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A Novel Pt(II)—Pt(IV) Mixed Valence Complex: The Crystal and Molecular Structure of $[LPt(\mu\text{-}I)(\mu\text{-}Me_2PCH_2PMe_2)_2PtMe_3][I_3]$, $L = 0.45I + 0.55Me$*

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X-ray structure determination of the title compound has shown that iodination of $[Pt_2Me_4\ (\mu\text{-}Me_2PCH_2PMe_2)_2]$ involves an oxidative addition reaction accompanied by methyl group transfer between the two platinum atoms. The crystal structure is built of symmetrical, linear $[I_3]^-$ anions and partially disordered cations, in which I^- or CH_3^- ligands occupy the L sites with nearly equal propability. In the cations the Pt(II) and Pt(IV) centres are characterised by square planar and octahedral coordination geometries; they are locked into close proximity [Pt . . . Pt 386.3(1) pm] by two bridging $Me_2PCH_2PMe_2$ ligands. The L-shaped $LPt(\mu\text{-}I)PtMe$ fragment [Pt-I-Pt 91.2(1)°] is perpendicular to the $Pt(1)P_2L(\mu\text{-}I)$ and $Pt(2)P_2C_2$ coordination planes. The overall geometry of the cation approximates to C_s symmetry.

Crystals of the title compound are triclinic, space group $P\overline{1}$, with two formula units in a unit cell of dimensions $a = 924.0(2)$, $b = 932.8(4)$, $c = 1804.4(7)$ pm, $\alpha = 102.39(4)$, $\beta = 94.63(3)$ and $\gamma = 96.93(3)°$. Least-squares refinement of the structural model defined by 221 parameters converged at a conventional R index on F of 0.049 for 5045 reflections with $I \geq 3\,\sigma\,(I)$.

INTRODUCTION

The ability of transition metal complexes stabilised by bridging bis(diphenylphosphino)methane (dppm) ligands to promote dimetallic activation and catalysis of small molecules, leading to useful organic products, has prompted intense interest in further exploration of their chemistry. With platinum dppm forms several types of dinuclear complexes, and examples of these have now been crystallographically characterised for the oxidation states 0[1], I,[2,3] II[4-6] and IV.[7] The $Pt_2(\mu\text{-dppm})_2$ complexes display diverse structural properties, reflecting the considerable stereochemical flexibility of the P—CH_2—P linkage. They adopt several modes of metal-metal interaction, including the novel Pt→Pt donor-acceptor bonding in the unique structure of the $[Me_2Pt(\mu\text{-dppm})_2PtMe]^+$ cation.[6] Structural data also indicate that steric effects may be of major importance in influencing the rich reactivity of these complexes.

It is therefore likely that by changing phosphine substituents of diphosphinomethane ligands, and thus modifying their steric as well as electronic properties, new molecules of novel structure and different, perhaps even

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* Dedicated to Professor D. Grdenić on occasion of his 65th birthday.

enhanced, reactivity may be obtained. A study of steric and electronic effects of related $R_2PCH_2PR_2$ ligands on the structures and reactivities of dinuclear complexes has recently been initiated by the synthesis and structural characterisation of $[Me_2Pt(\mu\text{-dmpm})_2PtMe_2]$ (*I*), the first dmpm ($Me_2PCH_2PMe_2$) bridged complex of platinum to be reported.[8] It has been found that (*I*) and its dppm analogue adopt different conformations of the $Pt_2P_4C_2$ dimetallacycles in the solid state, and show different fluxional behaviour in solutions. Different reactivities of the two compounds towards small moleclues, such as MeI, I_2 and Br_2, appear likely to be of predominantly steric origin. In continuation of this work we have now carried out an X-ray structure determination of the title compound.

The results we present here demonstrate that reaction of (*I*) with diiodine involves a new type of oxidative addition which is accompanied by a methyl group transfer between two metal centres. The title compound also provides the first example of a new type of mixed valence complex. A preliminary account of this work has been reported elsewhere.[9]

EXPERIMENTAL

Brown crystals of the title compound were obtained from a CH_2Cl_2/MeOH solution.

