Inorganica Chimica Acta, 214 (1993) 85–95

Reactivity of $[\text{Pt}(\text{CH}_2{=}\text{CH}_2)(\text{PPh}_3)_2]$ toward ethyldiazocetate. Synthesis and molecular structure of the diethyl fumarate complex $[\text{Pt}\{\textit{trans}\text{-CH}(\text{CO}_2\text{Et}){=}\text{CH}(\text{CO}_2\text{Et})\}(\text{PPh}_3)_2]$ and preparation of the analogous diethyl maleate compound

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(Received April 1, 1993)

Abstract

Treatment of $[\text{Pt}(\text{CH}_2{=}\text{CH}_2)(\text{PPh}_3)_2]$ with $\text{NN}{=}\text{CHCO}_2\text{Et}$ (ethyldiazoacetate) or with *trans*-$\text{CH}(\text{CO}_2\text{Et}){=}\text{CH}(\text{CO}_2\text{Et})$ (diethyl fumarate) affords $[\text{Pt}\{\textit{trans}\text{-CH}(\text{CO}_2\text{Et}){=}\text{CH}(\text{CO}_2\text{Et})\}(\text{PPh}_3)_2]$ (**1**), whereas $[\text{Pt}\{\textit{cis}\text{-CH}(\text{CO}_2\text{Et}){=}\text{CH}(\text{CO}_2\text{Et})\}(\text{PPh}_3)_2]$ (**2**) is obtained from the reaction with *cis*-$\text{CH}(\text{CO}_2\text{Et}){=}\text{CH}(\text{CO}_2\text{Et})$ (diethyl maleate). The molecular structure of **1** has been confirmed by X-ray diffraction analysis which indicates that the diethyl fumarate ligand binds to platinum via the olefinic bond, a weak metal–α-C(olefin)–H interaction also having been detected; the corresponding Pt–C distance is 2.110(3) Å, and the olefinic C=C bond length is 1.466(6) Å. The redox properties of these complexes, as studied by cyclic voltammetry and controlled potential electrolysis, are also described.

Introduction

Diazoalkanes ($\text{NN}{=}\text{CRR}'$) are versatile reagents in coordination chemistry and in synthesis. They can bind a metal centre in a variety of modes or generate free or coordinated carbene reactions products [1] in view of their propensity towards dinitrogen loss. In pursuit of our interest on the activation of small unsaturated-C or -N molecules [2], we have initiated the study of their reactivity at low-valent early transition metal centres and, in particular, from the reactions of $\text{N}_2\text{CHCOOEt}$ with *trans*-$[\text{M}(\text{N}_2)_2(\text{dppe})_2]$ (M = Mo or W, dppe = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$), the bisdiazoalkane complexes *trans*-$[\text{M}(\text{N}_2\text{CHCOOEt})_2(\text{dppe})_2]$ have been obtained [3], apart from some organonitrogenated products, i.e. benzene-azomethane or a phosphazene (for reactions carried out in benzene or in THF, respectively) [4]. We now report the extension of this study to a low-valent late transition metal Pt(0) centre.

Although a few examples are known of diazoalkane complexes of zerovalent Group 10 metal sites, such as $[\text{M}(\text{diazoalkane})\text{L}_2]$ (M = Ni or Pd; diazoalkane = $\text{N}_2\text{C}(\text{CN})_2$, N_2CPh_2 or diazofluorene; L = CNBu^t or PPh_3) [5, 6], with a π-bound (η^2) diazoalkane, complexes with diazoalkane-derived ligands have also been quoted for such a type of metal centre. In particular, the ketenimine complex $[\text{Ni}\{\text{Bu}^t\text{N}{=}\text{C}{=}\text{C}(\text{CN})_2\}(\text{CNBu}^t)_2]$ has been derived from $[\text{Ni}\{\text{N}_2{=}\text{C}(\text{CN})_2\}(\text{CNBu}^t)_3]$, upon metal-assisted addition of the diazoalkane-derived carbene to an isocyanide ligand [6]. Moreover, the azine compounds $[\overline{\text{M}\{\text{C}(\text{CF}_3)_2\text{N}}-\text{N}{=}\text{C}(\text{CF}_3)_2\}\text{L}_2]$ (M = Ni, Pd or Pt; L = tertiary phosphine or alkyl isocyanide) [7a, b] have been obtained from the reactions of $\text{NN}{=}\text{C}(\text{CF}_3)_2$ with $[\text{NiL}_4]$, $[\text{Pd}(\text{CNR})_2]$, $[\text{Pt}(\text{PR}_3)_3]$ or $[\text{Pt}(\text{stilbene})(\text{PPh}_3)_2]$. An azine complex of Pt(II), $[\text{Pt}(\text{C}_6\text{F}_5)_2\{\text{N}({=}\text{CPh}_2)\text{N}{=}\text{CPh}_2\}]$, in which the azine

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binds through one N atom and the π-system of a phenyl group (in a η^2-alkene-like mode), has also been reported from the reaction of $NN{=}CPh_2$ with $[Pt(C_6F_5)_2(THF)_2]$ [8], whereas products of insertions of carbenes (generated from diazo species) into metal–ligand bonds are known to occur in other cases [7].

In the present study we report the reaction of ethyldiazoacetate, $NN{=}CHCO_2Et$, with $[Pt(CH_2{=}CH_2)(PPh_3)_2]$ which leads to [Pt{*trans*-CH(CO_2Et)=CH(CO_2Et)}($(PPh_3)_2$)] (**1**) in which the diethyl fumarate ligand is derived from the diazoalkane and interacts with Pt(0) not only in the conventional way, by the C=C bond, but also via a weak C—H interaction which involves an olefinic α-C atom, as indicated by X-rays. The occurrence of such an interaction, which is *not* detected by NMR spectroscopy, is noteworthy in view of the rarity of the recognition [9] of agostic interactions at Pd(0) or Pt(0) species, which, moreover, are of different types from that observed in our case, as discussed below. For comparative purposes, the reactions of the ethylene complex with diethyl fumarate and the corresponding *cis* isomer (diethyl maleate) were also investigated.

Experimental

General procedures

All reactions were carried out under a dinitrogen atmosphere, through standard vacuum and inert gas flow techniques. The solvents were dried and freshly distilled before use by standard procedures. IR spectra were recorded with Perkin-Elmer 683 or 457 spectrophotometers, whereas the ^1H, ^{31}P and ^{13}C NMR spectra were recorded on a Varian Unity 300 spectrometer.

Electrochemistry

The electrochemical experiments were carried out either on an EG&G PAR 173 potentiostat/galvanostat and an EG&G PARC 175 Universal programmer or on an HI-TEK DT 2101 potentiostat/galvanostat and an HI-TEK PP RI waveform generator. Cyclic voltammetry was undertaken in a two-compartment three-electrode cell, at a platinum-wire working electrode, probed by a Luggin capillary connected to a silver-wire pseudo-reference electrode; a platinum or tungsten auxiliary electrode was employed. Controlled-potential electrolyses were carried out in a three-electrode H-type cell with platinum-gauze working and counter electrodes in compartments separated by a glass frit; a Luggin capillary, probing the working electrode, was connected to a silver-wire pseudo-reference electrode. The oxidation potentials of the complexes were measured by cyclic voltammetry in 0.2 mol dm^{-3} $[NBu_4][BF_4]/CH_2Cl_2$ (or NCMe) and the $E_p{}^{ox}$ values are quoted relative to the SCE by using as internal reference the $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$ couple ($E_{1/2}{}^{ox}=0.545$ or 0.42 V versus SCE, in 0.2 mol dm^{-3} $[NBu_4][BF_4]/CH_2Cl_2$ or NCMe, respectively).

The acid–base titrations of the electrochemically oxidized solutions were carried out by potentiometry, by using a solution of NaOH in CH_3OH which was standardized by titration against benzoic acid in NCMe. Background effects have been considered by performing also the titration of the blank solution of 0.2 mol dm^{-3} $[NBu_4][BF_4]$ which has been electrolyzed under identical conditions to those used for the corresponding complex solution.

