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Further X-ray and NMR investigations on bis-triphenylphosphinoplatinum complexes with polysubstituted olefins

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Abstract

Phosphine ^{13}C and ^{31}P NMR spectra are discussed for the compounds $Pt(PPh_3)_2(\eta^2\text{-olefin})$, with olefin = $CH(CN)=CH_2$, *trans*-$CH(CN)=CH(CN)$, $C(CN)_2=CH(CN)$, $C(CN)_2=C(CN)_2$, $CH(COOCH_3)=CH_2$, *trans*-$CH(COOCH_3)=CH(COOCH_3)$, $C(COOCH_3)_2=CH(COOCH_3)$, $C(COOCH_3)_2=C(COOCH_3)_2$, $C(CN)_2=C(CH_3)_2$. The chemical shifts of the phosphine *para* carbons reveal that CN or $COOCH_3$ groups bound to the olefin extend their electron-withdrawing effects as far as these carbons. The ^{195}Pt NMR spectrum of the last compound and the ^{31}P NMR spectrum of $Pt(PPh_3)_2[C(CN)_2=CH(OCH_3)]$ are also reported. For $Pt(PPh_3)_2[C(COOCH_3)_2=CH(COOCH_3)]$ the solid state structure, as determined by X-ray diffraction methods, is described. Cell parameters are: $a=14.275(5)$, $b=14.464(4)$, $c=12.172(4)$ Å, $\alpha=84.29(2)$, $\beta=81.44(2)$, $\gamma=63.86(2)°$, space group $P\bar{1}$. Substituents bending back occurs and conjugation results allowed only for the two *trans* carbonyls. A structural analysis is made for all of the title compounds so far studied by diffraction methods. This indicates that the P–Pt–P bond angle and the dihedral angle between the P–Pt–P and C–Pt–C planes are governed by intramolecular contacts between the olefin substituents and the phosphine ligands. For acyclic olefins, the P–Pt–P bond angle increases in the order $CX_2=CX_2<CX_2=CY_2<$ *trans*-$CHX=CHX<CH_2=CH_2$.

Introduction

A good amount of information on various aspects of Pt(0)[olefin] phosphino complexes is now available. Usually a simple representation of the platinum–olefin interaction is obtained through the Dewar–Chatt–Duncanson model (the metal causing a perturbation on the electronic structure of the olefin, whose π and π^* orbitals combine with the platinum orbitals to give more delocalized MOs). A prominent structural feature of these compounds is the 'bending back' [1] of the complexed olefin substituents with respect to the plane orthogonal to P–Pt–P and containing the olefin carbons. This increased the importance of the alternative cyclopropane description for the electronic structure. It is not clear which model gives a better overall simple representation, but in this context it is important to recall that both they allow for π interaction with olefin substituents, the former in an obvious way, and the latter taking into consideration the Walsh model for cyclopropane [2]. Subtler structural features imply the influence of substituents [3] on the P–Pt–P angle, on Pt–P, Pt–C and C–C distances and on the dihedral angle between the C–Pt–C and P–Pt–P planes [1]. Previous NMR studies [4, 5] on the title compounds indicated that when CN is the substituent the variations of ^{195}Pt and alkene ^{13}C chemical shifts can be explained through the effects of CN on the π antibonding MO energies and on the complexed olefin electron withdrawal, respectively. Noteworthy aspects of the ^{31}P spectra were the shielding effect of electron acceptor substituents and the internal differences between the two $^{1}J[P,Pt]$ in asymmetric compounds [4].

So far there has been no information about the geometry of $COOCH_3$ substituted olefins when complexed with Pt(0). However, it was known from an X-ray study that in free $C(COOCH_3)_2=C(COOCH_3)_2$ some substituents do not lie in the

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alkene plane, and from the ^{13}C spectra that also in $C(COOCH_3)_2{=}CH(COOCH_3)$ one of the substituents does not participate in conjugation [5, 6].

A better understanding of these complexes requires the examination of other effects originated by olefin substitution and a deeper knowledge of the factors having a significant role in determining the geometry. We present here the structure of $Pt(PPh_3)_2[C(COOCH_3)_2{=}CH(COOCH_3)]$, solved by diffraction methods, and the results of ^{13}C, ^{31}P and ^{195}Pt NMR investigations for this and related compounds.

