

Synthesis, structure and reactivity of *N,O*-metallacyclic (dicarbonyldiazene) platinum complexes

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Reaction of *cis*-Pt(PR¹)₂Cl₂ (R¹ = Me, Ph) with diacyl hydrazine R²OCNHNHCOR² (R² = Me, Ph) in refluxing ethanol and NaHCO₃ afforded platinum diazene diacyl complexes Pt(PR¹)₂(R²OCNNCOR²) (**1**, R¹ = R² = Ph; **3**, R¹ = Me, R² = Ph; **4**, R¹ = R² = Me). Reaction of Pt(PPh₃)₂(C₂H₄) with diazene dicarboxylates R²OCNNCOR² (R² = OEt, OPrⁱ) resulted in the formation of Pt(PPh₃)₂(R²OCNNCOR²) (**2**, R² = OEt; **5**, R² = OPrⁱ). Multinuclear NMR spectroscopy on **1–5** revealed that the dicarbonyl-substituted diazene ligand is coordinated asymmetrically, consistent with a five membered Pt—N—N—C—O ring. Compound **5** crystallises from THF–benzene as the solvate Pt(PPh₃)₂(PrⁱO₂CNNCO₂Prⁱ)·(C₆H₆)₂; its X-ray crystal structure shows that the coordination sphere of platinum is essentially square planar and coplanar with the five membered Pt1—O1—C5—N2—N1 ring. The Pt1—O1 distance is 2.027(4) Å and the Pt1—N1 distance is 2.050(5) Å. The N1—N2 distance is 1.421(6) Å while the N2—C5 and C5—O1 distances are 1.273(7) and 1.314(7) Å, respectively. Complexes **1–5** show sensitivity towards chlorinated solvents (CH₂Cl₂, CHCl₃) under photolysis conditions, forming the corresponding *cis*-platinum bis(phosphine) dichloride complexes; the same products are formed in a slower thermal reaction with **2** and **5**. Complexes **2** and **5** react photochemically with ethylene in [H₈]THF yielding Pt(PPh₃)₂(C₂H₄) but **1**, **3** and **4** are inert. Addition of an excess of dppe ligand to **2** and **5** resulted in the displacement of PPh₃ and the formation of Pt(dppe)(EtO₂CNNCO₂Et) and Pt(dppe)(PrⁱO₂CNNCO₂Prⁱ) [dppe = 1,2-bis(diphenylphosphino)ethane].

There are, in general, two ways in which a diazene (or azo) ligand can coordinate to transition metals.¹ The usual mode requires the diazene group to utilise its lone pair(s) on the nitrogen atom(s) (often the HOMO) to form σ bond(s) with the metal. This method of coordination can generate both mononuclear and binuclear complexes.^{1,2} The second mode involves the symmetrical binding of the diazene moiety to the metal by the transfer of electron density from the N=N π-bonding molecular orbital to the metal and from the metal to the N=N π-anti-bonding molecular orbital.³

Introduction of substituents other than simple alkyl or aryl groups into the diazene compound can provide additional coordination sites for the metal. A carbonyl-substituted diazene compound, for instance, can bind through oxygen as well as a diazene nitrogen.^{4,5} Ittel and Ibers have shown by X-ray crystallography that the azo ligand in the complex Pt(PPh₃)₂(PhOCNNCOPh) **1** coordinates to the metal as a metallacycle, binding to the metal through one oxygen and one nitrogen atom to form a five-membered ring.⁶ Bond lengths from the crystal structure of **1** revealed that the N=N double bond had lengthened to that of a single bond and one of the C—N bonds had shortened to a C=N bond when compared to the free ligand. Thus, this form can be described as a Pt^{II} complex with a substituted hydrazido ligand. Stone and co-workers in the late 1960s postulated that Pt(PPh₃)₂(EtO₂CNNCO₂Et) **2** adopts a symmetrical structure, where the diazene dicarboxylate ligand is coordinated to the metal in a η² fashion.⁷ Cenini and co-workers later revealed that **2** contains two inequivalent phosphorus nuclei,⁸ indicating that the diazene dicarboxylate ligand in **2** coordinates to platinum in the same way as the diazene dibenzoyl ligand found in **1**.

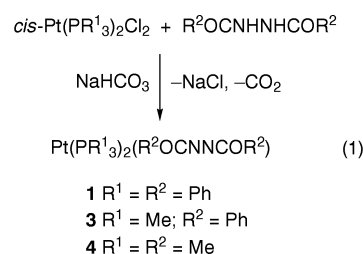
We report here the full characterisation of Pt(PMe₃)₂(PhOCNNCOPh) **3** and Pt(PMe₃)₂(MeOCNNCOME) **4**, the trimethylphosphine analogues of **1**. We have also developed a new route to the platinum diazene

dicarboxylate compounds Pt(PPh₃)₂(EtO₂CNNCO₂Et) **2** and Pt(PPh₃)₂(PrⁱO₂CNNCO₂Prⁱ) **5**. A crystal structure of **5** has been obtained, which provides unambiguous evidence on the binding mode of the diazene dicarboxylate ligand to the platinum centre. These compounds were synthesised in order to test their photochemical properties.