Starting compounds

The complex $[Pt(CH_2{=}CH_2)(PPh_3)_2]$ was prepared by a published method [10] whereas ethyldiazoacetate, diethyl fumarate and diethyl maleate were used as purchased from Aldrich.

Preparation of [Pt{trans-CH(CO_2Et)=CH(CO_2Et)}($(PPh_3)_2$)] (1)

From ethyldiazoacetate

Ethyldiazoacetate (0.087 cm^3, 0.84 mmol) was added to a CH_2Cl_2 solution (10 cm^3) of $[Pt(CH_2{=}CH_2)(PPh_3)_2]$ (0.30 g, 0.40 mmol) and the system was left stirring in a N_2 atmosphere for *c.* 4 h. Concentration *in vacuo* of the orange solution followed by addition of diethyl ether led to the precipitation of a yellow solid which was filtered off and thoroughly washed with acetone. The pale yellow residue was recrystallized from CH_2Cl_2/diethyl ether to give complex **1** as a pale yellow crystalline solid which was filtered off, washed with diethyl ether and dried *in vacuo*. Yield 0.13 g (45%). *Anal.* Calc. for $C_{44}H_{42}O_4P_2Pt\cdot\frac{1}{3}CH_2Cl_2$: C, 57.9; H, 4.7. Found: C, 57.8; H, 4.9%. This route provided the crystal which was analysed by X-rays (see below)

From diethyl fumarate

Diethyl fumarate (0.175 ml, 1.07 mmol) was added to a CH_2Cl_2 solution (20 cm^3) of $[Pt(CH_2{=}CH_2)(PPh_3)_2]$ (0.20 g, 0.27 mmol) and the system was left stirring in an N_2 atmosphere for 48 h. Concentration *in vacuo* followed by addition of diethyl ether led to the precipitation of yellow crystals of **1** which were filtered off, washed first with CH_2Cl_2/diethyl ether (3:1 vol. mixture), then with diethyl ether and dried *in vacuo*. Yield *c.* 0.20 g (*c.* 55%).

Preparation of [Pt{cis-CH(CO_2Et)=CH(CO_2Et)}($(PPh_3)_2$)] (2)

Diethyl maleate (0.090 ml, 0.53 mmol) was added to a CH_2Cl_2 solution (20 cm^3) of $[Pt(CH_2{=}CH_2)(PPh_3)_2]$ (0.20 g, 0.27 mmol), and the system was left stirring in an N_2 atmosphere for 48 h. Concentration *in vacuo* followed by addition of diethyl ether led to the precipitation of white crystals of **2** which were filtered off, washed with CH_2Cl_2/diethyl ether (1:1 vol. mixture), then with diethyl ether and dried *in vacuo*. Yield *c.* 0.18 g (*c.* 75%). *Anal.* Calc. for $C_{44}H_{42}O_4P_2Pt$: C, 59.3; H, 4.8. Found: C, 59.5; H, 4.4%.

X-ray structural determination

The crystal and refinement data for [Pt{*trans*-CH(CO_2Et)=CH(CO_2Et)}(PPh_3)$_2$] (**1**) are summarized in Table 1. A prismatic (white) crystal of dimensions 0.36×0.42×0.28 mm was lodged in a Lindemann glass capillary and centred on a four-circle Philips PW1100 diffractometer with graphite-monochromated Mo Kα radiation. The orientation matrix and preliminary unit cell dimensions were determined from 25 reflections found by mounting the crystal at random, varying each of the orientation angles χ and ϕ over a range of 120°, with $8 \leqslant \theta \leqslant 10°$. For the determination of precise lattice parameters, 25 strong reflections with $11 \leqslant \theta \leqslant 15°$ were considered. Integrated intensities for *hkl* reflections in the interval $h = \pm 11; k = \pm 14; l = 0 \rightarrow 18$ were measured, and two standard reflections, −4, 3, 3; and 3, 2, 1 were measured every 180 min. There were no significant fluctuations of intensities other than those expected from Poisson statistics. The intensity data were corrected for Lorenz–polarization effects and for absorption, by following the method of North *et al.* [11]; no correction was made for extinction. The structure was solved by using three-dimensional Patterson and Fourier techniques and refined with full-matrix least-squares; anisotropic thermal parameters were assigned to all the non-hydrogen atoms. Hydrogen atoms were introduced at calculated positions and were allowed to ride on associated carbon atoms during the least-squares refinement (d(C−H)=0.98 Å and U=0.07 Å^2), except for H(1) and H(2), of the fumarate ligand, which were derived from difference map and refined isotropically. The function minimized was $\Sigma w\Delta^2$ with $\Delta = (|F_o| - |F_c|)$. Final R values were $R = 0.024$ and $R_w = 0.026$. The two largest peaks in the final difference map (0.7 e Å^2) were located near the platinum atoms positions. Data processing and computation were carried out by using the SHELX 76 program package [12] with the atomic scattering factors taken from ref. 13 and for drawings ORTEP [14].

TABLE 1. Crystallographic data for [Pt{*trans*-CH(CO_2Et)=CH(CO_2Et)}PPh_3)$_2$] (**1**)

Formula	$C_{44}H_{42}O_4P_2Pt$
Molecular weight	891.85
Crystal system	triclinic
a (Å)	11.960(3)
b (Å)	12.442(3)
c (Å)	15.839(3)
α (°)	100.84(4)
β (°)	89.85(3)
γ (°)	116.43(4)
V (Å^3)	1932(1)
Space group	$P\bar{1}$
Z	2
D_{calc} (g cm^{-3})	1.48
F(000)	862
λ(Mo Kα) (Å)	0.71069
μ(Mo Kα) (cm^{-1})	35.5
Transmission coefficient (rel.)	71/100
Reflections measured	7055
Scan method	$\theta/2\theta$
Reflections ($I \geqslant 3\sigma(I)$)	6335
$R = \Sigma[F_o\| - \|F_c\|]/\Sigma\|F_o\|$	0.024
$R_w = [\Sigma(F_o\| - \|F_c\|)^2/\Sigma w\|F_o\|^2]^{1/2}$	0.026
Weighting scheme, w	$[\sigma^2(F_o) + 0.000714(F_o^2)]^{-1}$
Goodness of fit, S	1.09

The atomic coordinates are reported in Table 2, relevant bond distances and angles in Table 3, and torsion angles of the diethyl fumarate ligands in Table 4.

Results and discussion

Treatment of [Pt(CH_2=CH_2)(PPh_3)$_2$] in CH_2Cl_2 by ethyldiazoacetate, NN=$CHCO_2Et$, in a two-fold molar ratio, leads to the formation of the diethyl fumarate complex [Pt{*trans*-CH(CO_2Et)=CH(CO_2Et)}(PPh_3)$_2$] (**1**, eqn. (1)) which was isolated as a pale yellow crystalline solid (*c.* 45% yield).

$$[\mathrm{Pt(CH_2{=}CH_2)(PPh_3)_2}] + 2\mathrm{N_2CHCO_2Et} \longrightarrow [\mathrm{Pt}\{trans\text{-}\mathrm{CH(CO_2Et){=}CH(CO_2Et)}\}\mathrm{(PPh_3)_2}] + \mathrm{H_2C{=}CH_2} + 2\mathrm{N_2} \qquad (1)$$

The diethyl fumarate ligand formally results from the coupling of two carbene groups derived from the diazo compound, upon N_2 loss. However, its formation should involve the activation of the diazoalkane by the metal centre, since complex **1** is obtained by carrying out the reaction not only under W-filament light (thus favouring the decomposition of the free diazo compound towards N_2 loss) but also in the dark (in non-destabilizing conditions of the free diazo species). Moreover, coordination of $NNCHCO_2Et$ is also suggested by monitoring the reaction solution by IR spectroscopy (detection of a band, assigned to $\nu(N_2)$ of the coordination diazo compound, at 2035 cm^{-1}, a distinct wavenumber from that, 2105 cm^{-1}, of the free species).

