of bridging groups which have been characterized. A particular common structure feature is the nearly linear R_3PMMPR_3 unit which is often found with two bridging groups. For these the M–M separations fall into a relatively narrow range: 2.57–2.72 Å. A number of such compounds which have been characterized by x-ray diffraction are shown in Figure 1. Related complexes with other bridging ligands are shown in Figure 2. The range of bridging ligands runs from the classical examples of bridging halide, sulfide, phosphide and diphosphine through bridging carbonyl and on to bridging π-hydrocarbons including π-alkyl, π-cyclo-



Pd-Pd, 2.679 Å; ref. 7

Pd-Pd, 2.673 (1); ref 8

Pd-Pd, 2.720 Å; ref. 9

Pd-Pd, 2.609 (1) Å; ref. 10

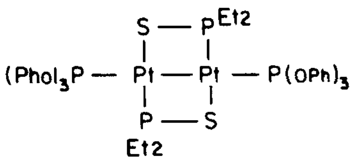
Pd-Pd, 2.686(7) Å; ref. 11

Pd-Pd, 2.582 (1) Å; ref. 12
Pt-Pt, 2.678 (1) Å; ref. 13
2.646 (1) Å

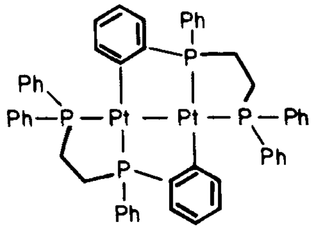
FIGURE 1 Drawings of crystallographically characterized compounds containing near linear $R_3PM^IM^IPR_3$ units. Hydrogen atoms are not indicated for structures containing borane units. (Figure continues on following page.)

pentadienide and π-benzene. Some unique hydroborane groups form bridging ligands and there are cases where the metallate anions $(\pi\text{-}C_5H_5)Mo(CO)_3^-$ and $Co(CO)_4^-$ function as bridging ligands.

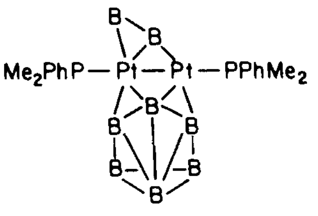
Unbridged compounds are as yet less abundant. Most of those



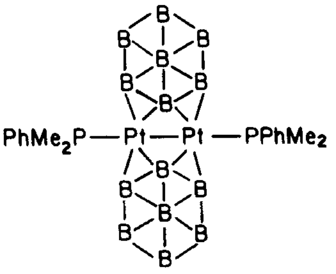
Pt-Pt, 2.628 (1) Å; ref. 14



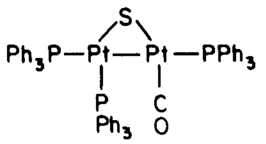
Pt-Pt, 2.628 (1) Å; ref 15



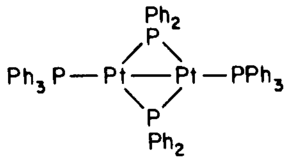
Pt-Pt, 2.621 (1) Å; ref. 16



Pt-Pt, 2.644 Å; ref. 17



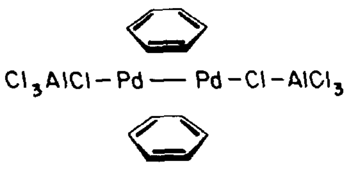
Pt-Pt, 2.647(2) Å; ref. 18

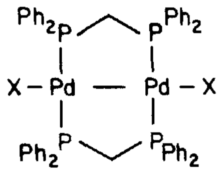


Pt-Pt, 2.604 Å; ref. 19

FIGURE 1 (continued)

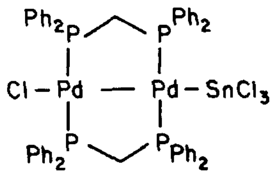
that are known are derivatives of[26] $(RNC)_6M_2^{2+}$ such as[27] $(CH_3NC)_4$ PdI_2 shown in Figure 3. Other examples include[28] $(Ph_3P)_2(RNC)_4$ M_2^{2+} and $Ph_2P(CH_2)_n(PPh_2)_2$- $(CH_3NC)_2Pd_2^{2+}$.[29] All have planar coordination about each metal and an unsupported metal-metal bond. The Pd–Pd bond lengths in these unsupported dimers, 2.5310(9) Å in[26] $(CH_3NC)_6Pd_2^{2+}$ and 2.533(1) in $(CH_3NC)_4Pd_2I_2$,[27] are somewhat shorter than those in the bridged complexes in contrast to $Pd_2(\mu\text{-}CO)_2Cl_4^{2-}$, $Pt_2(CO)_2Cl_4^{2-}$ adopts an unbridged structure with a dihedral angle of only 30° between the coordination planes of the two platinum atoms.[30]