Results

Preparation of Pt(PR¹)₂(R²OCNNCOR²) complexes (**1**, R¹ = R² = Ph; **3**, R¹ = Me, R² = Ph; **4**, R¹ = R² = Me)

The procedure reported by Dilworth and Kasenally⁹ for the preparation of the complex Pt(PPh₃)₂(PhOCNNCOPh) **1** was used to synthesise two analogues: Pt(PMe₃)₂(PhOCNNCOPh) **3** and Pt(PMe₃)₂(MeOCNNCOME) **4**. Reaction of the *cis*-platinum bis(phosphine) dichloride complex with the appropriate diacyl hydrazine in refluxing ethanol, in the presence of NaHCO₃, yielded air-stable crystals of the platinum complex after work up (60–70% yield, eqn. 1).



We have also synthesised **1** by the same method in order to obtain comparative spectroscopic data. All the above complexes are highly soluble in benzene, THF and chlorinated solvents. Multinuclear NMR characterisation of complexes **1**, **3**

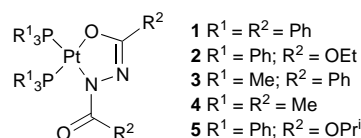
Table 1 ^1H and ^{31}P $\{^1\text{H}\}$ NMR (295 K) spectroscopic data of complexes 1–7

Compound	^1H , δ (J/Hz)	^{31}P , δ (J/Hz) ^a
1 ^b	7.00–8.00 (m, Ph)	3.1 [d, P ^O , $J(\text{PP}) = 22$, $J(\text{PtP}) = 3685$] 17.5 [d, P ^N , $J(\text{PP}) = 22$, $J(\text{PtP}) = 3261$] 6.2 [br d, P ^O , $J(\text{PtP}) \approx 3790$] 16.6 [d, P ^N , $J(\text{PP}) = 23$, $J(\text{PtP}) = 3166$]
2 ^c	1.14 (3H, br t, CH_2CH_3) 1.35 [3H, t, CH_2CH_3 , $J(\text{HH}) = 7.0$] 4.12 (2H, br, CH_2CH_3) 4.57 [2H, quart, CH_2CH_3 , $J(\text{HH}) = 7.0$] 7.00–8.00 (30H, m, Ph)	
3 ^b	1.80 [9H, d, PMe_3 , $J(\text{PH}) = 11.0$] ^d 1.90 [9H, d, PMe_3 , $J(\text{PH}) = 11.3$] ^d 7.00–8.00 (10H, m, Ph)	–20.1 [d, P ^O , $J(\text{PP}) = 26$, $J(\text{PtP}) = 3435$] –10.9 [d, P ^N , $J(\text{PP}) = 26$, $J(\text{PtP}) = 3028$]
4 ^b	1.70 [9H, d, $\text{P}^{\text{N}}\text{Me}_3$, $J(\text{PH}) = 10.7$] ^d 1.80 [9H, d, $\text{P}^{\text{O}}\text{Me}_3$, $J(\text{PH}) = 11.2$] ^d 2.01 [3H, d, COMe , $J(\text{PH}) = 0.9$] 2.23 (3H, s, COMe)	–38.0 [d, P ^O , $J(\text{PP}) = 27$, $J(\text{PtP}) = 3448$] –29.0 [d, P ^N , $J(\text{PP}) = 27$, $J(\text{PtP}) = 3010$]
5 ^e	0.75 [6H, d, $\text{CH}(\text{CH}_3)_2$, $J(\text{HH}) = 6.2$] 1.06 [6H, d, $\text{CH}(\text{CH}_3)_2$, $J(\text{HH}) = 6.2$] 4.08 [1H, sept, $\text{CH}(\text{CH}_3)_2$, $J(\text{HH}) = 6.2$] 4.12 [1H, sept, $\text{CH}(\text{CH}_3)_2$, $J(\text{HH}) = 6.2$] 7.00–8.00 (30H, m, Ph)	5.8 [d, P ^O , $J(\text{PP}) = 23$, $J(\text{PtP}) = 3859$] 16.5 [d, P ^N , $J(\text{PP}) = 23$, $J(\text{PtP}) = 3158$]
6 ^c	0.97 [3H, t, CH_2CH_3 , $J(\text{HH}) = 7.2$] 1.23 [3H, t, CH_2CH_3 , $J(\text{HH}) = 7.2$] 4.00 [2H, d, CH_2CH_3 , $J(\text{HH}) = 7.2$] 4.62 [2H, d, CH_2CH_3 , $J(\text{HH}) = 7.2$]	31.1 [d, P ^O , $J(\text{PP}) = 11$, $J(\text{PtP}) = 3839$] 38.1 [d, P ^N , $J(\text{PP}) = 11$, $J(\text{PtP}) = 3041$]
7 ^c	1.10 [6H, d, $\text{CH}(\text{CH}_3)_2$, $J(\text{HH}) = 6.2$] 1.36 [6H, d, $\text{CH}(\text{CH}_3)_2$, $J(\text{HH}) = 6.2$] 4.79 [1H, sept, $\text{CH}(\text{CH}_3)_2$, $J(\text{HH}) = 6.2$] 5.40 [1H, sept, $\text{CH}(\text{CH}_3)_2$, $J(\text{HH}) = 6.2$] 7.00–8.00 (30H, m, Ph)	31.0 [d, P ^O , $J(\text{PP}) = 12$, $J(\text{PtP}) = 3843$] 38.1 [d, P ^N , $J(\text{PP}) = 12$, $J(\text{PtP}) = 3023$]