This route for the fumarate complex (**1**), which can obviously be applicable only to the preparation of complexes with symmetric olefins, is distinct from that commonly followed for the synthesis of related olefinic Pd or Pt complexes by using the olefin itself as a starting material [15, 16]. However, this more direct procedure can also be applied to the synthesis of **1**, as well as

TABLE 2. Fractional atomic coordinates and their equivalent isotropic thermal parameters, with e.s.d.s in parentheses, for [Pt{*trans*-CH(CO_2Et)=CH(CO_2Et)}(PPh_3)$_2$] (**1**)

Atom	x	y	z	U_{eq}[a] (Å^2)
Pt	0.56617(1)	0.02917(1)	0.23835(1)	0.0295(1)
P(1)	0.77242(9)	0.19560(8)	0.26694(6)	0.0325(3)
P(2)	0.61490(8)	−0.13320(8)	0.20848(6)	0.0312(3)
C(9)	0.8394(4)	0.2306(3)	0.3793(2)	0.037(1)
C(10)	0.9537(4)	0.3392(4)	0.4148(3)	0.052(2)
C(11)	1.0017(5)	0.3588(4)	0.4992(3)	0.062(2)
C(12)	0.9368(6)	0.2748(5)	0.5497(3)	0.069(3)
C(13)	0.8230(5)	0.1692(5)	0.5158(3)	0.066(3)
C(14)	0.7740(4)	0.1473(4)	0.4307(3)	0.050(2)
C(15)	0.7895(4)	0.3453(3)	0.2536(3)	0.043(2)
C(16)	0.6940(5)	0.3801(4)	0.2859(4)	0.067(2)
C(17)	0.7062(6)	0.4960(5)	0.2819(4)	0.084(3)
C(18)	0.8100(7)	0.5748(4)	0.2460(4)	0.083(3)
C(19)	0.9069(7)	0.5433(5)	0.2149(4)	0.086(3)
C(20)	0.8956(6)	0.4272(4)	0.2191(3)	0.068(2)
C(21)	0.9017(3)	0.1810(3)	0.2020(2)	0.038(1)
C(22)	1.0277(4)	0.2040(3)	0.2356(3)	0.047(2)
C(23)	1.1198(4)	0.1915(4)	0.1807(3)	0.058(2)
C(24)	1.0877(4)	0.1563(4)	0.0924(3)	0.060(2)
C(25)	0.9628(5)	0.1330(4)	0.0587(3)	0.056(2)
C(26)	0.8710(4)	0.1450(4)	0.1130(3)	0.046(2)
C(27)	1.0033(4)	−0.0872(4)	0.2209(3)	0.056(2)
C(28)	1.0304(4)	−0.0810(4)	0.3058(3)	0.060(2)
C(29)	0.9331(4)	−0.0921(4)	0.3618(3)	0.060(2)
C(30)	0.8073(4)	−0.1108(4)	0.3320(3)	0.048(2)
C(31)	0.7786(3)	−0.1179(3)	0.2452(2)	0.036(1)
C(32)	0.8785(4)	−0.1050(4)	0.1902(3)	0.045(2)
C(33)	0.5920(4)	−0.2019(3)	0.0938(2)	0.040(2)
C(34)	0.5424(4)	−0.1553(4)	0.0377(2)	0.044(2)
C(35)	0.5162(5)	−0.2082(5)	−0.504(3)	0.062(2)
C(36)	0.5413(5)	−0.3071(5)	−0.0827(3)	0.068(2)
C(37)	0.5949(5)	−0.3511(4)	−0.0274(3)	0.068(2)
C(38)	0.6205(4)	−0.3008(3)	0.0597(3)	0.049(2)
C(39)	0.4996(3)	−0.2546(3)	0.2615(2)	0.038(1)
C(40)	0.4609(4)	−0.2208(4)	0.3411(3)	0.052(2)
C(41)	0.3747(5)	−0.3090(5)	0.3842(4)	0.069(3)
C(42)	0.3226(6)	−0.4295(5)	0.3476(5)	0.088(3)
C(43)	0.3616(6)	−0.4652(5)	0.2681(5)	0.095(3)
C(44)	0.4487(5)	−0.3783(4)	0.2257(4)	0.070(2)
C(1)	0.3550(3)	−0.0626(3)	0.2297(3)	0.039(1)
C(2)	0.4008(4)	0.0702(4)	0.2548(3)	0.043(2)
C(3)	0.3937(4)	0.1212(4)	0.3443(3)	0.051(2)
O(3)	0.3918(4)	0.2307(3)	0.3416(2)	0.073(2)
C(4)	0.3974(8)	0.2989(7)	0.4383(4)	0.116(5)
C(5)	0.2677(8)	0.2732(8)	0.4585(5)	0.120(7)
C(6)	0.2950(4)	−0.1241(4)	0.1420(3)	0.047(2)
C(7)	0.1877(5)	−0.3227(5)	0.0469(4)	0.073(2)
C(8)	0.1912(6)	−0.4422(5)	0.0411(5)	0.094(3)
O(1)	0.2840(3)	−0.0778(3)	0.0840(2)	0.065(2)
O(2)	0.2478(3)	−0.2478(3)	0.1324(2)	0.060(1)
O(4)	0.3900(4)	0.0759(3)	0.4060(2)	0.072(2)

[a] U_{ep} is the isotropic equivalent thermal parameter and is defined as one-third the trace of the orthogonalized U_{ij} tensor

TABLE 3. Selected bond distances (Å) and angles (°), with e.s.d.s in parentheses, for [Pt{*trans*-CH(CO_2Et)=CH(CO_2Et)}(PPh_3)$_2$] (**1**)

Pt–P(1)	2.285(2)	Pt–P(2)	2.285(1)
Pt–C(1)	2.110(3)	Pt–C(2)	2.132(5)
P(1)–C(9)	1.829(4)	P(1)–C(15)	1.838(5)
P(1)–C(21)	1.828(4)	P(2)–C(31)	1.840(4)
P(2)–C(33)	1.822(4)	P(2)–C(39)	1.842(4)
C(1)–C(2)	1.466(6)	C(1)–C(6)	1.455(6)
C(2)–C(3)	1.457(6)	C(3)–O(3)	1.355(7)
C(3)–O(4)	1.209(7)	O(3)–C(4)	1.458(8)
C(4)–C(5)	1.390(9)	C(6)–O(1)	1.206(6)
C(6)–O(2)	1.364(5)	C(7)–C(8)	1.490(9)
C(7)–O(2)	1.457(6)		
C(1)–Pt–C(2)	40.5(2)	P(2)–Pt–C(2)	141.4(2)
P(2)–Pt–C(1)	101.0(2)	P(1)–Pt–C(2)	115.1(2)
P(1)–Pt–C(1)	155.5(2)	P(1)–Pt–P(2)	103.4(1)
Pt–P(1)–C(21)	115.0(1)	Pt–P(1)–C(15)	119.0(2)
Pt–P(1)–C(9)	112.3(2)	C(15)–P(1)–C(21)	101.6(2)
C(9)–P(1)–C(21)	105.5(2)	C(9)–P(1)–C(15)	101.8(2)
Pt–P(2)–C(39)	108.6(2)	Pt–P(2)–C(33)	113.4(2)
Pt–P(2)–C(31)	121.2(2)	C(33)–P(2)–C(39)	106.3(2)
C(31)–P(2)–C(39)	101.7(2)	C(31)–P(2)–C(33)	104.2(2)
Pt–C(1)–C(6)	113.0(3)	Pt–C(1)–C(2)	70.6(3)
C(2)–C(1)–C(6)	118.1(4)	Pt–C(2)–C(1)	69.0(3)
C(1)–C(2)–C(3)	117.8(4)	Pt–C(2)–C(3)	112.9(3)
C(2)–C(3)–O(4)	126.8(5)	C(2)–C(3)–O(3)	111.0(4)
O(3)–C(3)–O(4)	122.2(4)	C(3)–O(3)–C(4)	117.5(5)
O(3)–C(4)–C(5)	109.0(6)	C(1)–C(6)–O(2)	110.1(4)
C(1)–C(6)–O(1)	127.6(4)	O(1)–C(6)–O(2)	122.3(4)
C(8)–C(7)–O(2)	107.7(5)	C(6)–O(2)–C(7)	116.9(4)

