

Monodentate-N Coordination of 1-aza-4-oxo-1,3-butadienes $[R^1N=C(R^2)C(R^3)=O]$ to Platinum(II). X-ray Structure of *trans*- $[PtCl_2(PEt_3)\{\sigma\text{-N}-(t\text{-BuN=CHC(Me)=O)}\}]$

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Abstract

Reaction of dimeric *trans*- $[PtCl_2(PR_3)]_2$ with 1-aza-4-oxo-1,3-butadienes $[R^1N=C(R^2)C(R^3)=O]$, $R^3 = \text{Me, Ph, OMe, NEt}_2$ in a 1:2 molar ratio results in almost quantitative formation of mononuclear complexes *trans*- $[PtCl_2(PR_3)\{\sigma\text{-N}-(R^1N=C(R^2)C(R^3)=O)\}]$. The ligands are bonded in the monodentate $\sigma\text{-N}$ bonding mode to the platinum(II) centre. This has been established by an X-ray structure determination of *trans*- $[PtCl_2(PEt_3)\{\sigma\text{-N}-(t\text{-BuN=CHC(Me)=O)}\}]$. Crystals of the latter compound are orthorhombic with space group $Pc2_1n$; cell constants are $a = 14.712(3)$, $b = 15.053(2)$, $c = 9.025(5)$ Å, $Z = 4$ and $R_w = 0.056$ for 3281 reflections. The 1-aza-4-oxo-1,3-butadiene (α -iminoketone for R^3 is alkyl or aryl) has the E-configuration about the imine bond (C=N 1.34(4) Å), with a C(5)–C(6) distance of 1.44(5) Å and a N=C(5)/C(6)=O torsion angle of $89(4)^\circ$. As a result of this ligand conformation, the acetyl hydrogen atoms are positioned (on average) into the neighbourhood of the Pt-atom above the Pt-coordination plane. Infrared and NMR (^1H , ^{13}C , ^{31}P) data show that these structural features are also predominant in solution.

Introduction

In recent years much attention has been paid to the study of the coordination properties of isoelectronic hetero-1,3-butadiene systems, e.g. tetraaza- and 1,4-diaza-1,3-butadienes [1]. Recently we found that the α -iminoketones, $R^1N=C(R^2)C(R^3)=O$, which also are members of this class of hetero-1,3-butadiene systems, have a versatile metal-mediated organic chemistry [2, 3]. Depending on the substitution pattern of the α -iminoketone and the

organometallic reagent used, *i.e.* organo-zinc or -aluminum, a variety of products could be made in a chemoselective way. Examples of selective transfer of alkyl groups from alkyl-aluminum or -zinc reagents to each of the four atoms of the 1,3-butadiene system have now been established [3, 4]. In order to understand the mechanistic details of these transfer reactions, more information on the coordination properties of the α -iminoketones is required than is available in the literature.

In principle, $R^1N=C(R^2)C(R^3)=O$ compounds may coordinate to a metal centre as a monodentate ligand that is bonded via the lone pairs of either the imino-N or the ketone-O donor atom. Prerequisite for this coordination mode, however, is that the N=C and C=O entities, through rotation around the central C–C bond, can be positioned in a transoid conformation. Alternatively the O and N donor atoms can be placed in a cisoid conformation, which is the ideal arrangement for the chelate bonding. In view of the observed chemoselectivity of the organo-zinc and -aluminum reactions with α -iminoketones, our primary interest concerned the monodentate bonding mode. For this reason we studied the coordination of α -iminoketones with d^8 metal centres with a square planar coordination geometry. The selection of this particular metal centre is based on the results of our previous studies of the factors that favour monodentate coordination of the isoelectronic α -diimine ligands $RN=C(R^1)C(R^1)=NR$ [19].

In this paper we report the molecular structure of *trans*- $[PtCl_2(PEt_3)\{\sigma\text{-N}-(t\text{-BuN=CHC(Me)=O)}\}]$ in the solid containing the α -iminoketone in the non-planar gauche conformation. It is demonstrated that for the α -iminoketones studied the monodentate N-coordination with platinum(II) is the preferred bonding mode, not only in the solid, but also in solution.