^a Couplings to Pt refer to the satellites from ^{195}Pt ; P^O indicates phosphorus *trans* to oxygen and P^N indicates phosphorus *trans* to nitrogen. ^b In CDCl_3 . ^c In C_6D_6 . ^d Contain overlapping satellites from ^{195}Pt . ^e In $[\text{C}_2\text{H}_5]_2\text{THF}$.

and 4 (Tables 1 and 2) supports the coordination of the diazene ligand $\text{R}^2\text{OCNNCOR}^2$ ($\text{R}^2 = \text{Me}$, Ph) to the platinum centre *via* the oxygen and nitrogen atoms (Scheme 1) as in the crystal structure of 1.⁶

The ^{31}P $\{^1\text{H}\}$ NMR spectrum of 4 in CDCl_3 shows two inequivalent phosphorus nuclei that are mutually coupled and possess ^{195}Pt satellites (Fig. 1). The two $^1J(\text{PtP})$ coupling constants of 4 differ by about 400 Hz. Generally, a phosphorus nucleus *trans* to an oxygen donor has a larger $^1J(\text{PtP})$ value compared to a phosphorus nucleus *trans* to a nitrogen donor.¹⁰ Following this general trend we can assign the resonance at $\delta_{\text{P}} - 38.0$ [$^1J(\text{PtP}) = 3448$ Hz] to the phosphorus

**Scheme 1**

nucleus *trans* to the oxygen donor and the resonance at $\delta_{\text{P}} - 29.0$ [$^1J(\text{PtP}) = 3010$ Hz] to the phosphorus nucleus *trans* to the nitrogen donor. The ^1H NMR spectrum of 4 in CDCl_3 shows the two methyl resonances on the diazene diacyl ligand as a singlet at δ_{H} 2.23 and a doublet at δ_{H} 2.01 [$^5J(\text{PH}) = 0.9$ Hz]. The two PMe_3 groups appear as separate doublets at δ_{H} 1.70 and δ_{H} 1.80, each possessing overlapping ^{195}Pt satellites. On selective phosphorus decoupling at $\delta_{\text{P}} - 38$ (phosphorus *trans* to oxygen) the doublet resonances at δ_{H} 2.01 (COMe) and δ_{H} 1.80 (PMe_3) in the ^1H NMR spectrum collapse into singlets. On selective phosphorus decoupling at $\delta_{\text{P}} - 29$ (phosphorus *trans* to nitrogen), only the doublet resonance at δ_{H} 1.70 (PMe_3) in the ^1H NMR spectrum collapses into a singlet. Hence the resonance at δ_{H} 1.70 is due to the PMe_3 *trans* to nitrogen and the resonance at δ_{H} 1.80 is due to the PMe_3 *trans* to oxygen. On changing the solvent to C_6D_6 we observe a substantial downfield shift of the diazene diacyl methyl resonances and an upfield shift of the PMe_3 doublets, with increased separation between them.

The ^{13}C $\{^1\text{H}\}$ NMR spectrum of 4 shows two CO resonances at δ_{C} 175.4 and δ_{C} 165.4, the former resonance being a doublet [$J(\text{PC}) = 3$ Hz] with ^{195}Pt satellites [$J(\text{PtC}) = 67$ Hz] and the latter a doublet of doublets [$J(\text{PC}) = 9$ Hz, 4 Hz] without detectable ^{195}Pt satellites. The diazene diacyl methyl carbon atoms can be detected as two doublet resonances at δ_{C} 22.1 [$J(\text{PC}) = 4$ Hz] and δ_{C} 16.5 [$J(\text{PC}) = 5$ Hz].