TABLE 4 Torsion angles (°) of the diethyl fumarate ligand in complex **1**

C2–C1–C6–O1	4.4(7)
C2–C1–C6–O2	−174.6(4)
C6–C1–C2–C3	148.2(4)
C1–C2–C3–O3	−158.0(4)
C1–C2–C3–O4	22.2(8)
C2–C3–O3–C4	−174.4(5)
O4–C3–O3–C4	5.4(8)
C3–O3–C4–C5	−95.4(7)
C1–C6–O2–C7	−178.3(4)
O1–C6–O2–C7	2.6(7)
C8–C7–O2–C6	158.8(5)

of the related diethyl maleate complex, i.e. [Pt{*cis*-CH(CO_2Et)=CH(CO_2Et)}(PPh_3)$_2$] (**2**), which was detected only in trace quantities from the reaction of the diazo compound with the ethylene complex. Compounds **1** and **2** can thus be obtained by treatment of a solution of [Pt(CH_2=CH_2)(PPh_3)$_2$] in CH_2Cl_2 by diethyl fumarate or diethyl maleate, *trans* or *cis*-CH(CO_2Et)=CH(CO_2Et), respectively, in a two- to four-fold molar ratio (eqn. (2)); these products were isolated as a pale yellow (**1**, *c.* 55% yield) or a white (**2**, *c.* 75% yield) crystalline solid.

$$\begin{aligned}&[\mathrm{Pt(CH_2{=}CH_2)(PPh_3)_2}]\\&\quad+\,\textit{trans}(\text{or }\textit{cis})\text{-}\mathrm{CH(CO_2Et){=}CH(CO_2Et)}\longrightarrow\\&\quad[\mathrm{Pt}\{\textit{trans}(\text{or }\textit{cis})\text{-}\mathrm{CH(CO_2Et){=}CH(CO_2Et)}\}\mathrm{(PPh_3)_2}]\end{aligned} \qquad (2)$$

In the IR spectra, the strong bands observed at 1690(sh) and 1680 cm^{-1} (**1**), or at 1710 and 1685(sh) cm^{-1} (**2**), are assigned to ν(C=O) of the olefinic ligand. Moreover, the *cis* geometry of the phosphines is suggested [17] by the detection of a medium intensity (and sharp) band at 530 or 525 cm^{-1} (**1** or **2**, respectively).

The equivalence of the phosphine ligands is indicated by the singlet ^{31}P NMR observed at δ 26.8 or 26.6 (**1** or **2**, respectively, in CD_2Cl_2, relative to external H_3PO_4), with the ^{195}Pt satellites (^1J(PPt) = 3848.8 (**1**) or 3769.0 (**2**) Hz) (Table 5). These data are comparable with those exhibited by [Pt($CH_2{=}CH_2$)(PPh_3)$_2$] (δ 31.98, ^1J(PtP) = 3718.8 Hz, in $CDCl_3$, as measured in this work) and those quoted [18a] for [Pt{*trans*-CH(CO_2Me)=CH(CO_2Me)}(PPh_3)$_2$] (δ 23.8, ^1J(PPt) = 3860 Hz, in $CDCl_3$); the somewhat higher field shift, relative to the ethylene complex, agrees with the commonly observed behaviour reported [18a] for other substituted ethylene complexes related to ours. However, complex **2**, with the *cis*-olefin, exhibits (see above) a somewhat lower value (by *c.* 80–90 Hz) of ^1J(PPt) than those for the related *trans*-olefin complexes (**1** and the dimethyl fumarate analogue).

In the ^{1}H NMR spectra (Table 5), the olefinic proton resonance (C*H*CO_2Et) is observed as an apparent doublet (at δ 3.54 (**1**, in $CDCl_3$) or 3.00 (**2**, in CD_2Cl_2), with line separation of 6.3 (**1**) or 3.6 (**2**) Hz, with the expected ^{195}Pt satellites (^2J(HPt) = 56.4 (**1**) or 57.6 (**2**) Hz). Each of those doublets corresponds to the deceptively simple M part of an AA'M spin system (A, A' = ^{31}P; M = ^{1}H) [19a], as indicated by the analysis (see below) of the ^{13}C–^{1}H undecoupled NMR spectrum of the olefinic carbons, *C*HCO_2Et, which was shown to correspond to the X part (^{13}C) of an AA'MX spin system. In fact, by using the coupling constants obtained from the analysis (see below) of the X (^{13}C) part of this AA'MX system (^3J(AM) = 24.5 (**1**) or 22.6 (**2**) Hz; ^3J(A'M) = −18.0 (**1**) or −19.1 (**2**) Hz; ^2J(AA') = 22.0 (**1**) or 27.0 (**2**) Hz, the simulated M part (^{1}H) was in agreement with the experiment (see Fig. 1 for complex **2**).

The chemical shift of C*H*CO_2Et (see above) occurs at a lower field than that exhibited by the analogous ethylene complex (δ 2.30, in $CDCl_3$, as measured in this study), whereas the former complexes present lower ^2J(HPt) values than that of the latter (60.3 Hz), as

TABLE 5. IR, ^{1}H NMR and ^{31}P NMR for [Pt{*trans*-CH(CO_2Et)=CH(CO_2Et)}(PPh_3)$_2$] (**1**) and [Pt{*cis*-CH(CO_2Et)=CH(CO_2Et)}(PPh_3)$_2$] (**2**)

Compound	IR[a] ν(C=O)	^{1}H NMR[b]				^{31}P NMR[c]
		δ	J	Integ	Assignment	δ
1	1690sh	7 34–7.17 (m)		30	C_6H_5, phosphine	−114.2(s)[d]
	1680s	3.81 (dq)[e]	$^2J(H_AH_B) = 10.5$ $^3J(H_AH) = 7.2$	2	$CHCO_2CH_AH_BCH_3$ (*H*$_A$)	
		3 54(AA'*M*)[f]	$^3J(AM) = 24.5$ $^3J(A'M) = -18.0$ $^2J(AA') = 22.0$ $^2J(HPt) = 56.4$	2	C*H*$CO_2CH_2CH_3$	
		3.37 (dq)[g]	$^2J(H_AH_B) = 10.5$ $^3J(H_BH) = 7 2$	2	$CHCO_2CH_A$*H*$_BCH_3$	
		0 86 (t)	$^3J(HH_{A,B}) = 7.2$	6	$CHCO_2CH_AH_BC$*H*$_3$	
2	1710s	7 19–7.03 (m)		30	C_6H_5, phosphine	−113.4(s)[h]
	1685sh	3.43 (dq)[i]	$^2J(H_AH_B) = 10.8$ $^3J(H_AH) = 7.0$	2	$CHCO_2C$*H*$_AH_BCH_3$	
		3.23 (dq)[j]	$^2J(H_AH_B) = 10.8$ $^3J(H_BH) = 7.0$	2	$CHCO_2CH_A$*H*$_BCH_3$	
		3.00 (AA'*M*)[k]	$^3J(AM) = 22.6$ $^3J(A'M) = -19.1$ $^2J(AA') = 27.0$ $^2J(HPt) = 57 6$	2	C*H*$CO_2CH_2CH_3$	
		0.68 (t)	$^2J(HH_{A,B}) = 7 0$	6	$CHCO_2CH_AH_BC$*H*$_3$	

[a] Spectra recorded in KBr disc, ν in cm^{-1}; bands diagnostic of *cis*-phosphines at 530m (**1**) and 525m (**2**) cm^{-1}; abbreviations: s = strong; m = medium; sh = shoulder [b] Spectra recorded in $CDCl_3$ (**1**) or CD_2Cl_2 (**2**); δ values (ppm) relative to Me_4Si; d = doublet; t = triplet, dq = doublet of quartets; m = multiplet; J in Hz. [c] Spectra recorded in CD_2Cl_2; δ values (ppm) relative to external P(OMe)$_3$. [d] 26.8 ppm relative to H_3PO_4; J(PtP) = 3848.8 Hz. [e] Quartets centred at δ *c.* 3.82 and 3 79. [f] M part of an AA'M spin system (A,A' = ^{31}P, see footnote g of Table 6 and the text) as a deceptively simple doublet (apparent J = 6 3 Hz). [g] Quartets centred at δ *c* 3 39 and 3.35 [h] 26.6 ppm relative H_3PO_4, J(PtP) = 3769 0 Hz. [i] Quartets centred at δ *c.* 3.44 and 3 41 ppm. [j] Quartets centred at δ *c.* 3.25 and 3.22. [k] M part of an AA'M spin system (A,A' = ^{31}P, see footnote l of Table 6, Fig. 1 and the text) as a deceptively simple doublet (apparent J = 3.6 Hz).