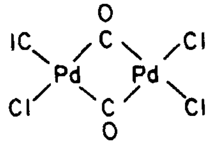




Pd–Pd, 2.57 Å; ref. 20

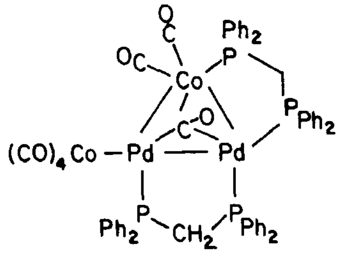
X = Br, Pd–Pd, 2.699(5) Å; ref. 21
X = Cl, Pt–Pt, 2.651(1) Å; ref. 22

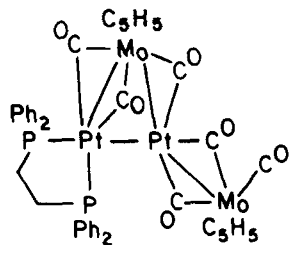




Pd–Pd, 2.644(2) Å; ref. 23

Pd–Pd, 2.697(3) Å; ref. 24





Pd–Pd, 2.586(1) Å; ref. 25

Pt–Pt, 2.672(2) Å; ref. 25

FIGURE 2 Other bridged binuclear M(I) compounds characterized by x-ray diffraction.

With such a diverse group of M(I) complexes involving a host of different ligands it is not surprising that the methods of their preparation are rather varied. Two routes are particularly common and somewhat suitable for general use. Reduction of a M(II) complex is a frequent route to M(I) complexes.[31] Both carbon monoxide[32] and methyl isocyanide[33] in aqueous solution will spontaneously reduce $PtCl_4^{2-}$ and $PdCl_4^{2-}$ to M(I) complexes $M_2(CO)_2Cl_4^{2-}$ or $(RNC)_6M_2^{2+}$ with carbon dioxide as the probable oxidation product in ei-

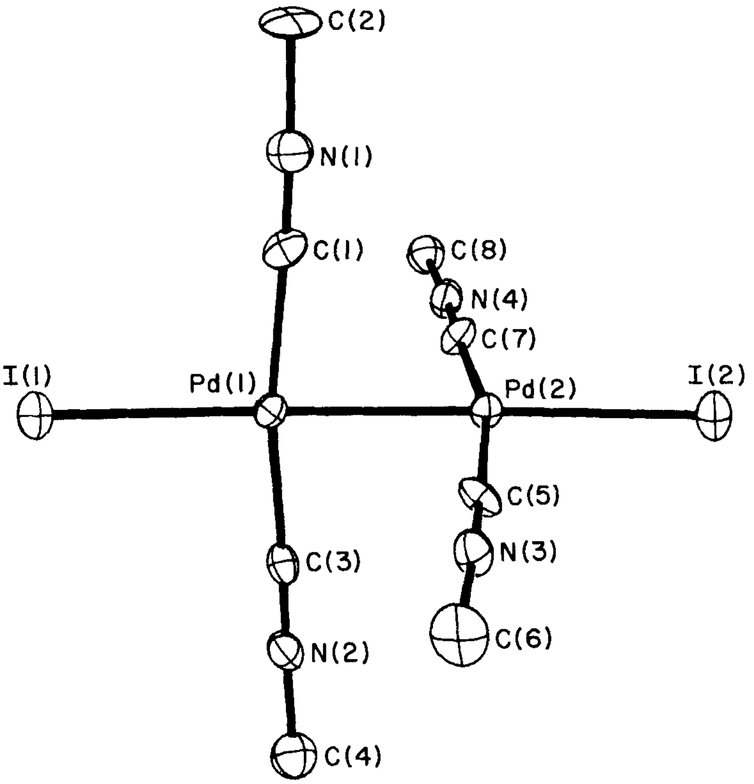
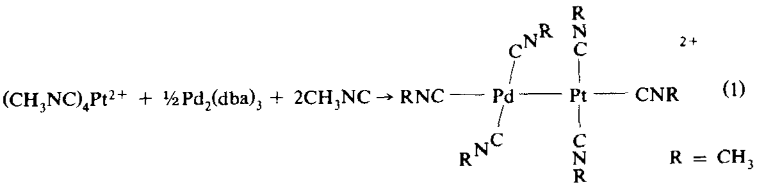