Crystal Data

$C_{13.5}H_{83.5}I_{4.5}P_4Pt_2$, $M_r = 1286.1$, triclinic, space group $P\bar{1}$, $a = 924.0(2)$, $b = 932.8(4)$, $c = 1804.4(7)$ pm, $\alpha = 102.39(4)$, $\beta = 94.63(3)$, $\gamma = 96.93(3)^\circ$, $U = 1.499$ nm^3, $Z = 2$, $D_X = 2.850$ Mg m^{-3}, Mo-K_α radiation, $\lambda = 71.069$ pm, $\mu = 14.33$ mm^{-1}, $T = 293$ K.

The choice of the centrosymmetric space group $P\bar{1}$ led to a successful structure analysis.

Measurements

All measurements were made with a crystal fragment of irregular habit, using graphite monochromated molybdenum X-rays and an Enraf-Nonius CAD4F diffractometer. The unit cell dimensions were obtained from a least squares fit to the setting angles of 25 automatically centred reflections. The intensities of 7590 reflections with $2 < \Theta$ (Mo-K_α) $\leq 27^\circ$ were measured by taking $\Theta/2\Theta$ scans of 1.0° in Θ.

The integrated intensities, I, and their variances, σ^2 (I), obtained as described earlier,[10] were corrected for Lorentz, polarisation, crystal decomposition (maximum correction 1.32 on F^2) and absorption effects. The absorption correction was performed by the empirical method of Walker and Stuart,[11] which derives a transmission function from the differences between F_o and F_c based on a structural model with isotropic thermal parameters. The correction factors on F were 0.71—1.40. Subsequent merging of 1798 equivalent intensities into 852 symmetry idependent ones gave R_{internal} of 0.039. Of the 6031 unique structure amplitudes observed, only 5045, for which $I \geq 3\,\sigma$ (I), were used in structure solution and refinement.

Structure Analysis

The structure was solved by Patterson and difference electron density techniques. It was refined by full-matrix least squares minimization of the function $\Sigma w (|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2$ (F) + $(0.03F)^2$.

During refinement it became apparent that the sites assigned to ligands L are disordered. Various disorder models were tried, but the one which allocates to L sites αI(2) and $(1-\alpha)$C(14), where α is an occupancy factor, was found to be satisfactory. The positions of I(2) and C(14) were allowed to vary independently, but the vibrational parameters of the two atoms were constrained to be equal. All non-hydrogen atoms were assigned anisotropic thermal vibrations. Complex, neutral atom scattering factors were used throughout.[12] The scattering of hydrogen atoms was not accounted for. The refinement converged at R of 0.049 and R_w of 0.068, with 221 structural parameters (including α) changing by less than 0.15 of their estimated standard derivations.

In the final difference synthesis the extreme function values were —2.4 and $+2.6 \times 10^{-6}$ e pm^{-3}; all peaks higher than 1.5×10^{-6} e pm^{-3} were close to the positions of Pt or I atoms. The occupancy factor α converged at 0.446(5), close to the value of 0.5 which was assumed in calculating the crystal data. The final atomic positional parameters are shown in Table I and selected interatomic distances and angles are presented in Table II.*

TABLE I

Atomic Fractional Coordinates and e.s.d.s. for $[LPt(\mu\text{-}I)(\mu\text{-}dmpm)_2PtMe_3]I_3$[a]