The UV/VIS spectra of complexes 1, 3 and 4 show a prominent low-energy band at around 300 nm (Table 3). Both complexes 1 and 3 show a band maximum at *ca.* 319 nm, whereas the band for 4 is shifted 15 nm to higher energy. This effect is observed on changing the diazene from the aryl PhOCNN-

Table 2 ^{13}C $\{^1\text{H}\}$ NMR (295 K) spectroscopic data of complexes 1 and 3–5

Compound	δ (J/Hz) ^a
1 ^b	127.1–135.2 (Ph) 163.2 [dd, CO, $J(\text{PC}) = 10$, 3] 171.7 [d, CO, $J(\text{PC}) = 4$]
3 ^b	16.6 [d, PCH_3 , $J(\text{PC}) = 38$, $J(\text{PtC}) = 33$] 19.7 [dd, PCH_3 , $J(\text{PC}) = 44$, 2; $J(\text{PtC}) = 43$] 124.2–131.8 (Ph) 163.4 [dd, CO, $J(\text{PC}) = 9$, 3] 174.6 [d, CO, $J(\text{PC}) = 4$]
4 ^b	16.3 [d, PCH_3 , $J(\text{PC}) = 38$, $J(\text{PtC}) = 33$] 16.5 [d, CH_3 , $J(\text{PC}) = 5$] 19.6 [dd, PCH_3 , $J(\text{PC}) = 45$, 2; $J(\text{PtC}) = 45$] 22.1 [d, CH_3 , $J(\text{PC}) = 4$] 165.4 [dd, CO, $J(\text{PC}) = 9$, 4] 175.4 [d, CO, $J(\text{PC}) = 3$, $J(\text{PtC}) = 67$]
5 ^c	23.8 (s, CH_3) 24.1 (s, CH_3) 67.6 (s, CH) 71.2 (s, CH) 128.8–136.6 (Ph)

^a Couplings to Pt refer to the satellites from ^{195}Pt . ^b In CDCl_3 . ^c In $[\text{C}_2\text{H}_5]_2\text{THF}$, no CO resonance was detected.

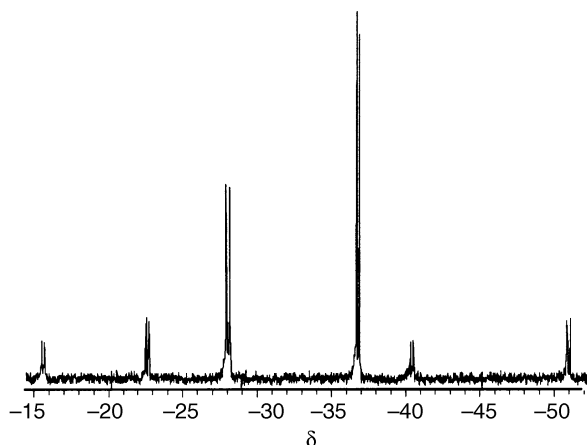
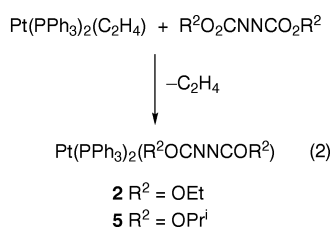


Fig. 1 ^{31}P $\{^1\text{H}\}$ NMR spectrum of $\text{Pt}(\text{PMe}_3)_2(\text{MeOCNNCOMe})$ (**4**) in CDCl_3 (295 K) consisting of two doublets, each with ^{195}Pt satellites

COPh ligand to the alkyl MeOCNNCOMe ligand. No such effects are observed on changing the phosphine ligand from PPh_3 to PMe_3 . Since the crystal structure of **1** shows a conjugated metallacycle,⁶ we assign this band to a transition of the metallacycle, rather than attempting to distinguish intra-ligand transitions from charge-transfer transitions.

Preparation of $\text{Pt}(\text{PPh}_3)_2(\text{R}^2\text{OCNNCOR}^2)$ complexes (**2**, $\text{R}^2 = \text{OEt}$; **5**, $\text{R}^2 = \text{OPr}^i$)

Reaction of $\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)$ with an equivalent amount or excess (up to threefold) of $\text{R}^2\text{OCNNCOR}^2$ ($\text{R}^2 = \text{OEt}$, OPr^i) in benzene at room temperature in the absence of light yields $\text{Pt}(\text{PPh}_3)_2(\text{R}^2\text{OCNNCOR}^2)$ ($\text{R}^2 = \text{OEt}$ **2**, OPr^i **5**) and ethylene gas (eqn. 2).



These compounds are yellow/orange in colour and relatively air stable as solids. They are slightly soluble in benzene and **5** is soluble in THF. Based on the evidence of Cenini *et al.*⁸ and our own, the binding mode of the diazene ligand in **2** corre-

sponds to that found in complexes **1**, **3** and **4**, co-ordinating via the nitrogen and oxygen atoms to form a metallacycle.

Multinuclear NMR spectra of $\text{Pt}(\text{PPh}_3)_2(\text{EtO}_2\text{CNCNCO}_2\text{Et})$ **2** and $\text{Pt}(\text{PPh}_3)_2(\text{Pr}^i\text{O}_2\text{CNCNCO}_2\text{Pr}^i)$ **5** confirm that both complexes have inequivalent phosphorus atoms as well as inequivalent alkyl groups on the diazene ligand (Tables 1 and 2). The ^{31}P $\{^1\text{H}\}$ NMR spectra of **2** and **5** again show two mutually coupled doublet resonances, both with ^{195}Pt satellites.