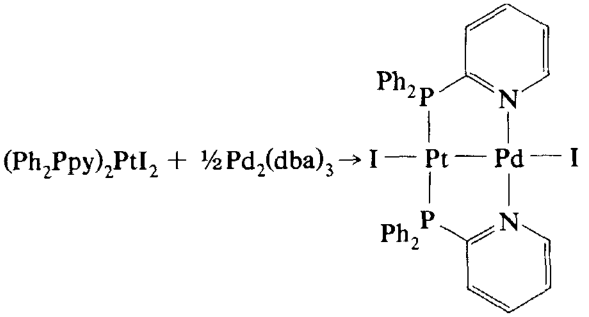
FIGURE 3 Perspective drawing of $(CH_3NC)_4Pd_2I_2$ (Ref. 27).

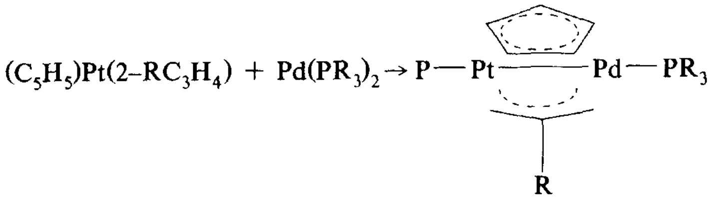
ther case. With methyl isocyanide this reduction proceeds smoothly even under aerobic conditions and the product, $(CH_3NC)_6Pd_2^{2+}$, and most of its derivatives are perfectly air stable materials which are readily handled by normal chemical techniques.

These reductive techniques have the general problem that overreduction to M(0) complexes or to the metal itself are also feasible outcomes. A more easily controlled reaction is the conproportionation reaction in which equal amounts of a suitable M(0) compound are used to reduce the M(II) reaction partner.[31,34] Not only does this procedure eliminate overreduction but it also allows for the controlled formation of heterobinuclear compounds as shown in Eqs. (1),[33] (2)[35] and (3).[31]

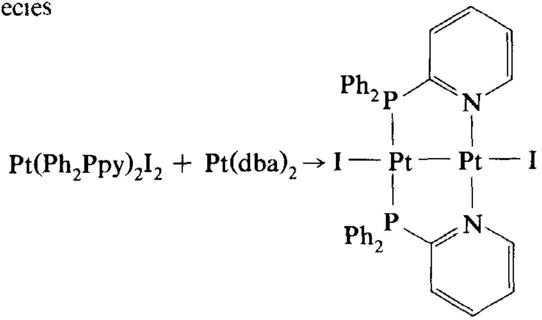

(1)

(dba is dibenzylideneacetone):


(2)


(3)

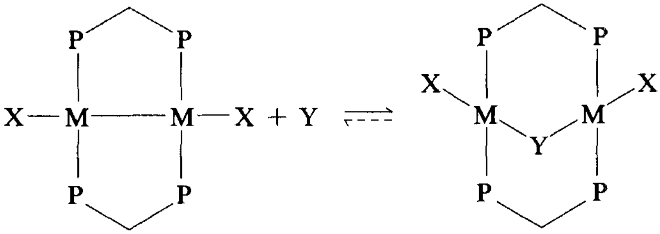
The stability of the products of these reactions attests to the strength of the metal–metal bonds. The products do not disproportionate readily into the two corresponding homobinuclear compounds [i.e., for Eq.(1) into $(CH_3NC)_6Pd_2^{2+}$ and $(CH_3NC)_6Pt_2^{2+}$]. Notice also that in Eq.(2) and (4)[35] this reaction has been used to create species


(4)

with different ligation at each metal. It appears likely that further exploration of this method of preparing unsymmetric dimers is warranted.