	x	y	z
Pt(1)	—0.16601(5)	0.04250(6)	0.13961(3)
Pt(2)	0.03342(5)	0.21356(6)	0.34146(3)
I(1)	0.05425(9)	0.25819(9)	0.19637(5)
I(2)	—0.37849(27)	—0.15991(31)	0.08446(18)
I(3)	—0.67528(13)	—0.46800(14)	0.09385(7)
I(4)	—0.56804(10)	—0.37732(11)	0.25534(6)
I(5)	—0.45992(14)	—0.29104(16)	0.41626(7)
P(1)	0.0016(4)	—0.1206(4)	0.1263(2)
P(2)	0.0448(4)	—0.0463(4)	0.3035(2)
P(3)	—0.3228(4)	0.2150(4)	0.1643(2)
P(4)	—0.2247(4)	0.2234(4)	0.3344(2)
C(1)	0.0334(14)	0.1956(19)	0.4599(8)
C(2)	0.2674(13)	0.2431(22)	0.3587(10)
C(3)	0.0546(18)	0.4545(17)	0.3818(9)
C(4)	0.1213(14)	—0.1064(16)	0.2130(7)
C(5)	—0.2872(14)	0.3229(15)	0.2611(8)
C(6)	0.1295(19)	—0.0943(20)	0.0557(10)
C(7)	—0.0669(20)	—0.3255(21)	0.0982(13)
C(8)	0.1744(18)	—0.1040(24)	0.3709(10)
C(9)	—0.1173(18)	—0.1875(19)	0.2965(12)
C(10)	—0.3036(17)	0.3545(19)	0.1066(10)
C(11)	—0.5225(13)	0.1558(18)	0.1505(9)
C(12)	—0.3549(15)	0.0585(19)	0.3225(9)
C(13)	—0.2775(19)	0.3262(22)	0.4210(9)
C(14)	—0.330(4)	—0.107(4)	0.081(2)

[a] $L = \alpha I + (1 - \alpha)\,Me$, where $\alpha = 0.446(5)$; dmpm = $Me_2PCH_2PMe_2$.

All calculations were performed on a SEL 32/27 minicomputer, using the locally developed GX (Glasgow X-ray) system of crystallographic programs.[13]

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* The anisotropic vibrational atomic parameters and a list of the observed and calculated structure amplitudes are available from the authors.

TABLE II

Interatomic Distances and Angles in [LPt(μ-I) (μ-dmpm)$_2$PtMe$_3$]I$_3$

(a) Distances (pm)			
Pt(1) — I(1)	265.2(1)	Pt(2) — I(1)	275.6(2)
Pt(1) — I(2)	252.9(3)	Pt(2) — P(2)	239.1(4)
Pt(1) — P(1)	229.0(4)	Pt(2) — P(4)	239.2(4)
Pt(1) — P(3)	229.0(4)	Pt(2) — C(1)	218(2)
Pt(1) — C(14)	199(4)	Pt(2) — C(2)	214(2)
P(1) . . . P(2)	310.5(6)	Pt(2) — C(3)	219(2)
P(3) . . . P(4)	311.1(5)	I(3) — I(4)	290.9(2)
P — CH$_3$	179(2)—188(2)	I(4) — I(5)	290.0(2)
P — CH$_2$	180(2)—187(2)	Pt(1) . . . Pt(2)	386.3(1)
(b) Angles (°)			
I(1) — Pt(1) — I(2)	179.0(1)	I(1) — Pt(2) — P(2)	93.6(1)
I(1) — Pt(1) — P(1)	88.2(1)	I(1) — Pt(2) — P(4)	93.6(1)
I(1) — Pt(1) — P(3)	88.1(1)	I(1) — Pt(2) — C(1)	174.7(4)
I(2) — Pt(1) — P(1)	92.7(2)	I(1) — Pt(2) — C(2)	88.2(5)
I(2) — Pt(1) — P(3)	91.1(2)	I(1) — Pt(2) — C(3)	87.8(4)
P(1) — Pt(1) — P(3)	174.6(2)	P(2) — Pt(2) — P(4)	102.8(2)
C(14) — Pt(1) — I(1)	170(2)	P(2) — Pt(2) — C(1)	89.8(5)
C(14) — Pt(1) — P(1)	94(2)	P(2) — Pt(2) — C(2)	86.7(6)
C(14) — Pt(1) — P(3)	91(2)	P(2) — Pt(2) — C(3)	172.2(5)
Pt(1) — I(1) — Pt(2)	91.2(1)	P(4) — Pt(2) — C(1)	89.7(4)
I(3) — I(4) — I(5)	179.2(1)	P(4) — Pt(2) — C(2)	170.2(6)
P(1) — C(4) — P(2)	116.7(8)	P(4) — Pt(2) — C(3)	84.7(5)
P(3) — C(5) — P(4)	116.1(8)	C(1) — Pt(2) — C(2)	87.9(6)
Pt — P — C	111(1)—122(1)	C(1) — Pt(2) — C(3)	88.3(6)
C — P — C	99(1)—107(1)	C(2) — Pt(2) — C(3)	85.7(7)