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Experimental

All reactions were carried out under dry, oxygen-free nitrogen. Solvents were carefully dried and distilled before use. The starting platinum dimers $trans\text{-}[\text{PtCl}_2(\text{PR}_3)]_2$ [5] and the α -iminoketones $[\text{R}^1\text{N}=\text{C}(\text{R}^2)\text{C}(\text{R}^3)=\text{O}]$ with $\text{R}^1 = t\text{-Bu}$, $\text{R}^2 = \text{H}$, $\text{R}^3 = \text{Me}$ (L1) [6] and with $\text{R}^1 = \text{Me}$, $i\text{-Prop}$, Ph , $\text{R}^2 = \text{R}^3 = \text{Ph}$ (L5, L6, L2, respectively) [7, 8] were prepared by published methods. A new α -iminoketone, having $\text{R}^1 = 2,4\text{-dimethyl-3-pentyl}$, $\text{R}^2 = \text{H}$ and $\text{R}^3 = \text{Ph}$ (L7), was synthesized starting from phenylglyoxal monohydrate and the corresponding amine, following the described procedure for L1. Yield 55%; b.p. 130°C (0.01 mm Hg); IR (Nujol, NaCl, cm^{-1}) $\nu(\text{C}=\text{O})$ 1706(vs), $\nu(\text{C}=\text{N})$ 1654(m); ^1H NMR (in CDCl_3 , RT, TMS internal, δ ppm) 0.86 (d, 12H, CH_3), 2.00 (sept, 2H, CH), 2.43 (m, 1H, NCH), 7.84 (s, 1H, $\text{N}=\text{CH}$), 7.80 (m, 5H, C_6H_5); ^{13}C NMR (in CDCl_3 , RT, TMS internal, δ ppm) 17.6/19.6 (q, CH_3), 28.8 (d, CH), 82.8 (d, NCH), 127.9 130.2 133.2 and 134.4 (C_6H_5), 158.6 (d, $\text{N}=\text{CH}$), 191.4 (s, $\text{C}=\text{O}$). The α -iminoester ($t\text{-BuN}=\text{CHCOOMe}$)(L3) was obtained starting from methylglyoxylate which could be prepared easily by the method described by Kelly *et al.* [9]. Yield 70%; b.p. 123°C (0.01 mm Hg); IR (Nujol, NaCl, cm^{-1}) $\nu(\text{COOMe})$ 1755(vs), $\nu(\text{C}=\text{N})$ 1648(s); ^1H NMR (in CDCl_3 , RT, TMS internal, δ ppm) 1.39 (s, 9H, $(\text{CH}_3)_3$), 3.88 (s, 3H, OCH_3), 7.68 (s, 1H, $\text{N}=\text{CH}$); ^{13}C NMR (in CDCl_3 , RT, TMS internal, δ ppm) 28.5 (q, $(\text{CH}_3)_3$), 58.7 (s, $\text{C}(\text{CH}_3)_3$), 52.0 (q, OCH_3), 147.9 (d, $\text{N}=\text{CH}$), 163.8 (s, $\text{C}=\text{O}$). The novel α -iminoimide ligand ($t\text{-BuN}=\text{CHCONEt}_2$)(L4) was prepared from the corresponding α -iminoester by applying a general procedure for the conversion of esters to imides using '*in situ*' prepared ($\text{Me}_2\text{AlN}(\text{Et})_2$) [10]. Yield 60%; b.p. 120°C (0.01 mm Hg); IR (Nujol, NaCl, cm^{-1}) $\nu(\text{CONEt}_2)$ 1630 (s), $\nu(\text{C}=\text{N})$ 1660 (m, sh); ^1H NMR (in CDCl_3 , RT, TMS internal, δ ppm) 1.20 (s, 9H, $(\text{CH}_3)_3$), 1.14 (t, 3H, CH_2CH_3 , $J = 7.05$ Hz), 1.15 (t, 3H, CH_2CH_3 , $J = 7.15$ Hz), 3.39 (q, 2H, CH_2CH_3 , $J = 7.15$ Hz), 3.50 (q, 2H, CH_2CH_3 , $J = 7.05$ Hz), 7.72 (s, 1H, $\text{N}=\text{CH}$); ^{13}C NMR (in CDCl_3 , RT, TMS internal, δ ppm) 12.2/14.2 (q, CH_2CH_3), 28.7 (q, $(\text{CH}_3)_3$), 40.3/42.1 (t, CH_2CH_3), 58.0 (s, $\text{C}(\text{CH}_3)_3$), 150.6 (d, $\text{N}=\text{CH}$), 165.9 (s, $\text{C}=\text{O}$).

Synthesis of $trans\text{-}[\text{PtCl}_2(\text{PR}_3)]\{\sigma\text{-N}-(\text{R}^1\text{N}=\text{C}(\text{R}^2)\text{C}(\text{R}^3)=\text{O})\}$

The synthesis of $trans\text{-}[\text{PtCl}_2(\text{PEt}_3)]\{\sigma\text{-N}-(t\text{-BuN}=\text{CHC}(\text{Me})=\text{O})\}$, **I**, is described as a typical example. A solution of 1-(tert-butylimino)propanone (0.7 mmol) in dichloromethane (10 ml) was slowly added to a stirred suspension of $trans\text{-}[\text{PtCl}_2(\text{PEt}_3)]_2$ (0.3 mmol) in dichloromethane (15 ml) at room temperature. After 5 min the colour of the reaction mixture

changed from orange to yellow. After additional stirring for 30 min the clear solution was concentrated to 5 ml. Hexane was added (20 ml) whereupon the new complex crystallized at -20°C as small, bright-yellow crystals. Yield 0.21 g (70%). Since this complex is very sensitive to hydrolysis, the whole procedure had to be carried out in an N_2 atmosphere. The elemental analytical data [found (calc.)] for **I** are: C 30.52 (30.53), H 5.67 (5.48), N 2.67 (2.74), O 3.31 (3.13). The elemental analytical data for the other complexes are: **II** C 35.02 (34.72), H 6.32 (6.15), N 2.36 (2.53), O 3.02 (2.89); **V**, C 29.62 (29.60), H 5.47 (5.31), N 2.75 (2.66), O 5.80 (6.07); **VI**, C 34.06 (33.80), H 6.70 (6.16), N 4.91 (4.93), O 2.80 (2.82); **VII**, C 41.66 (41.52), H 4.87 (4.61), N 2.22 (2.31), O 2.70 (2.64).

Physical Measurements

^1H NMR spectra were recorded on Bruker WM 250, Varian T 60, Varian A 60 or Varian XL 100 NMR spectrometers, ^{13}C NMR spectra on Bruker WM 250 and WP 80 and Varian CFT 20 NMR spectrometers (off-resonance ^{13}C spectra were recorded for all the compounds to aid assignment), and ^{31}P NMR spectra on a Bruker WP 80 spectrometer. IR spectra were obtained with a Perkin-Elmer 283 spectrophotometer. Elemental analyses were carried out by the Analytical Section of the Institute for Applied Chemistry TNO, Zeist, The Netherlands.

X-ray Data Collection, Structure Determination and Refinement

Crystal data and other numerical details of the structure determination are listed in Table I. Crystals of the title compound ($\text{C}_{13}\text{H}_{28}\text{Cl}_2\text{NOPPt}$) are orthorhombic, space group $Pc2_1n$, with 4 molecules in a unit cell of dimensions $a = 14.712(3)$, $b = 15.053(2)$, $c = 9.025(5)$ Å, $V = 1998.52$ Å³. 1307 reflections ($\theta \leq 30^\circ$) with intensities above the 2.5 $\sigma(I)$ level were measured on a NONIUS CAD 4 diffractometer using graphite monochromatised Mo K_α radiation. The structure was solved by means of the heavy atom technique. It was difficult to locate the ethyl groups, which are not very well defined. After isotropic block diagonal least-squares refinement, an empirical absorption correction was applied (DIFABS) [11] (crystal dimensions $0.15 \times 0.25 \times 0.30$ mm; $\mu = 74.4$ cm^{-1}). The refinement was continued anisotropically, except for the ethyl groups in the PEt_3 ligand, which resulted in a final R_w -value of 0.056. Unit weights were used and the anomalous scattering of Pt was taken into account.