Most of these binuclear complexes are coordinatively unsaturated with a 16 electron count at each of the two metal atoms. This generalization pertains not only to all of the unbridged dimers but also to most of the bridged dimers shown in Figures 1 and 2. Even $(C_5H_5)_2Pd_2(PR_3)_2$ conforms since each π-cyclopentadienyl group appears to be bonded to the Pd_2 unit in trihapto rather than pentahapto fashion.[31] This feature (coordination unsaturation) makes these molecules unique among metal–metal bonded compounds and, combined with the presence in some cases of flexible bridging ligands, leads to some remarkable chemical reactions.

One unusual feature of some of these molecules is the facile, sometimes reversible insertion of small molecules into the metal–metal bond as shown in Eq.(5). Here the small molecule Y may be carbon monoxide, an isocyanide,



(5)

sulfur dioxide, a sulfur atom (from cyclooctasulfur), a methylene group (from diazomethane) or an acetylene activated by electron withdrawing groups. In the process of insertion the M–M bond is broken and the metal–metal separation increases from ~ 2.6 Å to between 3.2 and 3.5 Å depending on the size of the small molecule and whether one (the case for CO, CNR, SO_2, S or CH_2 insertion) or two (the case for acetylene insertion) atoms are placed between the two metal ions. The structure of one of the products (a molecular A-frame) of this type of reaction is shown in Figure 4.[37] Flexibility of the bridging ligands, with an ability to span the range 2.5–3.5 Å, appears to be a critical requirement necessary to support this type of reaction. Investigations have specifically noted that other M(I) dimers, such as $Pd_2(\mu\text{-S-PPh}_2)_2(PR_3)_2$,[38] $Pd_2(\mu\text{-Ph}_2\text{Ppy})_2Cl_2$[39] and $(\overline{\text{Pt}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPhC}}_6\text{H}_4))_2$,[15] which possess less flexible bridges, as well as unbridged complexes, do not undergo similar in-

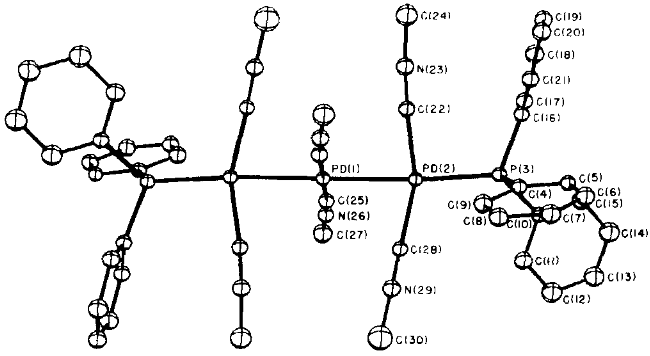
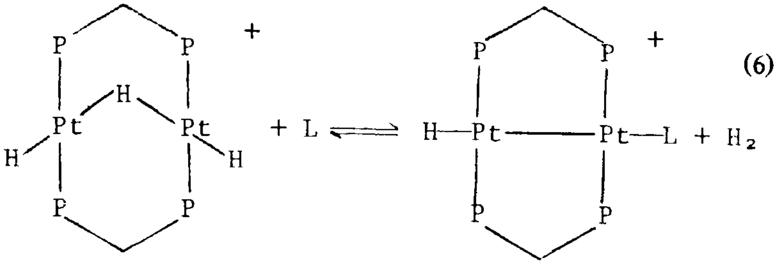


FIGURE 4 The first bis(diphenylphosphino)methane bridged A-frame, Pd_2 (μ-dpm)$_2$(μ-$CNCH_3$) $(CNCH_3)^{+}{}_2$ (Ref. 37).

sertion reactions. However, the unbridged dimer $(CH_3NC)_6Pd_2^{2+}$ does undergo one remarkable insertion reaction. Treatment of $(CH_3NC)_6Pd_2^{2+}$ with $Pd_2(dba)_3$ in the presence of triphenylphosphine or methyl isocyanide yields the linear, trinuclear cations $(Ph_3P)_2(CH_3NC)_6Pd_3^{2+}$ or $(CH_3NC)_8Pd_3^{2+}$, respectively. The structure of the former is shown in Figure 5. The three metal atoms have nearly planar coordination with the coordination planes perpendicular to one another. The insertion of metal atoms or ions into these reactive metal–metal bonds warrants further study.

Bridge flexibility also produces other novel reactions for these species. One of these is the reductive elimination of dihydrogen from Pt(II) species with the formation of binuclear Pt(I) compounds.[41,42] This is shown in Eq.(6). In some cases this is a reversible reaction. In addition it forms



(6)

part of a plausible scheme [shown as Eq.(7)] for the the water gas shift reaction which is catalyzed by these binuclear platinum complexes.