Experimental

The compounds were synthesized as previously described [4]. Colorless single crystals of $Pt(PPh_3)_2[C(COOCH_3)_2{=}CH(COOCH_3)]$, suitable for X-ray studies, were obtained by recrystallization from dichloromethane/n-hexane solutions.

Collection and reduction of X-ray data

Monitoring of four standard reflections (0,1,1; 0,−1,−1; 0,1,−1; 0,−1,1) taken every 100 reflections, indicated no decay during data collection and a ψ scan of some suitable reflections, with the χ angle close to 90°, did not show absorption phenomena. Data were corrected by Lorentz and polarization effects. Table 1 summarizes crystal parameters and details of data collection.

TABLE 1. Summary of crystal data and intensity measurements

Formula	$C_{44}H_{40}O_6P_2Pt$
Formula weight	881.15
a (Å)	14.275(5)
b (Å)	14.464(4)
c (Å)	12.172(4)
α (°)	84.29(2)
β (°)	81.44(2)
γ (°)	63.86(2)
V (Å^3)	2229(1)
Z	2
Space group	$P\bar{1}$
Crystal dimensions (mm)	0.30 × 0.25 × 0.10
Radiation	Mo
Diffractometer	Nicolet P3
Scan mode	2θ–θ
Scan range	1
Background counts	¼ of scan time at the end of scan
2θ limits (°)	3, 56
No. reflections collected	10626
No. unique data ($I > 3\sigma$)	6223
Final no. variables	478
Final R, R_w	0.051, 0.069

Solution and refinement of the structure

The structure was solved with the usual combination of Patterson function and Fourier maps to obtain all the non-H atoms. Refinements by least-square procedures were applied subsequently. The function minimized was $\Sigma\omega(|F_o| - |F_c|)$, with weights of the type $\omega = a + F_o + cF_o^2$, where a and c are of the order of $2F_o$ (min.) and $2/F_o$ (max.) [7]. In the final cycles of least-squares the H atoms were included at fixed positions (d(C–H) = 1 Å, C–C–H angle = 120 or 109.5°). Calculations were performed running the Caos program [8] on an Eclipse MV/8000II Data General computer. Atomic scattering factors and anomalous dispersion terms were taken from the International Tables for X-ray Crystallography.

NMR spectra

NMR spectra were recorded in deuterated dichloromethane solutions of complexes in 10 mm sample tubes with a spectrometer Bruker WP 80, operating in broad-band proton-decoupling. For ^{13}C spectra the solvent signal at δ 53.73 ppm from TMS was used as internal standard; spectral width was 4500 Hz, digital resolution 1.1 Hz/pt, flip angle 30°. For ^{31}P 10% H_3PO_4 was used as external reference; spectral width 5200 Hz; digital resolution 1.2 Hz/pt; flip angle 45°. For ^{195}Pt spectral width was 20 000 Hz, digital resolution 1.2 Hz/pt and flip angle 30°; platinum δ values are referred to a platinum resonating at exactly 21.4 HMz in a magnetic field where the TMS protons resonate at exactly 100 MHz.

Results and discussion

Crystal structure of $Pt(PPh_3)_2[C(COOCH_3)_2{=}CH(COOCH_3)]$

The crystal is built up from well separated discrete molecules with no crystallographically imposed symmetry. Figure 1(a) shows a computer generated drawing of the complex with H atoms omitted. Atomic coordinates are given in Table 2, and Table 3 contains relevant structural parameters. The metal coordination is approximately planar, platinum being out of the mean square plane of the four bound atoms, P(1), P(2), C(1), C(2), by 0.07 Å. If the olefin is considered as a monodentate ligand then the metal is 0.07 Å out of the plane given by P(1), P(2), mp (mp = mid-point of the ethylene C–C bond).