The IR spectra of **2** and **5** show CO/CN stretching bands in the 1610–1670 cm^{-1} region (Table 3); the bands were more intense than the corresponding bands of **1**, **3** and **4**. In the IR spectrum of **2** two broad peaks are observed at around 1600 cm^{-1} in dichloromethane, but in nujol we can observe up to five peaks in the same region. The UV/VIS spectra of **2** and **5** contain low-energy shoulders at *ca.* 330 and 460 nm (Table 3).

Crystal Structure of $\text{Pt}(\text{PPh}_3)_2(\text{Pr}^i\text{O}_2\text{CNCNCO}_2\text{Pr}^i) \cdot (\text{C}_6\text{H}_6)_2$ **5**

Crystals of **5** suitable for X-ray data collection were grown by slow evaporation of a 2:1 THF–benzene solution of **5** at room temperature. The structure of **5** consists of monomolecular units of the complex with two molecules of benzene per unit cell. The structure of **5** (Fig. 2) clearly shows that the diazene ligand coordinates to the platinum centre through the oxygen atom of one carbonyl group and the nitrogen atom of the diazene function remote from the coordinated carbonyl. The principal bond lengths and angles (Fig. 3) follow a very similar pattern to that reported for **1** and related diacyl diazene metal complexes.^{4,5,6} The platinacycle contains O–C and N–N bonds which are extended relative to those of the free ligand, while the C–N bond is shortened. The platinacycle containing Pt, O1, C5, N2 and N1 is planar within 0.012 Å and essentially coplanar with the coordinated atoms P1, P2, O1 and N1 which are planar within 0.037 Å. The exocyclic carbon atom C4 is coplanar with the metallacycle. The phosphorus–metal bond lengths differ only slightly [$\delta(\text{Pt}–\text{P}) = 0.012$ Å], but there is a substantial difference in the angles to adjacent ligands: $\text{P1}–\text{Pt}–\text{N1} = 97.5(1)^\circ$, $\text{P2}–\text{Pt}–\text{O1} = 87.1(1)^\circ$.

Reactions of $\text{Pt}(\text{PR}^1)_2(\text{R}^2\text{OCNNCOR}^2)$ complexes ($\text{R}^1 = \text{Me}$, Ph ; $\text{R}^2 = \text{Me}$, Ph , OEt , OPr^i)

Complexes **1**, **3** and **4** show no reactivity towards ethylene or diphenylacetylene when photolysed in $[\text{D}_8]\text{THF}$. Photolysis of complexes **1**, **3** and **4** in CDCl_3 resulted in the formation of the corresponding *cis*-platinum bis(phosphine) dichloride $\text{Pt}(\text{PR}^1)_2\text{Cl}_2$ complexes ($\text{R}^1 = \text{Ph}$, Me).

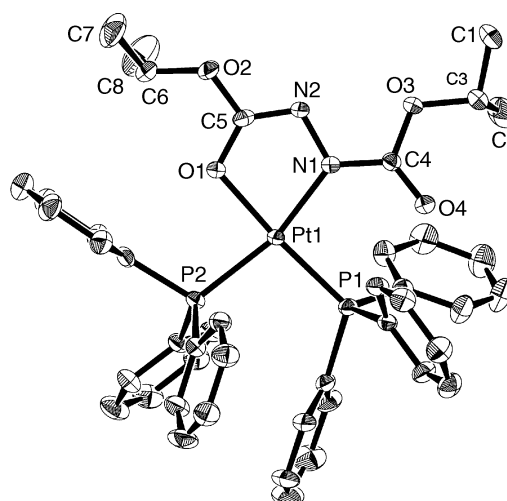


Fig. 2 ORTEP drawing¹⁹ of **5** showing non-hydrogen atoms with thermal ellipsoids at the 30% probability level. The two molecules of benzene of crystallisation are not shown

Table 3 UV/VIS and IR data for complexes **1**–**5**

Compound	UV/VIS in THF λ/nm ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)	IR, $\nu(\text{CO})$, $\nu(\text{CN})$ v/cm^{-1}
1	318 (12000)	1565 ^a 1595 ^a
2	333 (3100) 463 (400)	1618 ^b 1642 ^b 1610 ^c 1621 ^c 1629 ^c 1648 ^c 1668 ^c
3	319 (8700)	1561 ^a 1586 ^a
4	303 (4500)	1576 ^a 1612 ^a
5	337 (3100) 465 (400)	1613 ^c 1635 ^c

^a In KBr pellet. ^b In CH_2Cl_2 . ^c In nujol.