Results

The compounds $trans\text{-}[\text{PtCl}_2(\text{PR}_3)]\{\sigma\text{-N}-(\text{R}^1\text{N}=\text{C}(\text{R}^2)\text{C}(\text{R}^3)=\text{O})\}$ (**I**–**VII**) with R, R^1 , R^2 and R^3 as

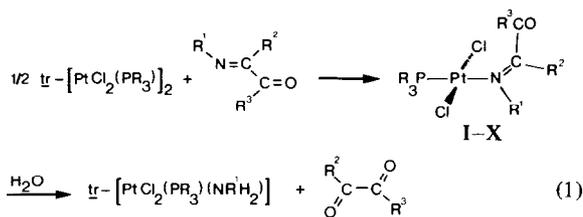
TABLE I. Crystal Data and Details of the Structural Analysis of *trans*-[PtCl₂(PEt₃){σ-N-(*t*-BuN=CHC(Me)=O)}]

Crystal data	
Formula	C ₁₃ H ₂₈ Cl ₂ NOPPt
<i>M_r</i>	511.3
Crystal system	orthorhombic
Space group	<i>Pc</i> 2 ₁ <i>n</i>
<i>a</i> (Å)	14.712(3)
<i>b</i> (Å)	15.053(2)
<i>c</i> (Å)	9.025(5)
β (°)	0
<i>V</i> (Å ³)	1998.52
<i>Z</i>	4
<i>D_c</i> (g cm ⁻³)	1.70
<i>F</i> (000) (electrons)	992
μ(Mo Kα) (cm ⁻¹)	74.4
Data collection (294 K)	
Radiation (Å)	Mo Kα, λ = 0.71069
θ _{min} , θ _{max} (°)	1.1, 30.0
Reference reflection	040
Total reflections	3281
Total unique reflections	3281
Observed data (<i>I</i> > 2.5σ(<i>I</i>))	1307
Refinement	
Number of refined parameters	200
Weighting scheme	unit
Final <i>R_F</i>	0.052
Final <i>R_{wF}</i>	0.056

indicated in eqn. (1) have been obtained in almost quantitative yield from the reaction of R¹N=C(R²)-C(R³)=O with the corresponding metal complexes *trans*-[PtCl₂(PR₃)₂] in a 2:1 molar ratio. The reaction does not occur in diethyl ether, probably because of the insolubility of the starting material. However, in dichloromethane the reaction is complete within 30 min. The isolated yellow crystals of **I–VII**, which according to elemental analyses have a 1:1 Pt/L stoichiometry, are soluble in dichloromethane, slightly soluble in aromatic solvents, but insoluble in diethyl ether and hexane. The new platinum complexes are very air- and moisture-sensitive and hydrolyse easily to give the *trans*-dichloroplatinum amine complexes and the corresponding α,β-diketones (see eqn. (1)). Attempts to synthesize these complexes starting from *cis*-[PtCl₂(PR₃)₂] or [PtCl₂(1,5-cyclo-octadiene)] failed.

It must be noted that only the 1:1 complexes could be isolated. Attempts to synthesize the 2:1 Pt/L complexes in order to obtain a dinuclear complex with a σ, σ-N, O bridging α-iminoketone were not successful, even when a tenfold excess of the platinum dimer was used.

Unambiguous proof for the σ-N monodentate coordination of the α-iminoketone to platinum in the



- I**, R = Et, R¹ = *t*-Bu, R² = H and R³ = Me
II, R = *i*-Pr, R¹ = *t*-Bu, R² = H and R³ = Me
III, R = Ph, R¹ = *t*-Bu, R² = H and R³ = Me
IV, R = Et, R¹ = Ph, R² = Ph and R³ = Ph
V, R = Et, R¹ = *t*-Bu, R² = H and R³ = OMe
VI, R = Et, R¹ = *t*-Bu, R² = H and R³ = NEt₂
VII, R = Et, R¹ = Me, R² = Ph and R³ = Ph
VIII, R = Et, R¹ = *i*-Pr, R² = Ph and R³ = Ph
IX, R = Et, R¹ = 2,4-dimethyl-3-pentyl, R² = H and R³ = Ph
X, R = Et, R¹ = Me, R² = Ph and R³ = Ph

solid state comes from the X-ray structure determination of *trans*-[PtCl₂(PEt₃){σ-N-(*t*-BuN=CHC(Me)=O)}] (**I**).

Molecular Geometry of *trans*-[PtCl₂(PEt₃){σ-N-(*t*-BuN=CHC(Me)=O)}]

Figure 1 gives a PLUTO view of the molecule. Positional parameters, some bond lengths and angles with their e.s.d.s are listed in Tables II and III. An important aspect of this novel type of α-iminoketone-metal complex is the observation that the α-iminoketone ligand is bonded via its N-atom with the N=C entity in the E conformation.

The N–C(5), C(5)–C(6) and C(6)–O distances in the non-planar NCCO skeleton (see discussion) of the α-iminoketone ligand differ only slightly as compared with the distances in free PhH(Me)CN=C(Ph)-C(Ph)=O (**XI**) [12]. The imine bond (N(1)=C(5), 1.34(4) Å) is somewhat larger than the corresponding distances in (**XI**) and *c*-HexN=CHCH=Nc-Hex (*c*-Hex-DAB) [13] of 1.268(2) and 1.258(3) Å, respectively. The central C(5)–C(6) bond length of 1.44(5) Å is somewhat smaller than the length of 1.530(2) Å in (**XI**), but similar to those in *c*-Hex-DAB (1.457(3) Å), [*trans*-PtCl₂(PBu₃)₂](*t*-Bu-DAB)

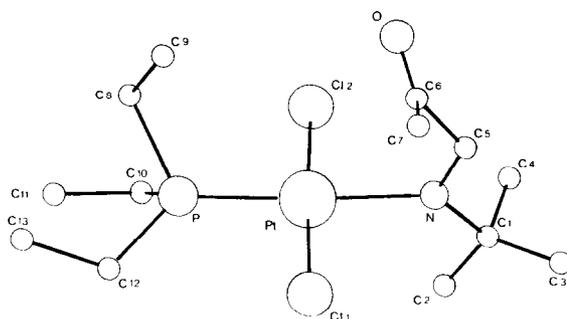


Fig. 1. Pluto drawing of *trans*-[PtCl₂(PEt₃){σ-N-(*t*-BuN=CHC(Me)=O)}]. The adopted numbering scheme is indicated.