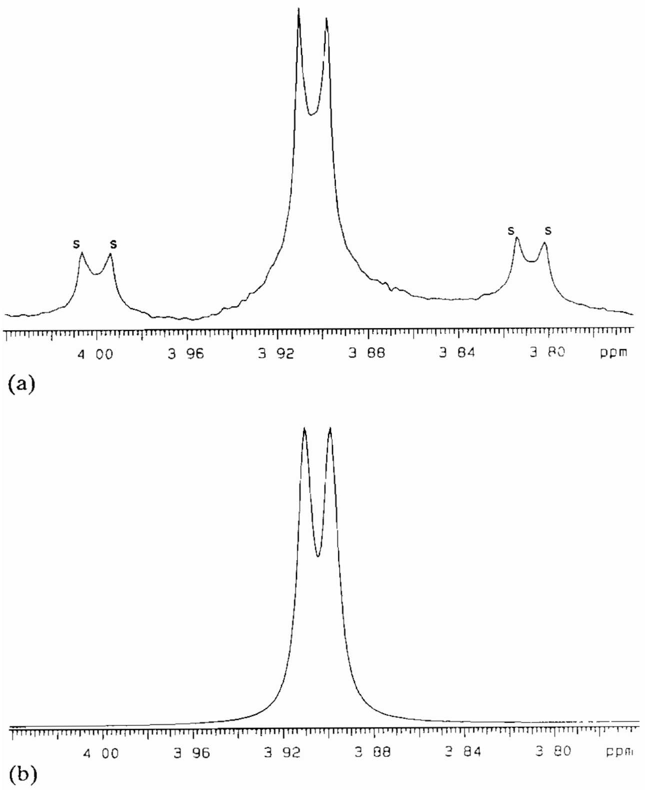

Fig. 1 (a) Experimental and (b) theoretical ^1H NMR spectra (M part of an AA'M (A,A' = ^{31}P, M = ^1H) spin system with $J(AM) = 22.6$, $J(A'M) = -19.1$ and $J(AA') = 27.0$ Hz) for the olefinic protons, $CH(CO_2Et){=}CH(CO_2Et)$, of complex 2 S = ^{195}Pt satellites.

known to occur [15] for related diphosphinic Pt(0) complexes with a substituted ethylene ligand (presenting an electron-acceptor substituent) ($^2J(HPt)$ in the common range 50–60 Hz); however, in these compounds, a more complex resonance pattern is observed [15] for the olefinic proton resonance due to the detected coupling with the two P nuclei and with protons of the phenyl rings of the phosphines, in second order spin systems

The methylene protons in **1** and **2** are not equivalent ($CHCO_2CH_AH_BCH_3$) and the resonance pattern for each of them is a doublet of quartets, due to coupling to the other one ($^2J(H_AH_B) = 10.5$ (**1**) or 10.8 (**2**) Hz) and to the three methyl protons ($^3J(HH_{A,B}) = 7.2$ (**1**) or 7.0 (**2**) Hz), respectively; these resonances are centred at δ 3.81 and 3.37 (**1**), or 3.43 and 3.23 (**2**). The methyl proton resonance occurs as a triplet ($^3J(HH_{A,B}) = 7.2$ (**1**) or 7.0 (**2**) Hz) at δ 0.86 (**1**) or 0.68 (**2**). Such couplings have been confirmed by ^1H-decoupling experiments. The inequivalence of the methylene protons is not unexpected since it is known [19b] that in a prochiral centre the paired 'ligands' (the two geminal methylene protons of the ethyl group, in our case) can be non-equivalent in chemical shift (anisochronous).

In the $^{13}C\{^1H\}$ NMR spectra of complexes **1** and **2** (Table 6), the resonance patterns for the olefinic carbons $CHCO_2Et$, centred at δ 47.77, were analysed as the X part of an AA'X (A,A' = ^{31}P) spin system [19b]. The values of the coupling constants were refined using a LAME iterative programme ($^2J(XA) = 36.7$, $^2J(XA') = -9.9$, $^2J(AA') = 22.0$ Hz (**1**); $^2J(XA) = 41.3$, $^2J(XA') = -10.7$, $^2J(AA') = 27.0$ Hz (**2**)), and the computed spectra were in accord with experiment (see Fig. 2 for **2**). In addition, ^{195}Pt satellites were also observed, corresponding to $J(CPt) = 212.1$ or 237.2 Hz, for **1** or **2**, respectively.

In the ^{13}C–^1H undecoupled spectra (Table 6), the $CHCO_2Et$ resonances were analysed as the X part of AA'MX (M = ^1H) spin systems corresponding to the above mentioned AA'X patterns observed in the $^{13}C\{^1H\}$ spectra, and the refinement by using a LAME iteractive programme provided, in addition, the coupling constants involving the olefinic proton $CHCO_2Et$ (M): $J(XM) = 161.7$, $^3J(AM) = 24.5$, $^3J(A'M) = -18.0$ Hz (**1**); $J(XM) = 156.3$, $^3J(AM) = 22.6$, $^3J(A'M) = -19.1$ Hz (**2**). These coupling constants were successfully applied in the simulation of the ^1H NMR doublet resonance for $CHCO_2Et$ (see above). The computed ^{13}C–^1H undecoupled spectra also agree with the experimental ones (see Fig. 3 for complex **2**).

The obtained values for $J(CH)$ (i.e. $J(XM)$, 161.7 (**1**) or 156.3 (**2**) Hz) are comparable with that reported, 156.5 Hz [20], for the related vinylidene ligand (=C=$CHCO_2Et$) of *trans*-[ReCl(=C=$CHCO_2Et$)(dppe)$_2$]. For both the fumarate and the maleate ligands, a pronounced high field shift (by *c.* 86 or 82 ppm, respectively) of the olefinic carbons is observed upon coordination (compared with δ 134.22 and 130.35, respectively, for the free olefins), in agreement with that observed [18b] in related systems.

In the ^{13}C–^1H undecoupled spectra of **1** and **2** (Table 6), the resonances of the methylene and methyl carbons of the olefin appear as the expected triplet ($J(CH)$) of quartets ($^2J(CH)$) and as a quartet ($J(CH)$) of triplets ($^2J(CH)$), centred at δ 58.74 (**1**) or 59.30 (**2**) (for the methylene carbon resonances) or at δ 13.96 (**1**) or 14.15 (**2**) (for the methyl carbons). All these multiplets coalesce into the expected singlets in the $^{13}C\{^1H\}$ spectra.

A fine structure has also been observed for the carbonyl carbon resonance of (**2**) which appears as a triplet ($^3J(CP) = 0.9$ Hz) at δ 172.76, whereas this pattern is not resolved for **1** in the broad singlet at δ 173.65; these resonances present the corresponding ^{195}Pt satellites with $^2J(CPt) = 37.3$ (**2**) or 39.1 (**1**) Hz Only a slight low field shift, by *c.* 7–8 ppm, results upon complexation of the olefin which, in the free state, presents such a resonance at δ 165.56 or 165.76 (diethyl fumarate or diethyl maleate, respectively).