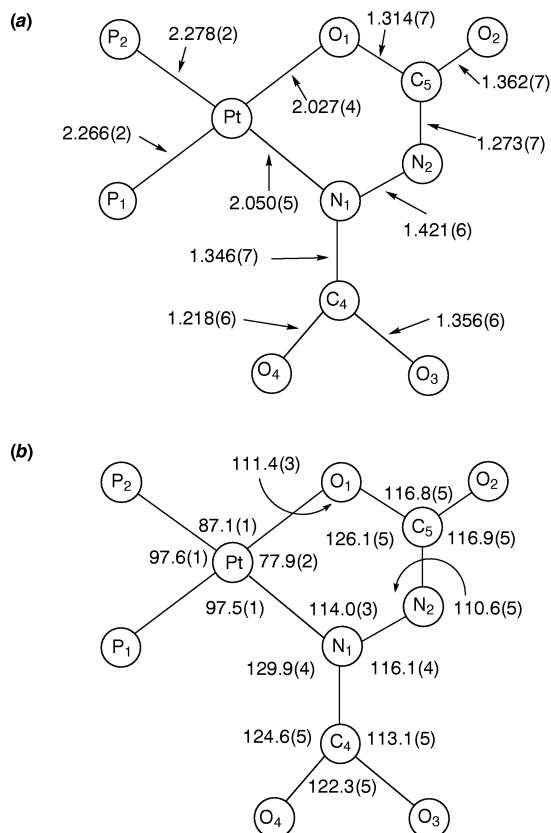


Fig. 3 Inner coordination sphere of **5**, showing (a) bond distances (Å) and (b) bond angles (degrees)

Both **2** and **5** react thermally with chlorinated solvents at room temperature to give *cis*-Pt(PPh₃)₂Cl₂ as the major product, with **5** being more readily converted. UV irradiation in CHCl₃ generated the same products more rapidly. Irradiation of **5** with ethylene or diphenylacetylene in [2H₈]THF resulted in the formation of Pt(PPh₃)₂(C₂H₄) [δ_{H} 2.2, $J(\text{PtH}) = 62$ Hz] or Pt(PPh₃)₂(PhC≡CPh) [δ_{P} 35, $J(\text{PtP}) = 3000$ Hz].¹¹ However, the same outcome can be achieved if the mixture is heated at 70 °C in the absence of light.

In addition to the organometallic species, some organic photoproducts are observed on irradiation of **5** in [2H₈]THF. Their ¹H NMR spectra exhibit similar features to the ¹H NMR data of the photoproducts from the free diazene ligand PrⁱO₂CNNCO₂Prⁱ. Further research to establish their identities is in progress. In general, diazene compounds initially undergo photochemically induced *trans*–*cis* isomerisation prior to degradation, involving the liberation of molecular N₂ and formation of a radical pair.¹² Diacyl diazene compounds are reported to form the corresponding diketone upon extrusion of N₂ on photolysis.¹³

On addition of an excess of 1,2-bis(diphenylphosphino)ethane (dppe) to complex **2** or **4**, a new singlet resonance was observed in the ³¹P {¹H} NMR spectrum at δ –4.7 (free PPh₃) and two new doublet resonances at *ca.* δ 38.1 and δ 31.1, both with ¹⁹⁵Pt satellites, which (Table 1) have been assigned as Pt(dppe)(EtO₂CNNCO₂Et) **6**. The complex Pt(dppe)(PrⁱO₂CNNCO₂Prⁱ) **7** is formed similarly. The displacement of triphenylphosphine with dppe is not uncommon in platinum complexes; for example, addition of dppe to *cis*-Pt(PPh₃)₂Cl₂ in chloroform produces Pt(dppe)Cl₂ in quantitative yield.¹⁴

Conclusion

This paper reports simple synthetic routes to complexes Pt(PR¹)₃(R²OCNNCOR²), containing the Pt–N–N–

C–O metallacyclic unit. The structural evidence indicates that the metallacycle is a fully conjugated planar system. The diazene ligand is readily displaced photochemically in chlorinated solvents. The diazene dicarboxylate ligand of Pt(PPh₃)₂(PrⁱO₂CNNCO₂Prⁱ) has also been replaced photochemically in THF and benzene, but the diazene diacyl complexes proved photostable in these solvents.

Experimental

General

All syntheses and manipulations were carried out under argon using standard Schlenk and high vacuum techniques. All preparative solvents (Fison AR grade) were dried over sodium–benzophenone and distilled under argon (chlorinated solvents were dried over P₂O₅, ethanol was dried over magnesium metal turnings and iodine). NMR solvents were obtained from Goss Scientific or Aldrich, and were dried over potassium metal under argon and distilled on a high vacuum line prior to use (chlorinated solvents were dried over molecular sieves or P₂O₅). Chemicals were obtained from the following sources and used without further purification: K₂PtCl₄, PPh₃, MeOCNNHNCOME, PhOCNNHNCOPh, EtO₂CNNCO₂Et and PrⁱO₂CNNCO₂Prⁱ were supplied by Aldrich; PMe₃ was supplied by Strem.