TABLE II. Positional Parameters of the Atoms in Fractional Coordinates of *trans*-[PtCl₂(PEt₃){ σ -N-(t-BuN=CHC(Me)=O)}] ^a

Atoms	$x(\sigma_x)$	$y(\sigma_y)$	$z(\sigma_z)$
Pt	-0.02155(7)	0.5000(0)	0.2201(1)
Cl(1)	0.0601(7)	0.4205(8)	0.3945(14)
Cl(2)	-0.1040(5)	0.5831(6)	0.0547(8)
P	0.0616(8)	0.4498(7)	0.030(2)
O	-0.253(2)	0.417(2)	0.236(3)
N	-0.108(2)	0.5450(14)	0.400(2)
C(1)	-0.097(3)	0.638(3)	0.471(4)
C(2)	-0.019(4)	0.676(3)	0.427(6)
C(3)	-0.122(3)	0.627(4)	0.640(4)
C(4)	-0.163(3)	0.700(2)	0.397(4)
C(5)	-0.181(2)	0.494(3)	0.428(3)
C(6)	-0.205(2)	0.414(2)	0.350(3)
C(7)	-0.188(3)	0.336(2)	0.440(6)
C(8)	0.001(4)	0.412(4)	-0.146(6)
C(9)	-0.063(4)	0.315(4)	-0.069(7)
C(10)	0.095(3)	0.535(3)	-0.105(4)
C(11)	0.165(7)	0.448(7)	-0.141(11)
C(12)	0.171(4)	0.402(4)	0.032(6)
C(13)	0.197(5)	0.324(5)	-0.092(8)

^ae.s.d.s in parentheses.TABLE III. Selected Bond Lengths (Å) and Bond Angles (°) of *trans*-[PtCl₂(PEt₃){ σ -N-(t-BuN=CHC(Me)=O)}] ^a

Pt-Cl(1)	2.314(12)	Cl(1)-Pt-Cl(2)	177.6(4)
Pt-Cl(2)	2.295(8)	Cl(1)-Pt-P	93.6(4)
Pt-P	2.239(13)	Cl(1)-Pt-N	87.6(6)
Pt-N	2.176(20)	Cl(2)-Pt-P	88.5(4)
N-C(1)	1.56(4)	Cl(2)-Pt-N	90.3(6)
N-C(5)	1.34(4)	P-Pt-N	177.0(6)
C(5)-C(6)	1.44(5)	Pt-N-C(1)	121.9(18)
C(6)-C(7)	1.45(5)	Pt-N-C(5)	115.6(19)
C(6)-O	1.25(4)	C(5)-N-C(1)	122(3)
		N-C(5)-C(6)	125(2)
		C(5)-C(6)-C(7)	111(3)
		O-C(6)-C(7)	126(3)
		C(5)-C(6)-O	121(3)

^ae.s.d.s in parentheses.

(1.48(2) Å) [14] and [PdCl₂(PPh₃)(t-Bu-DAB)] (1.485(10) Å) [13]. The C=O bond length of 1.25(1) Å is compatible with the length of 1.209(2) Å in (XI). As a result of the σ -N coordination and the non-planarity of the N=C-C=O skeleton, the acetyl hydrogen atoms are positioned (on average) into the neighbourhood of the Pt atom, above the Pt coordination plane, with a calculated Pt-H distance of 2.92 Å.

The imine-nitrogen atom and the P, Cl(1) and Cl(2) atoms are coordinated to platinum, resulting in an approximately square planar configuration. Only minor deviations of these atoms from their

least-squares plane were observed {Pt (0.012), Cl(1) (0.034), Cl(2) (0.035), P (-0.040) and N (-0.042)}. The Pt-Cl distances of 2.314(12) and 2.295(8) Å are similar to the Pt-Cl distances found in other *trans*-dichloro platinum complexes; e.g., 2.296(4) and 2.306(3) Å in [PtCl₂(PEt₃)(*cis*-2,3-dimethylpyrrolidine)] [15], 2.299(4) and 2.305(4) Å in [PtCl₂(PEt₃)pyrrolidine] [16] and 2.296(4) and 2.300(4) in [PtCl₂(PBu₃)₂(t-Bu-DAB)] [14]. The Pt-P distance which is *trans* to the α -iminoketone nitrogen atom is 2.239(13) Å, which is in the range of other *trans*-P-Pt(N) complexes; e.g., 2.227(5) Å in [PtCl₂(PBu₃)₂(t-Bu-DAB)] [14], 2.228(3) Å in [PtCl₂(PEt₃)(*trans*-2,5-dimethylpyrrolidine)] [16], 2.232(6) Å in [Pt(Ph₂Ppy)₂Pt₂Cl₂]-[Rh(CO)₂Cl₂] \cdot 0.5CH₂Cl₂] [17] and 2.220(2) Å in [Pt₂Cl₂(Pn-Pr₃)₂{C(=CH₂)CH₂NHMe}₂] [18]. Also the Pt-N distance of 2.176(20) Å is comparable with the Pt-N distances found in [PtCl₂(PEt₃)(*cis*-2,4-dimethylpyrrolidine)] (2.133(7) Å) [15] and [PtCl{C(=CH₂)CH₂NHt-Bu}(Pn-Pr₃)] (2.179(9) Å) [17].

Structure in Solution

The IR data obtained from solutions of *trans*-[PtCl₂(PR₃){ σ -N-(R¹N=C(R²)C(R³)=O)}] in CH₂Cl₂ are presented in Table IV. The observation of one strong ν (Pt-Cl), in the range 334 to 326 cm⁻¹, established the presence of a *trans*-MCl₂ unit in these [PtCl₂(PR₃)L] compounds [19] (*cf.* ν (Pt-Cl) of 339 cm⁻¹ in *trans*-[PtCl₂(PBu₃)₂(t-Bu-DAB)] [14]).