RESULTS

The diffraction study described here establishes that the reaction of [Me$_2$Pt(μ-dmpm)$_2$PtMe$_2$] (*I*) with two mole equivalents of I$_2$ produces a mixture (*V*) of the triiodide salts of [MePt(μ-I) (μ-dmpm)$_2$PtMe$_3$]$^+$ (*III*) and [IPt(μ-I) (μ-dmpm)$_2$PtMe$_3$]$^+$ (*IV*). In the crystals of (*V*), [LPt(μ-I) (μ-dmpm)$_2$PtMe$_3$] [*I*$_3$] (L = 0.45 I + 0.55 Me), the two salts are roughly in 1 : 1 ratio, and the cations (*III*) and (*IV*) are randomly distributed. This results in a partial disorder with the L sites occupied with nearly equal probability by methyl or iodo ligands. There is no direct experimental evidence suggesting that the disorder involves atoms other than I(2) and C(14), although the structural features of the cation imply that the site of I(1) may reflect a superposition of two slightly different, but not discernible positions of the bridging ligand (see later).

The crystal structure of (*V*) is built of cations and anions. The [I]$_3^-$ ions adopt a symmetrical, linear structure [I(3) — I(4) — I(5) 179.2(1)°], with I—I bond lengths [290.9(2) and 290.0(2) pm] in agreement with the value of 293 pm which is considered typical of unperturbed triiodide ions.[14] In the crystallochemical unit containing the atoms of Table I, the [I$_3$]$^-$ ion lies in the mirror plane of the cation, the individual displacements of I(3), I(4) and I(5) atoms from the $Pt_2I_2C(1)$ plane not exceeding ±5 pm. However, the shortest interatomic distances, I(3)...I(1) and I(3)...I(2) of 417.4(2) and 376.7(3) pm, do not appear indicative of a relatively strong association between the cations and anions. They can be compared with the shortest intermolecular I...I contact of 354 pm in solid diiodine.[15] In considering contacts between $[I_{16}]^{4-}$ ions, Herbstein and Kapon have suggested that a distance of 384 pm should not be regarded as evidence of interanionic association.[16]

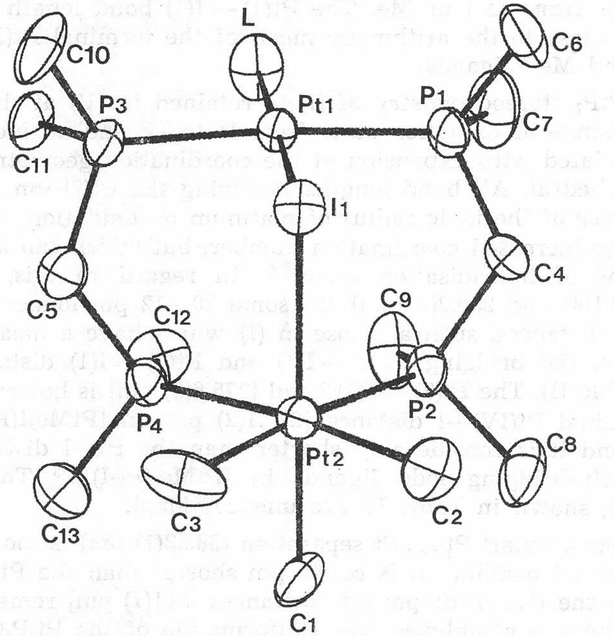


Figure 1. A view of the structure of $[LPt(\mu\text{-}I)(\mu\text{-dmpm})_2PtMe_3]^+$. The disordered site, L, is occupied with practically equal probability by I(2) or the methyl carbon C(14). The atomic vibrational ellipsoids display 50% probability.