TABLE 6. ^{13}C NMR data[a] for complexes **1** and **2**

Compound	δ	Pattern		J(CPt)	J(CP)	J(CH)	Assignment
		^{13}C{^{1}H}	^{13}C–^{1}H undecoupled				
1	173.65	s(br)	s(br)	39.1 (^2J)			CO_2Et
	134.91	AA′X[b]	m[c]	29 8 (^2J)	0.4 (J_{XA}) -47.6 ($J_{XA'}$)		PC (phosphines)
	133.69	t[d]	dm	21.1 (^3J)	[d]	162.4	*ortho-C* (phosphines)
	129.33	s	dt			160.5 7.3 (^2J)	*para-C* (phosphines)
	127.74	t[e]	dm		[e]	160.5	*meta-C* (phosphines)
	58.74	s	tq			146.5 4.2 (^2J)	$CHCO_2CH_2CH_3$
	47.77	AA′X[f]	AA′MX[g]	212.1	36 7 ($^2J_{XA}$) -9.9 ($^2J_{XA'}$)	161.7 (J_{XM})	$CHCO_2CH_2CH_3$
	13.96	s	qt			126.3 2.4 (^2J)	$CHCO_2CH_2CH_3$
2	172.76	t	t	37.3 (^2J)	0 9 (^3J)		CO_2Et
	135.98	AA′X[h]	m[c]	29.0 (^2J)	2.5 (J_{XA}) -49 0 ($J_{XA'}$)		PC (phosphines)
	134.21	t[i]	dm	20 0 (^3J)	[i]	162.3	*ortho-C* (phosphines)
	129.76	s(br)	dt			160.7 7 3 (^2J)	*para-C* (phosphines)
	128.11	t[j]	dm		[j]	163 2	*meta-C* (phosphines)
	59.30	s	tq			146 3 4 6 (^2J)	$CHCO_2CH_2CH_3$
	47.77	AA′X[k]	AA′MX[l]	237 2	41.3 ($^2J_{XA}$) -10.7 ($^2J_{XA'}$)	156.3 ($^2J_{XM}$)	$CHCO_2CH_2CH_3$
	14.15	s	qt			126.2 2.5 (^2J)	$CHCO_2CH_2CH_3$

[a] Spectra recorded in $CDCl_3$ (**1**) or CD_2Cl_2 (**2**); δ values (ppm) relative to Me_4Si; s = singlet, b = broad, d = doublet; t = triplet; q = quartet, m = complex multiplet; dd = doublet of doublets, dt = doublet of triplets, dm = doublet of multiplets; tq = triplet of quartets, qt = quartet of triplets, J in Hz.
[b] X part of an AA′X spin system (A,A′ = ^{31}P, see the text) with J(XA) = 0 4, J(XA′) = -47 6 and J(AA′) = 24 4 Hz.
[c] Unresolved multiplet, partially buried under the *ortho-C* (phosphines) resonances
[d] Due to virtual ^{31}P coupling, $1/2|^2J(CP) + {}^4J(CP)| = 6.8$ Hz.
[e] Due to virtual ^{31}P coupling, $1/2|^3J(CP) + {}^5J(CP)| = 5.3$ Hz
[f] X part of an AA′X spin system (A,A′ = ^{31}P, see footnote g).
[g] X part of an AA′MX spin system (A,A′ = ^{31}P, M = ^{1}H, see footnote f of Table 5 and the text) with J(XA) = 36.7, J(XA′) = -9 9, J(XM) = 161.7, J(AM) = 24.5, J(A′M) = -18.0 and J(AA′) = 22 0 Hz
[h] X part of an AA′X spin system (A,A′ = ^{31}P; see Fig 4 and the text) with J(XA) = 2.5, J(XA′) = -49.0 and J(AA′) = 27 1 Hz
[i] Due to virtual ^{31}P coupling, $1/2|^2J(CP) + {}^4J(CP)| = 6.5$ Hz.
[j] Due to virtual ^{31}P coupling, $1/2|^3J(CP) + {}^5J(CP)| = 5.0$ Hz
[k] X part of an AA′X spin system (A,A′ = ^{31}P; see footnote l, Fig. 2 and the text)
[l] X part of an AA′MX spin system (A,A′ = ^{31}P; M = ^{1}H, see footnote k of Table 5, Fig 3 and the text) with J(XA) = 41 3, J(XA′) = -10.7, J(XM) = 156.3, J(AM) = 22 6, J(A′M) = -19.1 and J(AA′) = 27.0 Hz.

The resonances of the different types of carbons at the aromatic rings of the phosphines have also been identified. Hence, the multiplets at the lower field region (δ *c.* 135) of the phenyl-carbon resonances are assigned to the carbons bonded to the phosphorus atoms. In the ^{13}C{^{1}H} NMR spectra they were analysed as the X part of an AA′X (A,A′ = ^{31}P; X = ^{13}C) spin system [19a], and the coupling constants (Table 6) were refined using a LAME iterative programme (J(XA) = 0.4, J(XA′) = -47.6 and J(AA′) = 24.4 Hz (**1**); J(XA) = 2.5, J(XA′) = -49.0 and J(AA′) = 27.1 Hz (**2**)), the computed spectra being in accord with the experimental ones (see Fig. 4 for complex **2**); moreover, the ^{195}Pt satellites were also detected (^2J(CPt) = 29.8 (**1**) or 29.0 (**2**) Hz). Such resonances have not been previously quoted [21] for related $[Pt(olefin)(PPh_3)_2]$ complexes.

The resonances of the *para*-carbons (Table 6) are broad singlets at δ 129.33 (**1**) or 129.76 (**2**), whereas those for the *ortho*- (δ = 133.69 or 134.21 for **1** or **2**, respectively) or *meta*-carbons (δ = 127.74 or 128.11 for **1** or **2**, respectively) are triplets due to virtual coupling with the P nuclei ($1/2|^2J(CP) + {}^4J(CP)| = 6.8$ (**1**) or 6.5 (**2**) Hz, *ortho*-C; $1/2|^3J(CP) + {}^5J(CP)| = 5.3$ (**1**) or 5.0 (**2**) Hz, *meta*-C). Such virtual couplings have not been quoted [21] for related complexes. In the ^{13}C–^{1}H undecoupled spectra, the resonances of the *para*-carbons split into a doublet (J(CH)) of triplets (^2J(CH)) due to coupling to the *para*- and the *meta*-protons, respectively. In addition, the resonances of the *meta*-carbons split into a doublet (J(CH)) of unresolved multiplets. ^{195}Pt satellites are observed for the resonances of the *ortho*-carbons (^3J(CPt) = 21.1

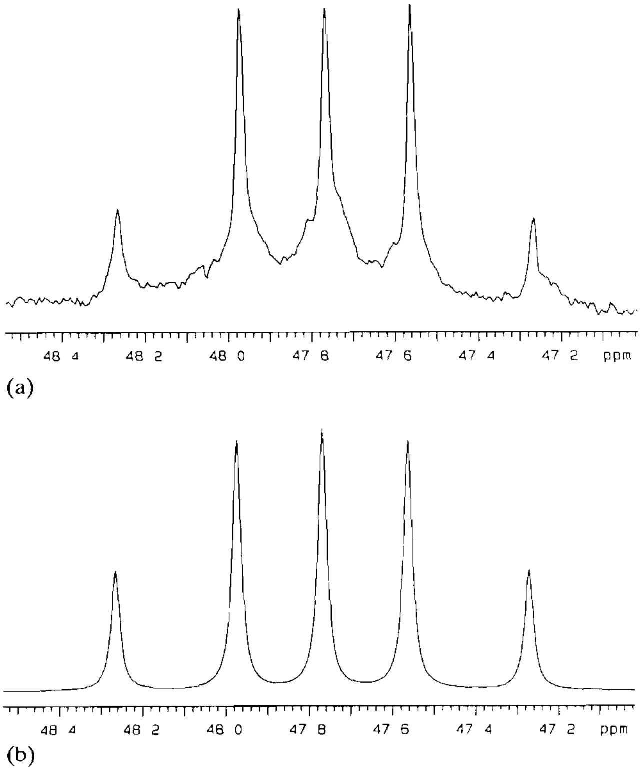

Fig. 2. (a) Experimental and (b) theoretical $^{13}C\{^1H\}$ NMR spectra (X part of an AA'X (A,A' = ^{31}P, X = ^{13}C) spin system with $J(XA) = 41.3$, $J(XA') = -10.7$ and $J(AA') = 27.0$ Hz) for the olefinic carbons, $CH(CO_2Et)=CH(CO_2Et)$, of complex **2**

