Diplatinum(III) tetrakis(β-diketonato) complexes exemplifying the unsupported Pt–Pt bond

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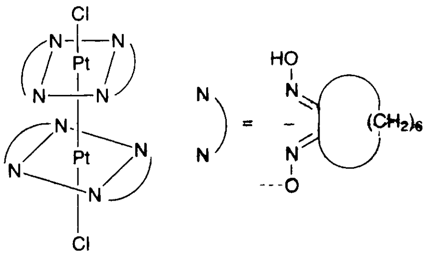
Coupling of tervalent ClPt(acac)$_2$ moieties to form diamagnetic, directly Pt–Pt bonded [Pt$_2$Cl$_2$(acac)$_4$] occurs in the course of oxidative addition of Cl$_2$ to [Pt(acac)$_2$] [acac = R(CO)CH(CO)R′ and R/R′ = Me/Me, Me/CF$_3$ or Ph/Ph].

The most familiar Pt^{III} compounds are 'lantern dimers' spanned by bidentate sulfato, *etc.*, bridges, with the Pt–Pt distance varying between 2.4 and 2.8 Å, according to ligand constraint.[1] However, a stable unsupported symmetric Pt^{III} dimer, [Pt$_2$Cl$_2$(C$_8$doH)$_4$] **I** where C$_8$doH = cyclooctane 1,2-dioxime, with Pt–Pt 2.6964(5) Å, was described recently,[2] after the independent discovery[3] of a closely related, more reactive analogue bearing two chloride ligands and two monodentate imines in the equatorial plane [Pt–Pt 2.694(1) Å]. The exact cyclododecane analogue of **I** has also been characterised.[4] We now report the extension of this previously unsuspected chemistry to common platinum β-diketonates.

Controlled Cl$_2$ addition† to a family of [Pt(acac)$_2$] complexes **II**, in chilled CH$_2$Cl$_2$ or CHCl$_3$ leads in certain cases (R/R′ = Me/Me, Ph/Ph, Me/CF$_3$) to the elusive orange–red, diamagnetic intermediate [Pt$_2$Cl$_2$(acac)$_4$] **III**. Further oxidation yields *trans*-[PtCl$_2$(acac)$_2$] **IV**, as expected.[5] At 290 K, solutions of **III** disproportionate efficiently to **II** and **IV**. These processes [eqn. (1) and (2)] are readily followed by ^{1}H or ^{195}Pt NMR. Dimeric **III** forms more rapidly than **IV** and is initially dominant in the reaction mixture. When isolated as an orange–red powder,‡ **III** is more stable than in solution, but is generally accompanied by **II** and/or **IV**.



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The constitution of **III** is established by: (*a*) direct observation of the molecular ion [Pt$_2$Cl$_2$(acac)$_4$]·M$^+$ (where M = H$^+$, Na$^+$), and abundant derived ions [Pt$_2$Cl(acac)$_4$]$^+$ and [(MeCN)Pt$_2$Cl(acac)$_4$]$^+$, by electrospray mass spectrometry of chilled CHCl$_3$–MeCN solutions. Innocent mixtures of **II** and **IV** do not form a molecular aggregate comparable in abundance with **III** in the ESMS experiment.§ (*b*) A prominent Raman-active band at 144 cm^{-1} in fresh orange–red powders at 77 K, due to the characteristic Pt–Pt symmetric stretching vibration.[2] Neither **II** or **IV** have nearby bands. (*c*) Highly characteristic ^{195}Pt NMR and simple ^{1}H NMR spectra, with Pt, R/R′ and C–H signals lying between those of **II** and **IV**. No ligand chlorination or Pt–C σ-bonding has occurred. (*d*) The instructive asymmetric CF$_3$/Me ligand system, where the mixed form of **II** (*cis* and *trans* isomers) leads to three NMR-distinguishable forms of **III**¶ (*cis*/*cis*, *trans*/*trans*, *cis*/*trans*) yielding in turn only two forms of **IV** (*cis* and *trans*). Pure *cis* or *trans* **II** gives the corresponding isomer of **III** which then yields exclusively *cis* or *trans* **IV** (and **II**); a lantern structure for **III** would invite scrambling reactions.