The expected bending back of the $COOCH_3$ groups is shown by the angles Pt–mp–C(3), Pt–mp–C(5) and Pt–mp–C(7) being larger than 90° (104.8°, 101.4° and 102.2°, respectively). Noticeably while the two *trans* carbonyls C(5)–O(3) and C(7)–O(5) are almost coplanar with C(2)–C(1)–C(5) and C(1)–C(2)–C(7), re-

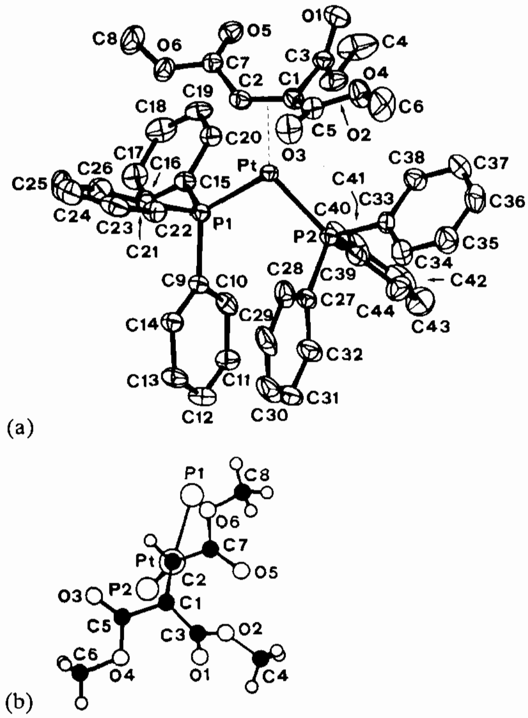


Fig. 1. (a) Computer generated drawing of $Pt(PPh_3)_2$-$[C(COOCH_3)_2{=}CH(COOCH_3)]$ with H atoms omitted. (b) A view of the structure along Pt–C(2) bond, with phenyl groups omitted.

TABLE 2. Atomic coordinates and isotropic thermal parameters with their e.s.d.s in parentheses

	x	y	z	B_{eq}[a]
Pt(1)	0.25922(4)	0.13096(3)	0.16784(3)	3.03(1)
P(1)	0.2605(2)	0.2785(2)	0.0153(2)	3.2(1)
P(2)	0.2166(2)	0.1906(2)	0.2916(2)	3.4(1)
O(1)	0.1849(8)	−0.1864(7)	0.2920(8)	5.8(4)
O(2)	0.0900(7)	−0.0291(8)	0.2514(9)	5.5(4)
O(3)	0.4699(8)	−0.0581(9)	0.2905(8)	6.1(4)
O(4)	0.3381(8)	−0.1444(8)	0.4023(7)	5.5(3)
O(5)	0.1843(7)	−0.0363(7)	0.0504(7)	4.9(3)
O(6)	0.3274(8)	0.0450(8)	−0.0466(7)	5.0(3)
C(1)	0.2856(9)	−0.0364(9)	0.2321(9)	3.7(4)
C(2)	0.3244(9)	0.0103(8)	0.1255(9)	3.7(4)
C(3)	0.184(1)	−0.0943(9)	0.263(1)	4.0(4)
C(4)	−0.011(1)	−0.074(2)	0.267(2)	10(1)
C(5)	0.3766(9)	−0.0804(9)	0.3090(9)	4.0(4)
C(6)	0.417(2)	−0.185(1)	0.482(1)	7.5(7)
C(7)	0.2690(9)	0.0025(9)	0.0418(9)	3.6(4)
C(8)	0.283(2)	0.049(1)	−0.137(1)	6.7(7)
C(9)	0.2515(8)	0.4101(8)	0.0083(8)	3.3(3)
C(10)	0.149(1)	0.4550(9)	0.034(1)	4.2(4)
C(11)	0.141(1)	0.552(1)	0.036(1)	4.6(4)
C(12)	0.234(1)	0.607(1)	0.013(1)	5.2(5)
C(13)	0.333(1)	0.564(1)	−0.013(1)	5.0(5)
C(14)	0.344(1)	0.4661(9)	−0.017(1)	4.1(4)
C(15)	0.1442(9)	0.2922(9)	−0.0646(9)	3.9(4)
C(16)	0.126(1)	0.380(1)	−0.159(1)	4.6(4)
C(17)	0.040(1)	0.385(1)	−0.218(1)	5.5(5)
C(18)	−0.027(1)	0.304(1)	−0.183(1)	6.0(6)
C(19)	−0.011(1)	0.221(1)	−0.092(1)	5.3(5)
C(20)	0.0749(9)	0.2133(9)	−0.0318(9)	3.9(4)
C(21)	0.389(1)	0.2697(9)	−0.0599(9)	3.8(4)
C(22)	0.4874(9)	0.233(1)	−0.006(1)	4.6(5)
C(23)	0.589(1)	0.225(1)	−0.059(2)	6.4(7)
C(24)	0.595(1)	0.251(1)	−0.159(2)	7.3(8)
C(25)	0.500(2)	0.289(1)	−0.213(1)	7.9(8)
C(26)	0.394(1)	0.299(1)	−0.165(1)	6.0(6)
C(27)	0.312(1)	0.2847(9)	0.2754(9)	4.1(4)
C(28)	0.425(1)	0.253(1)	0.267(1)	5.0(5)
C(29)	0.501(1)	0.322(1)	0.255(1)	6.5(6)
C(30)	0.470(2)	0.416(1)	0.251(1)	7.4(7)
C(31)	0.359(2)	0.451(1)	0.257(1)	7.1(7)
C(32)	0.279(1)	0.383(1)	0.272(1)	5.8(5)
C(33)	0.2346(9)	0.0913(9)	0.4274(8)	3.7(3)
C(34)	0.308(1)	0.094(1)	0.491(1)	5.1(5)
C(35)	0.313(1)	0.019(1)	0.593(1)	5.9(6)
C(36)	0.242(1)	−0.056(1)	0.631(1)	5.5(5)
C(37)	0.168(1)	−0.061(1)	0.568(1)	5.5(5)
C(38)	0.163(1)	0.014(1)	0.465(1)	4.8(5)
C(39)	0.074(1)	0.2521(9)	0.301(1)	4.6(4)
C(40)	−0.003(1)	0.272(1)	0.230(1)	5.3(4)
C(41)	−0.112(1)	0.316(1)	0.239(1)	6.3(5)
C(42)	−0.143(1)	0.338(1)	0.322(2)	7.8(7)
C(43)	−0.068(2)	0.320(1)	0.394(2)	8.4(9)
C(44)	0.042(1)	0.275(1)	0.385(1)	6.0(6)