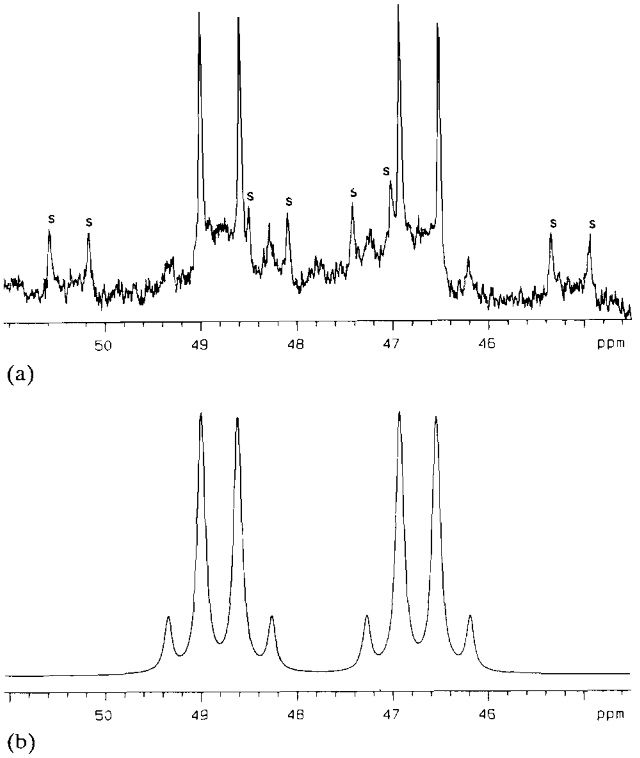

Fig. 3. (a) Experimental and (b) theoretical ^{13}C–^1H undecoupled spectra (X part of an AA'MX (A,A' = ^{31}P, X = ^{13}C, M = ^1H) spin system with $J(XA) = 41.3$, $J(XA') = -10.7$, $J(XM) = 156.3$, $J(AA') = 27.0$, $J(AM) = 22.6$ and $J(A'M) = -19.1$ Hz) for the olefinic carbons, $CH(CO_2Et)=CH(CO_2Et)$, of complex **2** S = ^{195}Pt satellites.

(**1**) or 20.0 (**2**) Hz), but not for those in the *para* position.

The chemical shifts of the *ortho*-, *para*- and *meta*-carbons (see above) are close to those reported by others [21] for related compounds, and correspond only to small complexation shifts of the phosphines.

The molecular structure of complex **1** has been authenticated by an X-ray diffraction analysis and is depicted in Fig. 5.

The crystal is constituted by well separated discrete molecules with no crystallographic imposed symmetry. The metal coordination is about planar, with the platinum atom 0.0465(8) Å apart from the mean plane of the four bonded atoms, P(1), P(2), C(1), C(2). The two *trans* carbonyls C(3)–O(4) and C(6)–O(1) are coplanar while the torsion angle C(3)–C(2)–C(1)–C(6) is 148.2(4)° indicating non-planarity for the C(3)–C(2)–C(1)–C(6) fragment. Selected geometrical parameters of the $[Pt(olefin)(PPh_3)_2]$ compounds have been revised in ref. 21.

The common Pt–P bond lengths range is 2.26–2.34 Å and these limit values are found in the complex $[Pt\{CCl_2=C(CN)_2\}(PPh_3)_2]$ [22] where the different substituents of the olefin are presumably responsible for the difference. In fact, in the present complex, to a symmetrically substituted olefin correspond equal Pt–P bond lengths (2.285(3) Å). The angle C(1)–Pt–C(2) (40.4(2)°) is the same as in the analogous ethylene complex (39.7(4)°) [18a], and the Pt–C distances (2.110(3), 2.132(5) Å) are close to those of the latter compound (2.11(1), 2.12(1) Å). Furthermore the dihedral angle, 3.3(1)°, between the P–Pt–P and Pt–C(1)–C(2) planes is small (it is 1.6° in the unsubstituted olefin compound [23]).

In the present structure the hydrogen atoms of C(2) and C(1) have been located from difference Fourier. This offers a unique opportunity to verify if some interaction with Pt could be responsible for the geometry of the coordination sphere: the Pt...H(1) contact distance is 2.52(3) Å and Pt...H(2) is 2.65(3) Å, while the corresponding Pt–C–H angles are 104(2) and 112(2)°, respectively. These non-symmetric values and the significant difference in the two Pt–C bond lengths, 2.110(3) and 2.132(5) Å, could be one the cause and the other the effect (or vice versa) of the observed asymmetry (Fig. 6). This was not investigated in the previous determinations of related compounds [21]. The relatively short Pt...H(1) distance of 2.52(3) Å is within the accepted range for a weak interaction [24, 25]. However, no diagnostic spectroscopic features of an

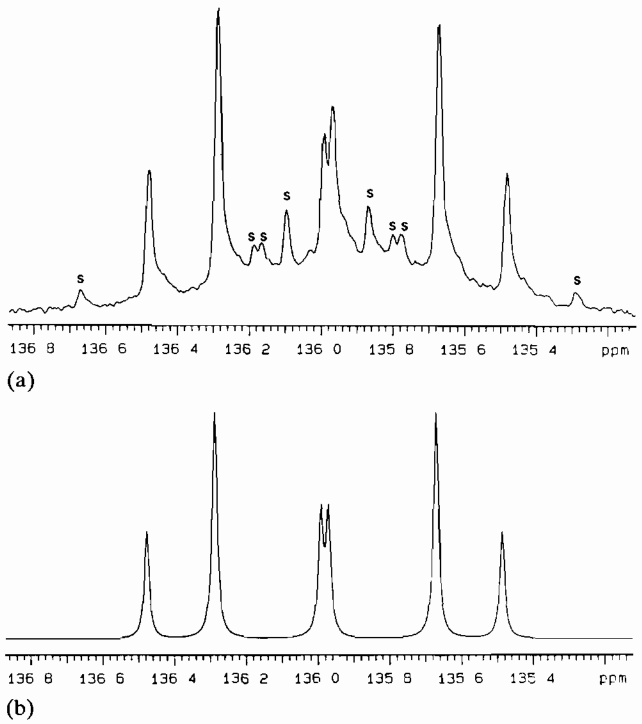

Fig. 4. (a) Experimental and (b) theoretical $^{13}C\{^1H\}$ NMR spectra (X part of an AA′X (A,A′ = ^{31}P; X = ^{13}C) spin system with $J(AX) = 2.5$, $J(A'X) = -49.0$ and $J(AA') = 27.1$ Hz) for the phenyl carbons bonded to the phosphorus atoms of complex **2**. S = ^{195}Pt satellites.