Another example of unusual reactivity involves the cyclo-

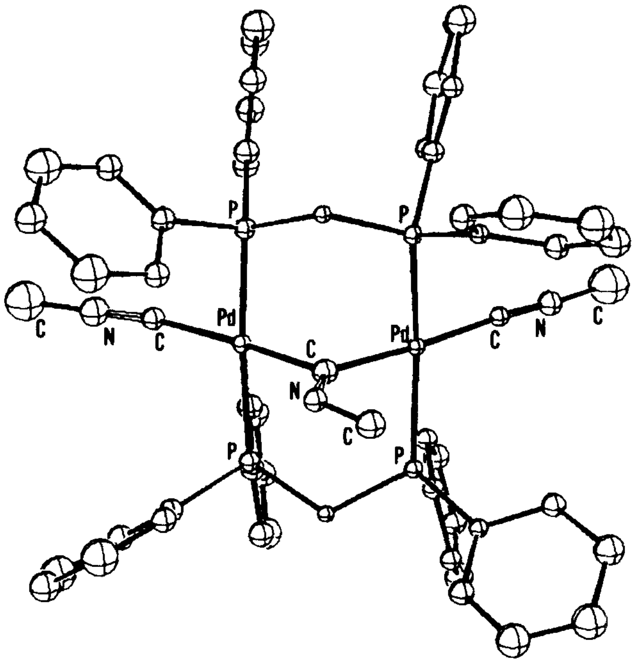
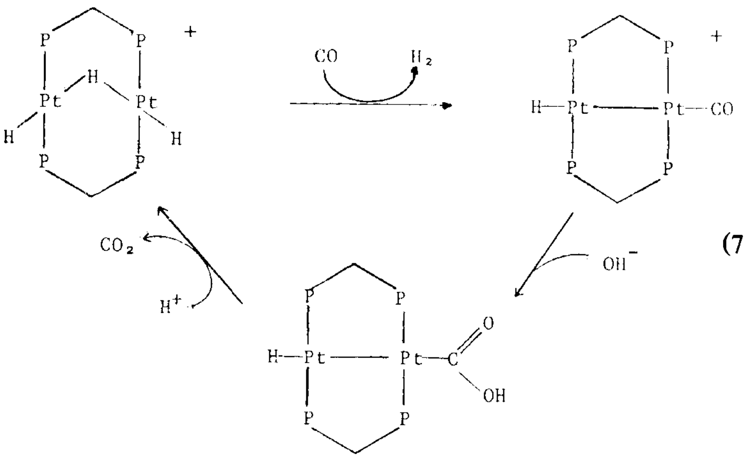
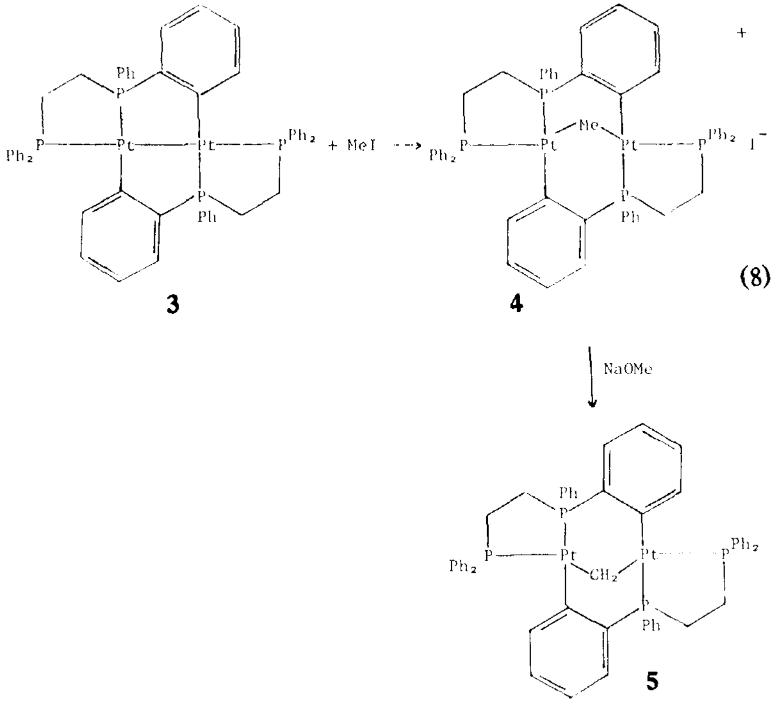


FIGURE 5 Structure of the cation in $[(Ph_3P)_2(CH_3NC)_6Pd_3][PF_6]_2$ (Ref. 40).