The imine stretching frequency, ν (C=N), shifted on complexation toward lower values by 10–17 cm⁻¹. The extent of this frequency decrease is comparable to that observed between free t-Bu-DAB and the coordinated ligand in, for example, [PtCl₂(PBu₃)₂(t-Bu-DAB)], $\Delta\nu$ = 13 cm⁻¹ [14]. The carbonyl stretching frequency, ν (C=O), shifted on coordination of the N donor site toward higher values by 0–10 cm⁻¹. These data suggest that while the bond order of the imine bond is reduced by coordination to platinum, the carbonyl one is somewhat increased. The basicity of the *trans*-phosphine ligand determines the extent of electron-withdrawing properties of the metal centre; the more basic the phosphine ligand, the less electron density is donated from the α -iminoketone ligand to platinum. Accordingly for the most basic ligand the electron density on the coordinated ligand will resemble that in the free ligand; this is reflected by the similarity of their ν (CN) and ν (CO) values.

The combined ¹H, ¹³C and ³¹P NMR spectroscopic data of the isolated (I–VII) and *in situ* prepared complexes (VIII–X) have been compiled in Tables V–VII. Since the respective compounds have comparable NMR data, the description of the ¹H NMR results will be restricted to those of *trans*-[PtCl₂(PEt₃){ σ -N-(t-BuN=CHC(Me)=O)}], which has a

TABLE IV. Infrared Data^a for *trans*-[PtCl₂(PR₃)₂{σ-N-(R¹N=C(R²)C(R³)=O)}] Complexes

Compound	$\nu(\text{C}=\text{O})$	$\Delta\nu$	$\nu(\text{C}=\text{N})$	$\Delta\nu$	$\nu(\text{M}-\text{Cl})$
Ligands					
<i>t</i> -BuN=CHC(Me)=O (L1)	1706s		1650w		
PhN=C(Ph)C(Ph)=O (L2)	1668vs		1623m		
<i>t</i> -BuN=CHC(OMe)=O (L3)	1755vs		1648s		
<i>t</i> -BuN=CHC(NEt ₂)=O (L4)	1630s		1660m		
Complexes					
<i>trans</i> -[PtCl ₂ (PEt ₃) ₂ {σ-N-(L1)}] (I)	1710vs	+4	1639w	-11	332s
<i>trans</i> -[PtCl ₂ (Pi-Pr ₃) ₂ {σ-N-(L1)}] (II)	1715vs	+9	1635w	-15	329s
<i>trans</i> -[PtCl ₂ (PPh ₃) ₂ {σ-N-(L1)}] (III)	1716vs	+10	1633w	-17	334s
<i>trans</i> -[PtCl ₂ (PEt ₃) ₂ {σ-N-(L2)}] (IV)	1675vs	+7	1608m	-15	334s
<i>trans</i> -[PtCl ₂ (PEt ₃) ₂ {σ-N-(L3)}] (V)	1755vs	-	1635vw	-13	331m
<i>trans</i> -[PtCl ₂ (PEt ₃) ₂ {σ-N-(L4)}] (VI)	1632s	+2	1650m	-10	326m

^aSolutions in CH₂Cl₂, ν (cm⁻¹). vs = very strong, s = strong, m = medium, w = weak, vw = very weak relative to the most intense peak.

TABLE V. ¹H NMR Data^a for *trans*-[PtCl₂(PR₃)₂{σ-N-(R¹N=C(R²)C(R³)=O)}]

Compound	R ¹	R ²	R ³	R
Ligands				
<i>t</i> -BuN=CHC(Me)=O (L1)	1.24s	7.42s	2.31s	
PhN=C(Ph)C(Ph)=O (L2)	6.5-8m	6.5-8m	6.5-8m	
<i>t</i> -BuN=CHC(OMe)=O (L3)	1.39s	7.68s	3.88s	
<i>t</i> -BuN=CHC(NEt ₂)=O (L4)	1.20s	7.72s	1.14t	3.39q ^b
			1.15t	3.50q ^c
Platinum dimers				
<i>trans</i> -[PtCl ₂ (PEt ₃) ₂] ₂				1.21d/t ^d 1.79d/q ^e
<i>trans</i> -[PtCl ₂ (Pi-Pr ₃) ₂] ₂				1.24d/d ^f 1.84m
Complexes				
<i>trans</i> -[PtCl ₂ (PEt ₃) ₂ {σ-N-(L1)}] (I)	1.65s ^g	7.80s ⁱ	3.27s ^h	1.26m 1.83m
<i>trans</i> -[PtCl ₂ (Pi-Pr ₃) ₂ {σ-N-(L1)}] (II)	1.73s ^j	8.20s ⁱ	3.12s ^k	1.37d/d ^l 2.9m
<i>trans</i> -[PtCl ₂ (PPh ₃) ₂ {σ-N-(L1)}] (III)	1.75s ^j	8.25s ^m	2.98s	7.4-7.7m
<i>trans</i> -[PtCl ₂ (PEt ₃) ₂ {σ-N-(L2)}] (IV)	7-9m	7-9m	7-9m	1.11d/t ^d 1.76d/q ^e
<i>trans</i> -[PtCl ₂ (PEt ₃) ₂ {σ-N-(L3)}] (V)	1.70s	8.20s ⁱ	3.90s	1.07d/t ^d 1.70d/q ^e
<i>trans</i> -[PtCl ₂ (PEt ₃) ₂ {σ-N-(L4)}] (VI)	1.72s ^g	8.02s ⁱ	1-1.3m	3.40q 3.51q