The structure of the $[LPt(\mu\text{-}I)(\mu\text{-dmpm})_2PtMe_3]^+$ cations in (*V*), shown in the Figure, reveals the presence of Pt(II) and Pt(IV) metal centres, characterised by square planar and octahedral co-ordination geometries. The metal atoms are spanned by two bridging dmpm ligands to form a $Pt_2(\mu\text{-PCP})_2$ nucleus of yet another, previously not observed structural type. They are also linked by a bridging iodide ligand, thus forming an L-shaped $LPt(\mu\text{-}I)PtMe$ linkage [Pt—I—Pt 91.2(1)°] perpendicular to the $Pt(2)P_2C(2)C(3)$ and $Pt(1)P_2L(\mu\text{-}I)$ coordination planes. The overall geometry of the cation approximates to C_s symmetry with the mirror plane passing through the planar $LPt(\mu\text{-}I)PtMe$ fragment.

The *cis*-square planar stereochemistries of both PtP_2Me_2 fragments in the parent dimer (*I*) (the Scheme) are radically altered by the reaction with diiodine, albeit in different ways. In (*V*) the square-planar coordination geometry typical of d^8 platinum ions is retained at the Pt(1) centre, the atoms Pt(1), P(1), P(3), I(1) and I(2) being coplanar within ±5 pm, but the Pt—P bonds have rearranged into a *trans*-PtP_2 linkage. The Pt(1)—P bond lengths equal to each other at 229.0(4) pm, are typical of values usually found for Pt(II)—P(*trans* to P) bonds.[17] The Pt(1) — I(2) distance of 252.9(3) pm is unusually short and may be in some error, arising from the disorder of the crystal structure. Terminal Pt(II)—I distances are expected to range from 261 pm, when *trans* to I,[18] a ligand of low *trans*-influence in d^8 platinum complexes,[19] up to 271 pm, when *trans* to σ-carbon donors.[20] The position of the bridging ligand I(1) might therefore be expected to change by about 10 pm, depending on whether it lies *trans* to I or Me. The Pt(1) — I(1) bond length of 265.2(1) pm found here is close to the arithmetic mean of the terminal Pt(II)—I distances *trans* to I[18] and Me[20] ligands.

The *cis*-PtP_2 stereochemistry of (*I*) is retained in (*V*) at the Pt(2) centre, despite the change of oxidation state from II to IV and an increase in steric demands associated with expansion of the coordination geometry from square planar to octahedral. All bond lengths involving the Pt(2) ion are compatible with an increase of the ionic radius of platinum on oxidation, an effect which may reflect the increased coordination number, but which can also be rationalised in terms of hybridisation effects.[21] In regard to this, the Pt(2) — P distances [239.1(4) and 239.2(4) pm] are some 10—12 pm longer than Pt(II)—P (*trans* to Me) distances, such as those in (*I*) which have a mean value of 227 pm.[8] Similarly, the bridging Pt(2) — I(1) and Pt(1) — I(1) distances differ by *ca.* 10 pm (Table II). The Pt(2) — I(1) bond [275.6(2) pm] is however comparable with the terminal Pt(IV)—I distance [277.1(2) pm] in $[PtMe_3I(PhMeAsCH_2CH_2AsMePh)]$,[22] and it is considerably shorter than the Pt—I distances [283 pm] involving triply-bridging iodo ligands in $[PtMe_3(\mu_3\text{-}I)]_4$.[23] The Pt—C bond lengths in (*V*), shown in Table II, are unexceptional.