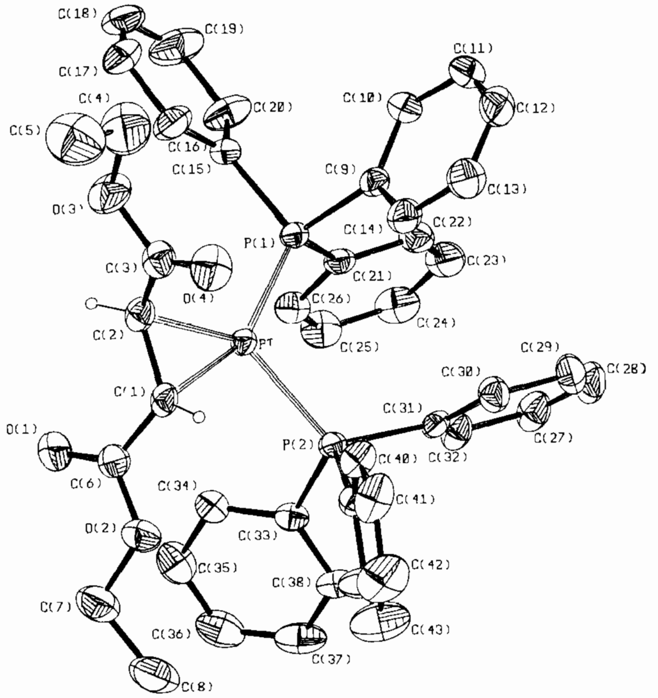

Fig. 5. Molecular structure of [Pt{*trans*-CH(CO$_2$Et)=CH(CO$_2$Et)}(PPh$_3$)$_2$] (**1**) (ORTEP view, ellipsoids at 50% probability).

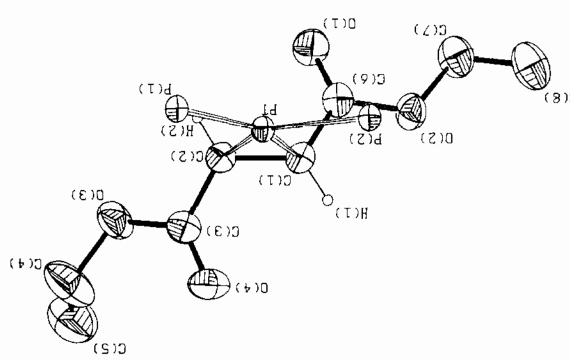

Fig. 6. A view of the structure of complex **1** on the C(1)–C(2)–C(3) plane, with the phenyl groups omitted.

agostic interaction [24] have been detected for complexes **1** or **2**, in particular IR ν(C–H) bands at low frequencies (2250–2800 cm^{-1}) (which, nevertheless, have been reported only in a limited number of cases), a lower value of ^1J(CH) (60–90 Hz) or a high field ^1H resonance for the agostic proton ($\delta < 0$ ppm). The lack of these NMR criteria for an agostic hydrogen, in our complexes, could result [24] from the occurrence of a fluxional agostic system. Other complexes are known where such criteria have also not been met, in particular for some Pd(II) or Pt(II) complexes with quinoline-8-carbaldehyde or 2-(benzylideneamino)-3-methylpyridine ligands [26], with a weak C–H agostic interaction which, however, has been monitored by the detection of a J(PtH) coupling constant (in the 8–20 Hz range).

Moreover, both J(HPt) (56.4 or 57.6 Hz) and J(HP) ($\leqslant 25$ Hz) (Table 5) for the olefinic proton in complexes **1** or **2**, respectively, are considerably smaller than those quoted [27] for the β-C–H agostic moiety of the norbornyl ligand at [Pt(C$_7$H$_{11}$)L$_2$]$^+$ (L$_2$ = peralkyldiphosphine) (*c*. 79–324 and 52–80 Hz, respectively), although some of our estimated values for J(HP), viz. J(AM) = 24.5 (**1**) or 22.6 (**2**) Hz (Table 6), are well above that reported (7.9 Hz) [27] for the non-agostic proton of the σ-alkyl group of the norbornyl ligand (complex with L$_2$ = Bu$_2^t$PCH$_2$CH$_2$PBu$_2^t$). This complex [27] and the analogous [Pt(C$_2$H$_5$)(diphosphine)]$^+$ [28] with an agostic ethyl group present typical values of J(CH) for the agostic β-C–H moieties.

Therefore, it appears there is no clear spectroscopic evidence for a typical agostic interaction in our complexes **1** or **2**. Moreover, only very rare examples of agostic Pd(0) or Pt(0) systems have been reported, and they include the otherwise highly unsaturated (two-coordinate and 14-electron) quasi-linear complexes [ML$_2$][M = Pd or Pt; L = PBu$_2^t$Ph] [9] in which the agostic interactions involve *ortho*-hydrogens of the phenyl rings and hydrogens of the tert-butyl groups.

In complex **1**, the C(1)–C(2) distance is 1.466(6) Å, a value comparable with those of the adjacent distances, C(1)–C(6), 1.455(6), and C(2)–C(3), 1.457(6) Å, which are shorter than the expected values for single bonds [29]. The non-planarity of the C(3)–C(2)–C(1)–C(6) fragment makes difficult an explanation in terms of electron delocalization, considering also the usual C=O bond lengths, 1.209(7) and 1.206(6) Å, for the adjacent carbonyl groups. The conformation of the substituted fumarate ligand is characterized by the torsion angles shown in Table 4, indicative of an overall *trans* geometry. In the analogous $C(COOCH_3)_2=CH(COOCH_3)$ complex, the bonds adjacent to the 'double bond' have a single-bond character [21].

The redox behaviour of complexes **1** and **2**, as well as of the parent ethylene compound, $[Pt(CH_2=CH_2)(PPh_3)_2]$, has been investigated by cyclic voltammetry and controlled potential electrolysis, at a Pt-disc or -gauze electrode, respectively, in 0.4 M $[Bu_4N][BF_4]/CH_2Cl_2$ or NCMe. They undergo an irreversible anodic wave at $E_p^{ox} = 1.02$, 1.07 or 0.82 V versus SCE, respectively, although, for compound **2**, another anodic wave is detected, as a shoulder of the main one, at scan rates below *c*. 0.6 V s^{-1} (at $E_p^{ox} = 0.97$ V, measured at 100 mV s^{-1}).

The higher oxidation potentials of **1** and **2** compared with the ethylene complex agree with the electron-withdrawing ability of the ester substituents with a conceivable resulting stabilizing effect on the HOMO. Moreover, the anodic process is believed to be metal centred since we did not detect, by cyclic voltammetry, an oxidation wave of free diethyl fumarate or maleate.

By controlled potential electrolysis, the anodic processes of these complexes involve 1.8, 1.3 or 1.4 electrons, respectively, possibly corresponding to the overall oxidation (although incomplete) of Pt(0) to Pt(II) with associated chemical reactions. These processes do not appear to involve anodically-induced proton evolution, as indicated by potentiometric titration of an electrolyzed solution of **1**. This contrasts with the behaviour observed for some diamino- or aminooxy-carbene complexes of Pd(II) or Pt(II), e.g., $[MCl_2\{CN(R)CH_2CH_2X\}(L)]$ (M = Pd or Pt, R = alkyl or aryl, X = NH or O, L = PR_3 or CNR) [30], as well as for the hydrido complexes $[PtHCl(PEt_3)_2]$ [31] or $[PtHR(PPh_3)_2]$ (R = C_3H_6CN, C_6H_5 or CH_2CF_3) [32], in which proton loss was observed upon anodic oxidation, generated from the carbene or the hydride ligand, respectively. Therefore, both the bonded fumarate and maleate derivatives in complexes **1** and **2** are not anodically activated towards proton loss, in contrast with the above-mentioned carbene and hydride ligands.

Conclusions

In this study, a diazo compound was activated by a Pt(0) metal centre towards N_2 loss and a coupling reaction to give a symmetric olefin in the *trans* isomeric form. Although the mechanism is unknown, diazo and derived carbene complexes can be postulated as intermediates and such a possibility will be investigated, as well as the mechanistic significance of the isomeric form of the product.

Moreover, X-ray data suggest that an α-hydrogen atom of the olefin ligand (i.e. an H atom bound to the olefinic coordinated C atom) can be involved in a weak interaction with the Pt(0) centre; such a rare type of interaction is elusive to detection by NMR and other spectroscopic methods, thus ruling out the possibility of involvement of, at least, a typical agostic interaction.

Acknowledgements

This work has been partially supported by the INIC/JNICT (Portugal)/CNR (Italy) cooperative research programme, and MURST (Italy). We also thank Professor Alberto Scrivanti (University of Venice) for helpful and stimulating discussions.

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