Ample evidence is presented above for the oxidative coupling of planar Pt(acac)$_2$ moieties which retain their identity in

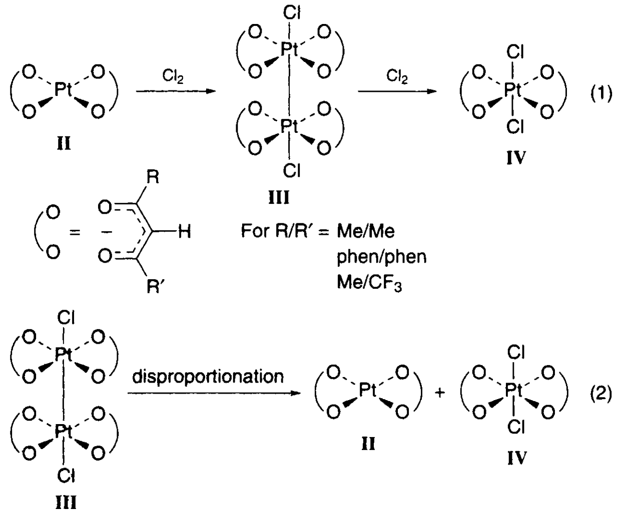

Table 1 Selected NMR data for platinum–diketonate and –dioximate complexes in oxidation state II–IV[a]

Diketonate (R, R′)	Σ Taft[b] 2 (R + R′)	PtL$_4$ (II)[c] δ_{Pt}	PtL$_4$ (II)[c] δ_{CH}	{PtClL$_4$}$_2$ (III)[d] δ_{Pt}	{PtClL$_4$}$_2$ (III)[d] δ_{CH}	PtCl$_2$L$_4$ (IV)[c] δ_{Pt}	PtCl$_2$L$_4$ (IV)[c] δ_{CH}	Δδ(II/III)	Δδ(II/IV)
Bu^t, Bu^t	−1.2	−471	5.75	undetected		1936	5.85	—	2407
Me, Me	0	−440	5.50	1296	5.50	1958	5.75	1736	2398
phen, phen	2.4	−329	6.86	1252	6.24	1940	6.93	1581	2269
Me, CF$_3$[e,f]	5.4	−216	6.00	1305[g]	5.98	1925[h]	6.19	1521	2141
CF$_3$, CF$_3$	10.8	23	6.48	undetected		1854	6.65	—	1831
Pt(C$_8$doH)$_2$	—	−3371	—	−1694[i]	—	−782	—	1677	2589
Pt(C$_{12}$doH)$_2$	—	−3401	—	−1746[i]	—	−829	—	1655	2572

[a] All ^{195}Pt chemical shifts referenced to PtCl$_4^{2-}$ (δ −1630). [b] Ref. 9. Spectra recorded at 298 K. [d] Spectra recorded at 243 K. [e] *Cis* and *trans*. [f] Isomers not resolved except as stated. [g] Four resonances observed at 298 K: δ 1360, 1352, 1349, 1342. [h] δ 1924 and 1926 for the two isomers. [i] 298 K.

binuclear **III** and throughout the transformations of eqn. (1) and (2). Single crystals of **III** (Me/Me) have been grown, but so far their instability has prevented X-ray structural determination of the precise molecular geometry.

The formation of **III** parallels the analogous restricted chlorination of [Pt(C_8doH)$_2$] to form red **I**,[2,4] with markedly similar Pt–Pt stretch (139 cm^{-1}) and ^{195}Pt resonance properties (see Table 1). Accordingly, the Pt–Pt single bond length is expected to be close to 2.7 Å in the new systems as well. Mutual rotation of the planar moieties is permitted, in accord with geometry-optimised MO calculations[6] where ω = 35°. This conforms with the isoelectronic {LRh^{II}(acac)$_2$}$_2$ system,[7] where an unsupported Rh–Rh bond is observed [with Rh–Rh 2.590(1) Å and torsion angle 42°] despite the prevalence of lantern-type Rh$^{II}_2$ carboxylates.

The formation of **III** is associated with the growth of a characteristic absorption band near 24 000 cm^{-1}, dwarfing the weaker [Pt(acac)$_2$] ^{3}MLCT feature (see Fig. 1). Upon further oxidation to **IV**, this near-UV band collapses again. The various indications of **III** [(*a*)–(*c*), above] disappear collectively as samples lose their red colour and the 24 000 cm^{-1} band.

These compounds and their [Pt_2Cl_2($C_n$doH)$_4$] analogues provide an instructive comparison with previous studies[1,8] restricted to strapped, structurally constrained Pt^{III} dimers, and a rare chance to survey ^{195}Pt NMR shifts in structurally related complexes spanning three oxidation states. A characteristic chemical shift difference of 1500–1700 ppm between Pt^{II} and Pt^{III} is observed, which is distinctly greater than that between Pt^{III} and Pt^{IV}.

Voltammetry in CH_2Cl_2 reveals the onset of irreversible oxidation of **II** near +1.2 V *vs.* Ag–AgCl, consistent with its capacity for reaction with Cl_2. Accordingly, **III** (R/R′ = Me/Me) can be generated (though accompanied by **IV**) by direct oxidation of **II** at a platinum electrode at +1.5 V in the presence of equimolar Cl^-. This is confirmed by detection of the 24 000 cm^{-1} band in an optically transparent thin-layer electrolysis cell at 233 K.[9] On electroreduction at −0.5 V, **III** rapidly gives way to **II**, and any **IV** present than follows suit (giving only **II**).