^aRecorded at ambient temperature in CDCl₃. All values are in ppm to internal TMS; s = singlet, d = doublet, t = triplet, q = quartet, sept = septet and m = multiplet. ^b³J(H-H) = 7.15 Hz. ^c³J(H-H) = 7.10 Hz. ^d³J(H-H) = 7.5 Hz, ³J(³¹P-H) = 18 Hz. ^e²J(³¹P-H) = 12 Hz. ^f³J(H-H) = 8 Hz, ³J(³¹P-H) = 20 Hz. ^g⁴J(¹⁹⁵Pt-H) = 3 Hz. ^h⁵J(¹⁹⁵Pt-H) = 6 Hz. ⁱ³J(¹⁹⁵Pt-H) = 64 Hz, ⁴J(³¹P-H) = 12 Hz. ^j⁴J(¹⁹⁵Pt-H) = 2 Hz. ^k⁵J(¹⁹⁵Pt-H) = 4 Hz. ^l¹³J(H-H) = 7.2 Hz, ³J(³¹P-H) = 14 Hz. ^m³J(¹⁹⁵Pt-H) = 37 Hz, ⁴J(³¹P-H) = 8 Hz. ⁿ³J(H-H) = 7 Hz, ²J(³¹P-H) = 12 Hz.

known molecular structure in the solid form (*vide supra*).

In the ¹H NMR spectra both the imine and the *t*-butyl protons are shifted downfield. The imine proton appears as a six-line pattern due to large phosphorus and platinum couplings ($\delta = 7.80$ ppm, ⁴J(³¹P-H) = 12 Hz, ³J(¹⁹⁵Pt-H) = 64 Hz); the platinum coupling was also observed on the *t*-butyl protons ($\delta = 1.65$, ⁴J(¹⁹⁵Pt-H) = 3 Hz).

Interestingly the acetyl protons are also shifted downfield and have platinum coupling ($\delta = 3.27$ ppm, ⁵J(¹⁹⁵Pt-H) = 6 Hz).

The ¹³C NMR spectra of all complexes showed that the ¹³C resonances of the imine part of the ligand were shifted to lower field (± 10 ppm) upon coordination. Platinum coupling was observed on the carbon resonance of the substituents at nitrogen (e.g. VII; R¹ = Me, $\delta = 45.3$ ppm, ²J(¹⁹⁵Pt-¹³C) =

TABLE VI. ^{31}P NMR Data for $\text{trans-}[\text{PtCl}_2(\text{PR}_3)\{\sigma\text{-N}(\text{R}^1\text{N}=\text{C}(\text{R}^2)\text{C}(\text{R}^3)=\text{O})\}]$

Compound	δ ^{31}p
Platinum dimers	
$\text{trans-}[\text{PtCl}_2(\text{PEt}_3)_2]$	10.16(3858)
$\text{trans-}[\text{PtCl}_2(\text{Pi-Pr}_3)_2]$	31.91(3891)
Complexes	
$\text{trans-}[\text{PtCl}_2(\text{PEt}_3)\{\sigma\text{-N}(\text{t-BuN}=\text{CHC}(\text{Me})=\text{O})\}]$ (I)	-1.37(3455)
$\text{trans-}[\text{PtCl}_2(\text{Pi-Pr}_3)\{\sigma\text{-N}(\text{t-BuN}=\text{CHC}(\text{Me})=\text{O})\}]$ (II)	17.41(3528)
$\text{trans-}[\text{PtCl}_2(\text{PEt}_3)\{\sigma\text{-N}(\text{PhN}=\text{C}(\text{Ph})\text{C}(\text{Ph})=\text{O})\}]$ (IV)	1.02(3520)
$\text{trans-}[\text{PtCl}_2(\text{PEt}_3)\{\sigma\text{-N}(\text{t-BuN}=\text{CHC}(\text{OMe})=\text{O})\}]$ (V)	-1.67(3610)
$\text{trans-}[\text{PtCl}_2(\text{PEt}_3)\{\sigma\text{-N}(\text{t-BuN}=\text{CHC}(\text{NEt}_2)=\text{O})\}]$ (VI)	-2.74(3510)
$\text{trans-}[\text{PtCl}_2(\text{PEt}_3)\{\sigma\text{-N}(\text{MeN}=\text{C}(\text{Ph})\text{C}(\text{Ph})=\text{O})\}]$ (VII)	-1.76(3440)
$\text{trans-}[\text{PtCl}_2(\text{PEt}_3)\{\sigma\text{-N}(\text{i-PrN}=\text{C}(\text{Ph})\text{C}(\text{Ph})=\text{O})\}]$ (VIII)	-2.44(3506)
$\text{trans-}[\text{PtCl}_2(\text{PEt}_3)\{\sigma\text{-N}(\text{R}^1\text{N}=\text{CHC}(\text{Ph})=\text{O})\}]$ (IX)	-2.14(3464)

($\text{R}^1 = 2,4\text{-dimethyl-3-pentyl}$).

$^a\text{H}_3\text{PO}_4$ as external standard, δ ppm, RT. Solvent $\text{C}_6\text{D}_6:\text{CH}_2\text{Cl}_2$, 1:5. Values of $^1J(^{195}\text{Pt}-^{31}\text{P})$ in Hz in parentheses.

TABLE VII. ^{13}C NMR Data^a for $\text{trans-}[\text{PtCl}_2(\text{PR}_3)\{\sigma\text{-N}(\text{R}^1\text{N}=\text{C}(\text{R}^2)\text{C}(\text{R}^3)=\text{O})\}]$ Complexes