[a] $B_{eq} = (4/3)\Sigma_{ij}[A_iA_jB_{ij}]$.

spectively (the dihedral angle between C(2)–C(1)–C(5) and C(1)–C(5)–O(3) is 15° and between C(1)–C(2)–C(7) and C(2)–C(7)–O(5) is 5°), the carbonyl C(3)–O(1) is in a plane almost perpendicular to C(2)–C(1)–C(3) (the dihedral angle between C(2)–C(1)–C(3) and C(1)–C(3)–O(1) is 86°). This lets the geminal oxygen atom O(2) be near the metal (Pt–O(2) = 3.06 Å) but prevents conjugation between the carbonyl and residual C(1)–C(2) π bonding (see Fig. 1(b)).

Selected geometrical parameters of $Pt(PPh_3)_2$-(olefin) compounds reported so far in the literature are given in Table 4 for comparison purposes. The Pt–P bond distances range is 2.26–2.34 Å, these values belonging to the complex $Pt(PPh_3)_2[CCl_2{=}C(CN)_2]$ [11] where the asymmetry of the olefin is presumably responsible for the difference. On the contrary in our complex the olefin asymmetry is not reflected on these parameters, the bond lengths being equal, i.e. 2.283(4) and 2.286(3) Å. The C(1)–Pt–C(2) bond angle range is 39.7–47.1°, these values belonging to the complexes $Pt(PPh_3)_2(C_2H_4)$ [15] and $Pt(PPh_3)_2(CCl_2{=}CCl_2)$ [9], respectively.