UV/VIS spectra were recorded on a Perkin-Elmer Lambda 7 spectrophotometer. Infrared spectra were recorded on a Mattson RS FTIR instrument. Mass spectra were recorded on a VG Auto-Spec mass spectrometer. NMR spectra were recorded on a Bruker MSL 300 MHz spectrometer. ¹H NMR spectra (300.13 MHz) were referenced relative to the peaks of the residual protio solvents: benzene (δ 7.15), chloroform (δ 7.30), dichloromethane (δ 5.30), tetrahydrofuran (δ 1.73, δ 3.85). ³¹P {¹H} NMR spectra (121.94 MHz) were referenced to external H₃PO₄ (85%). ¹³C {¹H} NMR spectra (75.47 MHz) were referenced to the solvent peak: benzene (δ 128.0), dichloromethane (δ 54.5), chloroform (δ 77.7) and tetrahydrofuran (δ 25.2, δ 67.4). Elemental analyses were performed by Elemental Microanalysis Ltd, Devon, UK.

Photolysis of samples was carried out in sealed Pyrex NMR tubes ($\lambda > 290$ nm) using a Philips HPK 125 W medium pressure mercury lamp at room temperature. Typically, both a cut-off filter (295–410 nm) and a water filter were placed in front of the lamp output. Prior to photolysis, samples were kept for 24 h at room temperature shielded from ambient light. Their NMR spectra were then recorded in order to ensure that there was no competing thermal reaction at room temperature.

Syntheses

The complexes *cis*-Pt(PPh₃)₂Cl₂,¹⁵ *cis*-Pt(PMe₃)₂Cl₂¹⁶ and Pt(PPh₃)₂(C₂H₄)¹⁷ were synthesised according to literature procedures. Mass spectral peaks are quoted only when they have a major contribution from ¹⁹⁴Pt.

Preparation of Pt(PPh₃)₂(PhOCNNCOPh) 1. This synthesis follows the procedure of Dilworth and Kasenally.⁹ Pt(PPh₃)₂Cl₂ (0.20 g, 0.2 mmol) and PhOCNNHNCOPh (0.06 g, 0.2 mol) were suspended in ethanol (20 mL) with sodium hydrogen carbonate (0.06 g). The mixture was refluxed under argon for 4 h. During this time the white suspension gradually dissolved, yielding a yellow solution. The solvent was removed under vacuum. The crude product was dissolved in benzene, and hexane was added until precipitation began. Yellow crystals formed overnight (0.13 g, 70% yield). Mass spectrum (FAB): m/z 956 (M^+ , ¹⁹⁴Pt, 63%); 957 (M^+ , ¹⁹⁵Pt and $[M + H]^+$, ¹⁹⁴Pt, 100%).

Table 4 Crystallographic data for complex **5**

<i>Crystal Data</i>	
Empirical formula	C ₅₆ H ₅₆ N ₂ O ₄ P ₂ Pt
<i>M</i>	1078.06
Temperature/K	293(2)
Crystal dimensions/mm	0.4 × 0.4 × 0.4
Crystal description	Brown block
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$ (No. 2)
Unit cell dimensions ^a	<i>a</i> = 15.395(10) Å α = 104.86(3)° <i>b</i> = 15.885(7) Å β = 95.38(3)° <i>c</i> = 11.481(2) Å γ = 66.95(3)°
Volume/Å ³	2497(2)
<i>Z</i>	2
<i>F</i> (000)	1092
Density (calcd)/g cm ⁻³	1.434
μ /cm ⁻¹	29.21
<i>Data Collection</i>	
Diffractometer	Rigaku AFC6S
Radiation	MoK α , graphite monochromated
Wavelength/Å	0.7107
Scan type	ω –2 θ
Scan rate/min ⁻¹	16.0°
Scan width/°	(1.21 + 0.30 tan θ)
2 θ range for data collection/°	5.18–50.02
Reflections collected	9336 (including 195 standard reflections)
Independent reflections ^b	8783 [<i>R</i> ² (int) = 3.12]
Transmission coefficients	0.90 (min), 1.00 (max), 0.96 (average)
Data corrections	Lorentz-polarisation
Average intensity change of standard reflx:	–0.9% (3 reflections checked every 150 data)
Index ranges	0 ≤ <i>h</i> ≤ 18, –16 ≤ <i>k</i> ≤ 18, –13 ≤ <i>l</i> ≤ 13
<i>Structure solution</i>	Patterson methods with SAPI91 ^c expanded with DIRDIF ^d
<i>Refinement method</i>	Full-matrix least-squares on <i>F</i> ² with SHELXL93 ^e
Non-hydrogen atoms	Anisotropic
Hydrogen atoms	Riding model, isotropic
Weighting scheme	$w = [\sigma^2(F_o^2) + (0.0457P)^2]^{-1}$ $P = [\max(I_{obs}, 0) + 2F_c^2]/3$
Data ^f /restraints/parameters	8783/0/586
Data-to-parameter ratio	14.98
Goodness-of-fit ^g on <i>F</i> ²	1.00
<i>R</i> (%) ^h indices	
[<i>I</i> _o > 2 σ (<i>I</i> _o)]	<i>R</i> 1 = 0.0391, <i>wR</i> 2 = 0.0854
All data	<i>R</i> 1 = 0.0650, <i>wR</i> 2 = 0.0932
Final difference map	
Largest diff. peak ⁱ and hole/e Å ⁻³	0.77 and –0.64
Largest shift/esd in final cycle	0.00