A faithful linear relationship is found between the ^{195}Pt chemical shift for **II**, which spans an exceptional 500 ppm, and the nett Taft[10] inductive parameter (see Table 1), mirroring the immense tunability of isostructural [Pt(SacSac)$_2$] systems[11] and of β-diketonates in general. Electron-deficient CF_3/CF_3 and bulky, electron-rich Bu^t/Bu^t forms of **II** both give **IV** as the only observed oxidation product, while the CF_3/Me and Ph/Ph forms of **III** are more persistent in solution than the Me/Me archetype. Alternative R/R′ substitution may yet lead to robust analogues. Kinetic factors are clearly crucial, given that the diketonate-based Pt^{III} dimers so far detected all eventually undergo spontaneous disproportionation.

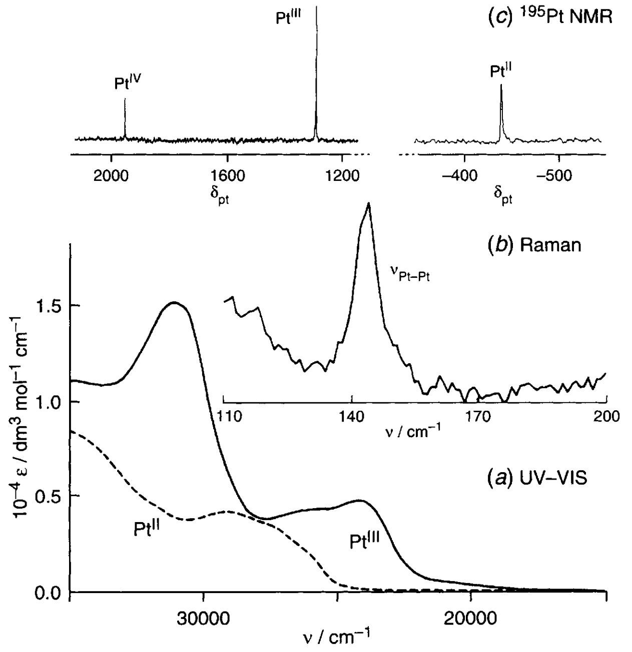

Fig. 1 (*a*) 243 K UV–VIS spectra of **II** and **III** in $CHCl_3$; (*b*) 77 K Raman spectrum of solid **III**; (*c*) 64.4 MHz ^{195}Pt NMR spectrum of **II**, **III** and **IV** in $CDCl_3$ (243 K)

The nett strength of the eight Pt–O bonds on either side of eqn. (2) should be roughly equal, and so the thermodynamic stability of the binuclear intermediate entails a trade-off between the formation of the Pt–Pt bond in **III** and the increased stability of two Pt^{IV}–Cl bonds over their Pt^{III}–Cl counterparts. This may explain the failure to observe bromo-capped dimers in this work and in the dioximato systems.[2] Equally, replacement of Cl^- by MeCN might stabilise **III** against disproportionation, echoing the ESMS observations. The present enquiry suggests that discrete Pt–Pt bonded intermediates might play an important role in other apparently simple Pt^{II}/Cl_2 oxidative-addition reactions, particularly where transient red colours are noted.[12]

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Footnotes

† Crystalline $ClC_6H_4I{\cdot}Cl_2$ is a convenient source of Cl_2. In a typical NMR experiment, 20 mg of **II** (R/R = Me/Me) in 0.5 ml $CDCl_3$ was cooled to 243 K in a capped 5 mm NMR tube, and $ClC_6H_4I{\cdot}Cl_2$ (8 mg) was added. The tube was promptly immersed in crushed solid CO_2 to freeze the solvent, then transferred to the pre-cooled (243 K) probe. The ^{1}H and ^{195}Pt NMR spectra were recorded once the solvent had thawed. The same transformations were observed with Cl_2 (g) as oxidant.

‡ Analysis (C, H, Cl) of the orange–red solids gave values consistent with **III** (except when contaminated with excess of relatively insoluble **IV**), but this is inconclusive, given the ease of disproportionation to equimolar **II** and **IV**.

§ Solutions of **III** (50 : 50 $CHCl_3$–MeCN; 1% HCO_2H) give peaks for these dinuclear species at 40% of the [Pt(acac)$_2$]·H$^+$ base peak (B1 = 35–75 V), while mixtures of **II** and **IV** show oligomer peaks at the 1% level only. We are exploring whether these represent weaker aggregates or true analogues of **III** formed under ESMS ionisation.

¶ At 298 K separate ^{195}Pt NMR signals were found for the *cis*/*cis**, *trans*/*trans**, *cis**/*trans* and *cis*/*trans** isotopomers (* = ^{195}Pt, 33% natural abundance). The statistically unfavoured *cis**/*trans** isotopomer [from which, in principle, *J*(Pt–Pt) could be measured directly] has not been detected so far.

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