Compound	T (°C)	R	R ¹	R ²	R ³	N=C	C=O
Ligand							
t-BuN=CHC(Me)=O L1	+35		28.7(Me)	58.0(CMe ₃)	23.9	154.3	200.1
MeN=C(Ph)C(Ph)=O L5	+35		40.7		126-135 ^b	168.0	198.7
i-PrN=C(Ph)C(Ph)=O L6	+35		23.5(Me)	53.7(CHMe ₂)	126-135 ^b	163.7	198.6
Platinum dimers							
$\text{trans-}[\text{PtCl}_2(\text{PEt}_3)_2]$	+35	7.4 ^c	14.5 ^d				
Complexes							
$\text{trans-}[\text{PtCl}_2(\text{PEt}_3)\{\sigma\text{-N}(\text{L1})\}]$ (I)	-60	7.4 ^e	11.5 ^f	31.2(Me)	66.4(CMe ₃)	31.2	163.8
	+35	7.4 ^e	14.0 ^f	31.1(Me)	66.5(CMe ₃)	31.2	164.3
$\text{trans-}[\text{PtCl}_2(\text{PEt}_3)\{\sigma\text{-N}(\text{L5})\}]$ (VII)	-50	7.3 ^e	13.0 ^f	45.5 ^h		126.8-135.7 ^m	173.9
	+35	7.4 ^e	13.7 ^f	45.3 ^h		127.4-135.3 ^m	175.0
$\text{trans-}[\text{PtCl}_2(\text{PEt}_3)\{\sigma\text{-N}(\text{L6})\}]$ (VIII)	-40	7.1 ^e	12.5 ^f	23.9(Me)	61.6(CHMe ₂)	128.1-135.5 ^m	174.2
	+35	7.1 ^e	13.5 ^f	23.9 ⁱ (Me)	61.6 ⁱ (CHMe ₂)	128.0-135.2 ^m	174.8
$\text{trans-}[\text{PtCl}_2(\text{PPh}_3)\{\sigma\text{-N}(\text{L5})\}]$ (X)	-50			46.2		127.2-135.8 ^m	174.9
	+35			46.3		126.9-136.1 ^m	175.2

^aIn CH_2Cl_2 ; all values are in ppm relative to internal TMS. Multiplicity, obtained from off-resonance spectra, is in agreement with the proposed assignments. ^b8 lines pattern. ^c $^2J(^{31}\text{P}-^{13}\text{C}) = 3$ Hz, ^d $^3J(^{195}\text{Pt}-^{13}\text{C}) = 23.4$ Hz. ^e $^1J(^{31}\text{P}-^{13}\text{C}) = 41$ Hz, ^f $^2J(^{195}\text{Pt}-^{13}\text{C}) = 37.4$ Hz. ^g $^4J(^{31}\text{P}-^{13}\text{C}) = 6$ Hz. ^h $^2J(^{195}\text{Pt}-^{13}\text{C}) = 3$ Hz, ⁱ $^3J(^{195}\text{Pt}-^{13}\text{C}) = 22$ Hz. ^j $^1J(^{31}\text{P}-^{13}\text{C}) = 40$ Hz, ^k $^2J(^{195}\text{Pt}-^{13}\text{C}) = 34$ Hz. ^l $^4J(^{31}\text{P}-^{13}\text{C}) = 6$ Hz. ^mMultiplet.

12 Hz). The carbonyl-C resonances were not shifted, except for the compounds VII-X which showed an upfield shift of ± 5 ppm for these resonances.

The δ ^{31}P of the PEt_3 ligand shifted by about 11 ppm upon coordination of the α -iminoketone ligand (e.g. +10.16 ppm in $\text{trans-}[\text{PtCl}_2(\text{PEt}_3)_2]$ and -1.37 ppm for compound I, respectively). Moreover, the $^1J(^{195}\text{Pt}-^{31}\text{P})$ decreased from 3860 Hz in $\text{trans-}[\text{PtCl}_2(\text{PEt}_3)_2]$ to 3455 Hz in $\text{trans-}[\text{PtCl}_2(\text{PEt}_3)\{\sigma\text{-N}(\text{t-BuN}=\text{CHC}(\text{Me})=\text{O})\}]$; this is

the expected shift for a change from Cl *trans* to P to N *trans* to P.

On the basis of the combined IR and temperature-independent NMR spectroscopic data of the 1:1 Pt/L complexes, a picture of the nature of the metal/ α -iminoketone interactions in solution was obtained. The reduced imine bond order, the large downfield shift of the imine- ^{13}C and ^{-1}H resonances, as well as the ^{195}Pt and ^{31}P coupling on the t-BuN=CH part of the molecule, establish that the ligand is

σ -N coordinated. The unchanged carbonyl bond order supports the view that there is no interaction between the oxygen atom and the platinum centre. Furthermore, the downfield shift of the R³.¹³C and ¹H resonances and the observation of platinum and phosphorus couplings with protons and carbon atoms throughout the whole ligand skeleton demonstrate that in solution, as in the solid, the σ -N monodentate coordinated ligand possesses a rigid structure which places the R³ substituents above the platinum coordination plane.

Discussion

Heterobutadienes containing the N=C–C=O skeleton are expected to have a versatile coordination behaviour because they can use the electron pairs on the hetero atoms as well as the π electrons of the N=C and C=O groupings for coordination. For the related 1,4-diaza-1,3-butadienes (R-DAB), all possible coordination modes, *i.e.* 2e, 4e, 6e and 8e bonding, have been achieved [1]. The metal–R-DAB complexes contain the R-DAB ligand bonded either in its E-*s-trans*-E conformation or the E-*s-cis*-E one, but in either case the R-DAB ligand skeleton is flat or nearly flat. The actual conformation of the coordinated N=C–C=O skeleton is difficult to predict because steric constraints of substituents may have a large influence on the relative stability of the flat (planar-*syn* or planar-*anti*) and non-planar gauche (N=C/C=O torsion angles of about 90°) conformations. (An extensive discussion of this aspect is given in ref. [20, 21]). For the present discussion two examples may illustrate this point. In the only crystal structure known for a free aza-oxo-butadiene compound, *i.e.* PhH(Me)CN=C(Ph)C(Ph)=O, the N=C/C=O torsion angle is 97.7(2)° [12] (see Fig. 2B), whereas the corresponding N=C/C=N angles in *c*-Hex-DAB and *t*-Bu-DAB are virtually 0°. However, in the case of smaller substituents, the N=C–C=O skeleton may adopt a nearly flat conformation, as indicated by the structure of [Fe₂(CO)₆(PhH(Me)CN=CHCOEt)] [22]. In this complex an ethyl N- α -methylbenzyliminoacetate is coordinated in a nearly-flat planar *syn* conformation to the Fe₂(CO)₆ unit as a 6e donating ligand.