^a Unit cell parameters and their esds were determined from a least-squares fitting of the setting angles of 20 reflections in the range 13.96° ≤ 2 θ ≤ 15.82°. ^b *R*(int) = $\Sigma |F_o^2 - F_c^2(\text{mean})| / \Sigma [F_o^2]$; 358 reflections measured twice. ^c Ref. 18(a). ^d Ref. 18(b). ^e Ref. 18(c). ^f Zero reflections suppressed in the refinement. ^g GOF = $\{\Sigma [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$ where *p* = number of parameters, *n* = number of data. ^h *R*1 = $\Sigma |F_o| / \Sigma |F_c|$, *wR*2 = $\{\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [w(F_o^2)^2]\}^{1/2}$. ⁱ Located 1.10 Å away from Pt(1).

Preparation of Pt(PPh₃)₂(EtO₂CNNCO₂Et) 2. Pt(PPh₃)₂(C₂H₄) (0.64 g, 0.9 mmol) and EtO₂CNNCO₂Et (0.60 g, 3.4 mmol) were dissolved in benzene (20 mL) under an atmosphere of argon at room temperature. On mixing the two compounds together, gas evolved and the solution changed from yellow to red. Within 1 h of addition, a yellow precipitate began to form. The mixture was shielded from ambient light and left stirring for 12 h. The product was collected and recrystallised from ethanol to form yellow crystals (0.53 g, 69% yield) (Found: C, 56.1; H, 4.6; N, 3.1. Calcd for C₄₂H₄₀N₂O₄P₂Pt: C, 56.4; H, 4.5; N, 3.1%). Mass spectrum (FAB): *m/z* 892 (*M*⁺, ¹⁹⁴Pt, 18%); 893 (*M*⁺, ¹⁹⁵Pt and [*M* + *H*]⁺, ¹⁹⁴Pt, 79%).

Preparation of Pt(PMe₃)₂(PhOCNNCOPh) 3. This complex was prepared by the same procedure as **1**. The product was recrystallised by addition of hexane to a benzene solution of **3** until precipitation began. The benzene–hexane mixture gave light yellow crystals (68% yield) (Found: C, 40.3;

H, 4.5; N 4.5. Calcd for C₂₀H₂₈N₂O₂P₂Pt: C, 41.0; H, 4.8; N, 4.9%). Mass spectrum (FAB): *m/z* 584 (*M*⁺, ¹⁹⁴Pt, 55%); 585 (*M*⁺, ¹⁹⁵Pt and [*M* + *H*]⁺, ¹⁹⁴Pt, 100%).

Preparation of Pt(PMe₃)₂(MeOCNNCOMe) 4. This complex was prepared by a procedure similar to that of **1**. The product was recrystallised by addition of hexane to a benzene solution of **4** until precipitation began. The benzene–hexane mixture yielded light brown crystals (65% yield) (Found: C, 26.3; H, 5.4; N, 6.1. Calcd for C₁₀H₂₄N₂O₂P₂Pt: C, 26.0; H, 5.2; N, 6.1%). Mass spectrum (FAB): *m/z* 460 (*M*⁺, ¹⁹⁴Pt, 53%); 461 (*M*⁺, ¹⁹⁵Pt and [*M* + *H*]⁺, ¹⁹⁴Pt, 100%).

Preparation of Pt(PPh₃)₂(PrⁱO₂CNNCO₂Prⁱ) 5. This complex was prepared as for **2**. The product was recrystallised from THF giving orange crystals (70% yield) (Found: C, 57.3; H, 4.8; N, 3.0. Calcd for C₄₄H₄₄N₂O₄P₂Pt: C, 57.3; H, 4.8; N, 3.0%). Mass spectrum (FAB): *m/z* 920 (*M*⁺, ¹⁹⁴Pt, 12%);

921 (M^+ , ^{195}Pt and $[M + H]^+$, ^{194}Pt , 73%).

X-Ray crystallographic study of 5

Crystals of compound **5** were grown at ambient temperature by the slow evaporation of a 2 : 1 THF–benzene solution. The resulting crystal was cut to size and mounted on a glass fibre using epoxy cement. X-ray data were collected on a Rigaku AFC6S diffractometer. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement of the positions of 20 automatically centred reflections. Equivalent reflections were merged, and data were corrected for Lorentz and polarisation factors.

The structure of compound **5** was solved using Patterson methods with SAPI91 and expanded using Fourier techniques with DIRDIF. Full-matrix least-squares refinement on F^2 was carried out with SHELXL 93. Programs used are given in ref. 18 and 19. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were refined on all structures using a riding model with isotropic temperature factors 1.2 times that of their carrier atoms (1.5 times for methyl groups). Crystallographic details are summarised in Table 4.

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