(7)

metalated compound **3** which undergoes addition of methyl iodide as shown in Eq.(8).[43] The product **4** appears to contain a bridging methyl group, although the alternative of rapid migration of the



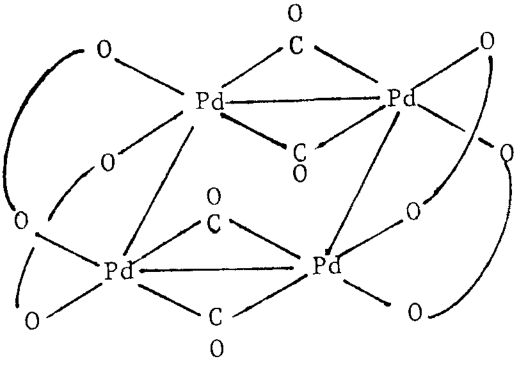
3 4 5

(8)

methyl group from one platinum center to the other has not been totally ruled out. On treatment with base (sodium methoxide) **4** is transformed into the bridged methylene complex **5**.[44] Crystallographic udies show that the Pt–Pt separation has enlongated from 2.628(1) Å in **3** to 2.915(1) in **5**.

Despite the unusual reactivity of the metal–metal bonds of some of these binuclear M(I) complexes, sometimes rather typical behavior is exhibited. Cleavage of the M–M bond by halogens to give monomeric M(II) complexes is a fairly characteristic reaction.[33,45] Photolysis is also known to cleave metal–metal bonds, and photolysis of $(CH_3NC)_6Pd_2^{2+}$ has been interpreted to result in the formation of T-shaped $(CH_3NC)_3Pd^+$.[46] Thus irradiation of $(CH_3NC)_6Pd_2^{2+}$ in the presence of halogen atom donors (CCl_4, CBr_4) yields $(CH_3NC)_3PdX^+$. Moreover, photolysis reversibly interconverts $(CH_3NC)_6PtPd^{2+}$ and a mixture of $(CH_3NC)_6Pd_2^{2+}$ and $(CH_3NC)_6Pt_2^{2+}$. While photolysis does represent a means to reacting metal–metal bonds, it is not yet clear whether the metal–metal bonds in bridged binuclear complexes can be activated in this fashion. The ligand bridges should hold the radical fragments together and may promote rapid recombination with no net chemical change.

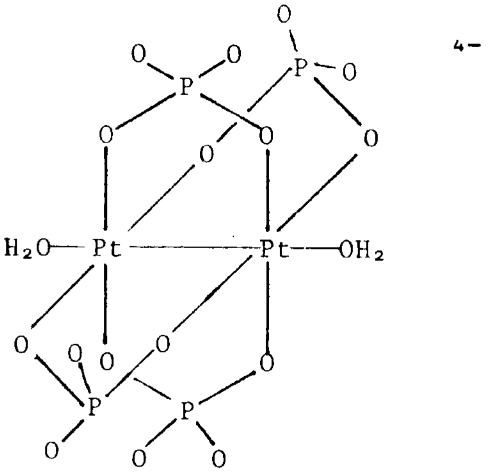
Not all diamagnetic Pd(I) compounds are dinuclear. A tetranuclear structure has been found for $Pd_4(\mu\text{-}O_2CCH_3)_4(\mu\text{-}CO)_4$, **6**.[47] Here, there are two types



6

of Pd–Pd interactions. Those bridged by acetate (2.909 Å) are considerably longer than those bridged by carbonyl (2.663(1) Å). In effect it consists of two closely linked Pd(I) centers (with carbonyl bridges) which are more loosely connected by the acetate bridges.