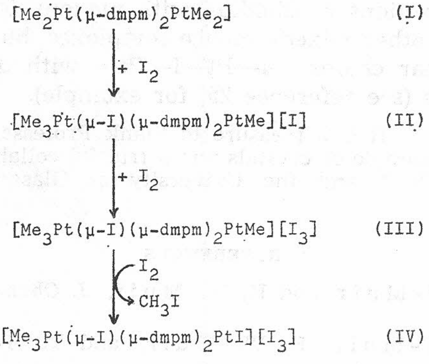
The 'intramolecular' Pt ... Pt separation (386.3(1) pm] is too long to permit direct metal-metal bonding. It is *ca.* 40 pm shorter than the Pt ... Pt distance in (*I*),[8] despite the P ... P dmpm bite distances [311(1) pm] remaining virtually the same in the two complexes. The conformation of the $Pt_2P_4C_2$ 8-membered dimetallacycle changes from that of C_{2h} symmetry in (*I*) to that of reduced C_s symmetry in (*V*). It thus appears that the distances separating the metal centres in these complexes change predominantly with conformations around P—CH_2 bonds. In (*I*),[8] Pt—P—CH_2—P torsion angles are all close to 45° and those involving the same dmpm ligand are of the same sign; in (*V*) the torsion angles across the P(1) — C(1) and P(2) — C(4) bonds are 30.0(6) and —77.4(8)°, while those across P(3) — C(5) and P(4) — C(5) are —34.3(6) and 83.2(8)°, respectively. It is therefore obvious that, in analogy with dppm, the ability of the dmpm ligand to respond to changes in stereochemical demands of the metal centres stems mainly from the conformational flexibility of the P—CH_2—P linkage.

Iodination of (*I*) does not relieve molecular steric overcrowding, and indeed it appears to increase it. The presence of considerable steric strain in (*V*) is evident from short intramolecular contacts coupled with distortions of bond angles, especially those subtended at the Pt(2), P(2), P(4), C(4) and C(5) atoms (Table II). Short Me ... Me distances are particularly obvious around the Pt(2) centre, where the C(8) atom makes contacts of 337(3) and 331(3) pm with C(1) and C(2), and C(13) approaches C(1) and C(3) at 333(2) and 334(2) pm. The atoms C(9) and C(12), lying close to the plane defined by the Pt(2)—P bonds, are separated by a distance of 335 pm only; their contact is somewhat relieved by distortion of the P—Pt(2)—P angle to 102.8(2)° and by opening of the Pt(2)—P—C(Me) angles to 122(1) and 121(1)°, for C(9) and C(12), respectively. Around the Pt(1) centre, steric crowding is less extensive: the atoms C(7) and C(11) lie close to the Pt(1) coordination plane and make respective contacts at 344(2) and 340(2) pm with I(2) [330(4) and 339(4) pm with C(14)]. The methylenic carbon atoms C(4) and C(5) are separated from Pt(1) by 344(1) and 340(1) pm, respectively. It is thus apparent, and especially obvious from an inspection of a structural model, that in (*V*) the internuclear region and also the inner coordination sphere of one metal centre, Pt(2), are efficiently shielded by the CH_3 and CH_2 groups; while the other metal centre, Pt(1), remains relatively open to the external environment.

DISCUSSION

Available diffraction studies of dppm and dmpm complexes permit some discussion of the inter-relationship between their molecular structure and reactivity.

The solid state structures of (*I*)[8] and (*V*), where (*V*) is a mixture of (*III*) and (*IV*), and the analytical and spectroscopic (NMR) characterisation of (*II*) to (*IV*),[9] indicate that (*I*) reacts with diiodine as shown in the Scheme.



Some of the changes involved here, such as oxidation of platinum(II) to platinum(IV) by diiodine and formation of the polyiodide ions, are well established reactions.[24] Oxidative addition to a dinuclear methylplatinum complex which occurs with transfer of a methyl group from one metal centre to the other, provides a new type of reaction in the chemistry of dinuclear complexes of platinum. As regards the mechanism of methyl group transfer, the solid state structure of (*I*) does not favour an intramolecular process. The steric crowding in (*I*) is particularly severe in the area encapsulating the Pt . . . Pt distance.