The present complexes are the first examples of complexes containing a monodentate coordinated aza-oxo-butadiene ligand. The aza-oxo-butadienes are ambident nucleophiles with the carbonyl (ester, imide) and imino groups as the two reactive sites for σ -coordination. In the case of the *trans*-PtCl₂-(PR₃) moiety with the phosphine substituent *trans* to the vacant coordination site, it is the stronger σ -donating imine N-donor site of the aza-oxo-butadiene that coordinates. This σ -N monodentate

coordination makes the imine bond very susceptible to hydrolysis as shown in equation (1).

It is interesting to find that the monodentate bonded α -iminoketone ligand in *trans*-[PtCl₂(PEt₃){ σ -N-(*t*-BuN=CHC(Me)=O)}] (I) has a non-planar gauche conformation with a torsion angle of 89° between the CN and CO chromophores (see Fig. 2A). This conformation is similar to the conformation found for the free N=C–C=O ligand having the bulkier Ph substituent instead of the H and Me substituents in the central C atoms (in I). This suggests that any substitution of a H atom at the central C atoms results in stabilization of the non-planar gauche over the planar *syn* and planar *anti* conformations. Accordingly, in this 2e- σ -N bonding mode, the CN and CO chromophores in aza-oxo-butadienes may be considered as isolated nucleophilic entities, due to the near-orthogonality between these entities. Only when there is extensive coordination of both chromophores to the same metal centre (e.g. the chelate 4e or the bridging 6e bonding modes) can similar electron delocalisations occur as have been found for the R-DAB ligands [1, 23].

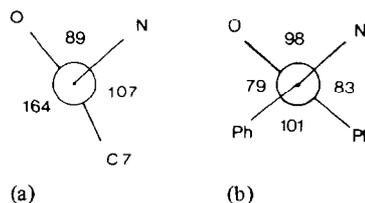


Fig. 2. Newman projections along the C(5)–C(6) axis of *trans*-[PtCl₂(PEt₃){ σ -N-(*t*-BuN=CHC(Me)=O)}] (A) and of PhH(Me)CN=C(5)(Ph)C(6)(Ph)=O (B).

IR and NMR data showed that the solution structures of the compounds *trans*-[PtCl₂(PR₃)L] (I–III) have structural features similar to those established for I in the solid. Moreover, the fact that the NMR spectra appeared to be temperature independent showed that the ligand conformation is rigid on the NMR time scale. An interesting consequence of this rigidity is apparent from the downfield ¹H chemical shift of the acetyl protons in compounds I–III. With the adoption of the non-planar gauche conformation, the structure of I–III (see Fig. 3A) shows that a C–H bond of the acetyl group is brought in the neighbourhood of the Pt atom above its coordination plane. Assuming free rotation of the CH₃ group about the H₃C–C(6) bond, each of these hydrogen atoms can equally experience the magnetic anisotropy of the planar complex, resulting in the observed deshielding of these protons (see Table V, $\Delta\delta = 0.96$ ppm for I). The calculated distance between the Pt centre and the acetyl hydrogen atoms (see Fig. 3A) is 2.92 Å, which is within the distance

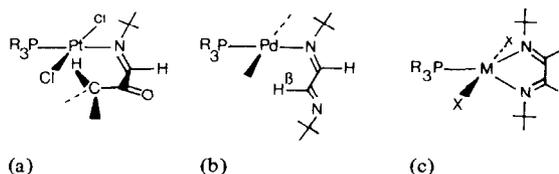


Fig. 3. (A) Acetyl-H in sixth atom position of a six-membered ring including PtNC(5)C(6)C(7)H; (B) imine-H in the fifth atom position of a five-membered ring including Pd-NCCH [13]; and (C) transition state of the fluxional process [19] observed for the complexes with M = Pt or Pd.

of 3.2 Å expected for the van der Waals contacts [24] (assuming sp³ hybridization at the acetyl C centre and a C—H distance of 1.10 Å). This Pt···H distance is comparable to that of the β-(imino) C—H···Pd distance of 2.6 Å in *trans*-PdCl₂(PPh₃)(*t*-Bu-DAB), which contains a monodentate bonded *t*-Bu-DAB ligand in the planar *anti* conformation (see Fig. 3B) [13]. Likewise a downfield shift of about 2.0 ppm was observed for the β-N=CH hydrogen nuclei in these complexes, which have in solution at the slow exchange limit (*vide infra*) a structure as shown in Fig. 3B.

A notable exception to the rigid *trans*-[PtCl₂(PR₃){σ-N-(R¹N=C(R²)C(R³)=O)}] (I-X) complexes is the dynamic behaviour observed for the *trans*-[MCl₂(PR₃)(*t*-Bu-DAB)] (M = Pt, Pd) complexes in solution [19]. It was shown that the fluxional process by which the metal M changes its point of attachment to the imino N-atoms in these complexes involves the five-coordinated situation shown in Fig. 3C. During this fluxional process the latter molecules are switching back and forth between enantiomeric configurations (*cf.* Fig. 3B for one of these enantiomers) which thus have the same energy. A similar process for the [PtCl₂(PR₃)(N=C—C=O)] complexes would require not only a flattened N=C—C=O skeleton when passing a five-coordinated transition state similar to the one shown in Fig. 3B for the *t*-Bu-DAB complexes, but also the involvement of an isomer having the iminoketone ligand mono-dentate bonded via the O-donor site. It is most probably the latter factor which contributes to the rigidity of the complexes I-X in solution, since it is very unlikely that the isomers having the iminoketone ligand either monodentate-N or -O bonded have equal energies.

Finally, it is interesting to note that the acetyl hydrogens (in compounds I–III) show a ⁵J(¹⁹⁵Pt–H) coupling of 6 Hz. A similar coupling of the N=CH hydrogen nucleus in [PtCl₂(PBU₃)(*t*-Bu-DAB)], which would be a ⁴J(¹⁹⁵Pt–H) coupling, is not observed [14, 19]. It is known that long-range coupling can occur if the molecular skeleton (in particular the dihedral angles) between a pair of nuclei with *J* =

1/2 is well-defined [25–27]. Since the observed value for a coupling between ¹⁹⁵Pt and ¹H over five bonds is rather large, it can be concluded that the molecule has a rigid molecular structure on the NMR time-scale.

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