Binuclear M(III) compounds These are considerably less common than their M(I) counterparts. Those that have been characterized by x-ray diffraction all fit into a common structural pattern in which each platinum atom is bound to five ligands and the other platinum atom in a crudely octahedral arrangement. In $[Pt_2(HPO_4)_4(H_2O)_2]^{4-}$, **7**, the Pt–Pt bond length of 2.486(2) Å is consistent with the presence of a Pt–Pt single bond and a $\sigma^2\pi^4\delta^2\delta^{*2}\pi^{*4}$electronic configuration.[48] In the corresponding sulfato complex $Pt_2(SO_4)_4(H_2O)^{4-}{}_2$, it is also short, 2.466 Å.[49] Other structurally characterized PT(II) compounds, **8**–**11**, have similar, though less symmetric structures. Their Pt–Pt distances: **8**,2.557(1),[50] **9**,2.539 (1),[51] **10**,2.547(1),[52] **11**, 2.575(1),[52] are indicative of the presence of a Pt–Pt single bond. Note that in accord with the higher oxidation state and smaller ionic radius of Pt(III) than Pt(I), the Pt–Pt bond lengths in these Pt(III) compounds are shorter than the Pt–Pt



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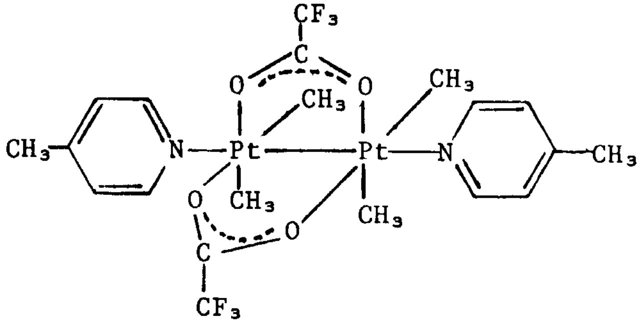

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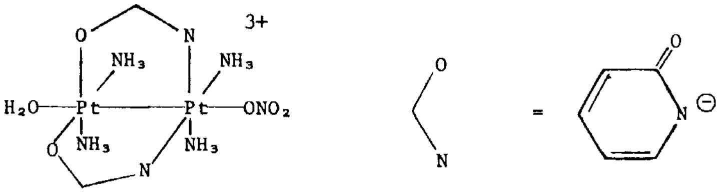

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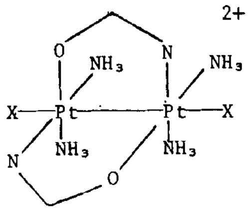
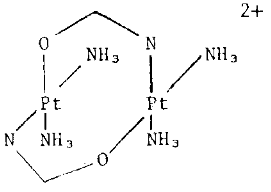


10 X = ONO_2

11 X = NO_2

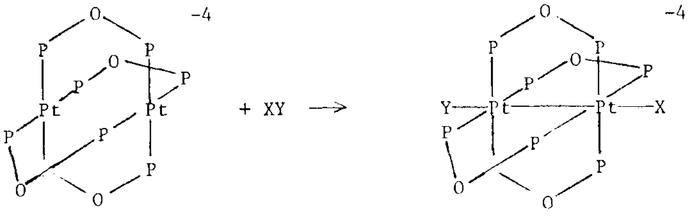
bond lengths in Pt(I) compounds. The 0.028(1) Å difference in Pt–Pt bond length between **10** and **11** has been ascribed to the difference in axial ligand (nitrate versus nitrite).[52]

Oxidative addition of halogens and related species to face-to-face oriented pairs of Pt(II) complexes should represent a general route for the preparation of Pt(III) complexes. Both **10** and **11** have been prepared from oxidation of a face-to-face, α-pyridonate bridged Pt(II) complex **12**.



12

Similar oxidation of the Pt(II) dimer **13** with halogens or methyl iodide gives binuclear Pt(III) complexes *via* Eq.(9).[53] In the process the Pt–Pt



(9)

13 P-O-P is $HO_2POPO_2H^{2-}$ **14**

separation decreases from 2.925(1) Å in **13** to 2.695(1) Å in **14** in accord with the idea that a Pt–Pt single bond is formed.

All of these binuclear Pt(III) complexes conform to the 18 electron rule and are coordinatively saturated. As a result it is anticipated that the metal–metal bonds found here will be less reactive toward insertion [Eq.(5)] than their M(I) counterparts. However, these simple Pt(III) dimers form only a small part of the story of extended linear arrays of platinum complexes, and the formation of metal–metal bonds in these arrays as well as their one-electron redox properties will continue to attract research efforts.

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