One might have expected that the final product of the reaction of (*I*) with diiodine would be a Pt(IV) — Pt(IV) species. Indeed, such a species, $[Me_2Pt(\mu\text{-}Br)_2(\mu\text{-dppm})(\mu\text{-}o\text{-}CH_2C_6H_4CH_2)PtMe_2]$ (but with one dppm ligand only) has recently been reported.[7] We however believe that steric effects in iodination of (*I*) play a major role in stabilising the discrete mixed valence cations. It is now obvious from the molecular structures of (*I*) and (*V*) that formation of a *fac*-$PtMe_3$ fragment at one metal centre of the parent dimer results in a considerable increase of steric crowding around the octahedral Pt(IV) ion and especially in the area between the metal centres. Although the Pt(II) ion in (*V*) remains relatively exposed to the external environment *(vide supra)* and to approach of reagents, the cation as a whole appears sterically saturated and may not be capable of accommodating further steric demands, such as those that would follow oxidation and increased coordination number of the second metal centre. Thus addition of the second mole equivalent of diiodine converts (*II*) into (*III*), a triiodide salt (Scheme); further reaction leads to regiospecific replacement of the methyl by iodo ligand at the Pt(II) centre, to form (*IV*), rather than to oxidative addition at the second metal centre.

We also note that reactivity of (*I*) towards diiodine differs from that of its dppm analogue $[Me_2Pt(\mu\text{-dppm})_2PtMe_2]$,[4] in which substantially increased steric crowding, arising from the bulky phenyl substituents of the μ-$R_2PCH_2PR_2$ ligands, precludes oxidative addition. Instead, the dppm dimer undergoes electrophilic cleavage of a methyl group to yield the $[Me_2Pt(\mu\text{-dppm})_2PtMe]^+$ cation,[6] in which both platinum ions retain d^8 configuration, and their mutual approach is sufficiently close to permit formation of a donor-acceptor metal-metal bond.

The discrete binuclear cation described here, (*V*), provides the first structurally characterised example of a novel type of Pt(II) — Pt(IV) mixed-valence complex. Reactions of diiodide with mononuclear complexes of platinum have produced other mixed-valence complexes, but these are invariably based on infinite linear chains —I—Pt—I—Pt— with disorder involving the Pt(II) and Pt(IV) sites (see reference 25, for example).

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SAŽETAK

Novi Pt(II) — Pt(IV) kompleks miješane valencije: Kristalna i molekuska struktura [LPt(μ-I)(μ-$Me_2PCH_2PMe_2$)$_2$$PtMe_3$] [$I_3$], L = 0,45I + 0,55Me

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Struktura spoja u naslovu, određena metodom rendgenske difrakcije, pokazala je da jodiranje [Pt_2Me_4(μ-$Me_2PCH_2PMe_2$)$_2$] uključuje oksidativnu adiciju popraćenu prijenosom metilne skupine između dva atoma platine.

Kristalna struktura izgrađena je od simetričnih, linearnih aniona [I_3]$^-$ i djelomično nesređenih kationa, u kojima ligandi I^- ili CH_3^- s gotovo jednakom vjerojatnošću zauzimaju položaj L. Centri Pt(II) i Pt(IV) u kationu imaju kvadratnu planarnu i oktaedarsku koordinaciju [Pt...Pt 386,3(1) pm], a premošteni su s dva $Me_2PCH_2PMe_2$-liganda. Fragment LPt(μ-I)PtMe ima L-oblik [Pt-I-Pt 91,2(1)°] i okomit je na ravnine Pt(1)P_2L(μ-I) i Pt(2)P_2C_2. Geometrija cijelog kationa odgovara približno simetriji C_s.

Kristali su triklinski, prostorne grupe $P\bar{1}$, s dvije formulske jedinice u elementarnoj ćeliji dimenzija: a = 924,0(2), b = 932,8(4), c = 1804,4(7) pm, α = 102,39(4), β = 94,63(3) i γ = 96,93(3)°. Struktura je riješena na osnovi 5045 refleksa [$I > 3\sigma(I)$] i utočnjena metodom najmanjih kvadrata do faktora R = 0,049.