This angle in our complex (39.9(6)°) is the same as in the ethylene derivative (39.7(4)°). Also Pt–C distances in our complex (2.10(1), 2.13(2) Å) are close to the ones of the ethylene derivative (2.11(1), 2.12(1) Å). The asymmetry of $C(COOCH_3)_2{=}CH(COOCH_3)$ seems to have just a small influence on these parameters. Furthermore the dihedral angle between P–Pt–P and Pt–C(1)–C(2) planes (D.A.) is

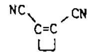
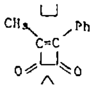
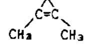
TABLE 3. Selected interbond distances and angles for the complex $Pt(PPh_3)_2[C(COOCH_3)_2{=}CH(COOCH_3)]$

Distances (Å)	
Pt-P(1)	2.283(4)
Pt-P(2)	2.286(3)
Pt-C(1)	2.13(2)
Pt-C(2)	2.10(1)
P(1)-C(9)	1.82(1)
P(1)-C(15)	1.85(1)
P(1)-C(21)	1.83(1)
P(2)-C(27)	1.83(1)
P(2)-C(33)	1.86(2)
P(2)-C(39)	1.84(1)
C(1)-C(2)	1.44(2)
C(1)-C(3)	1.51(2)
C(1)-C(5)	1.51(2)
C(2)-C(7)	1.49(2)
C(3)-O(1)	1.19(2)
C(3)-O(2)	1.34(2)
C(4)-O(2)	1.42(2)
C(5)-O(3)	1.20(2)
C(5)-O(4)	1.34(2)
C(6)-O(4)	1.43(2)
C(7)-O(5)	1.21(1)
C(7)-O(6)	1.33(2)
C(8)-O(6)	1.44(2)
Angles (°)	
P(1)-Pt-P(2)	105.3(1)
C(1)-Pt-C(2)	39.9(6)
P(1)-Pt-C(2)	103.1(5)
P(2)-Pt-C(1)	112.2(4)
Pt-P(1)-C(9)	122.8(5)
Pt-P(1)-C(15)	111.5(5)
Pt-P(1)-C(21)	109.8(5)
C(9)-P(1)-C(15)	101.9(6)
C(9)-P(1)-C(21)	103.1(6)
C(15)-P(1)-C(21)	106.5(6)
Pt-P(2)-C(27)	108.9(4)
Pt-P(2)-C(33)	116.3(4)
Pt-P(2)-C(39)	119.0(4)
C(27)-P(2)-C(33)	103.3(6)
C(27)-P(2)-C(39)	107.4(6)
C(33)-P(2)-C(39)	100.3(7)
C(2)-C(1)-C(3)	120(1)
C(2)-C(1)-C(5)	115(1)
C(3)-C(1)-C(5)	116(1)
C(1)-C(2)-C(7)	123(1)
C(1)-C(3)-O(1)	125(1)
C(1)-C(3)-O(2)	112(1)
O(1)-C(3)-O(2)	123(1)
C(1)-C(5)-O(3)	125(1)
C(1)-C(5)-O(4)	111(1)
O(3)-C(5)-O(4)	124(1)
C(2)-C(7)-O(5)	127(1)
C(2)-C(7)-O(6)	109.7(9)
O(5)-C(7)-O(6)	124(1)
C(3)-O(2)-C(4)	116(1)
C(5)-O(4)-C(6)	115(1)
C(7)-O(6)-C(8)	117(1)

noticeable large (13.2°). One of the main factors determining the observed variations of geometrical parameters in Table 4 can be the steric interaction between the coordinated molecules. Therefore we have made calculations for all of $Pt(PPh_3)_2$(olefin) complexes so far studied by diffraction methods to check intramolecular repulsions between H of phosphine phenyls and substituents of the olefins. H positions were calculated for the compounds of Table 4, whether not published, after generation of rigid phenyl groups (C–C–H angle 120°, d(C–H) = 1 Å), using Shelx program [18]. In relation to these calculations, we have maintained the labelling of the original references; in any case C(1) and C(2) are the olefin C atoms. The resulting intramolecular contacts are: (a) Cl(4)–H(of C(6)R1C) = 2.74 Å, being the van der Waals distance = 1.80 (Cl) + 1.20 (H) = 3.00 Å with reliability within 0.10 Å [19], in addition quasi-contacts are: Cl(1)–H(of C(6)R2B) = 3.15 Å, Cl(1)–H(of C(6)R1B) = 3.22 Å and Cl(2)–H(of C(6)R1C) = 3.11 Å; (b) N(4)–H(of C(34)) = 2.70 Å, being van der Waals distance = 1.50 (N) + 1.20 (H) = 2.70 Å [19], in addition quasi-contacts are: N(2)–H(of C(38)) = 3.00 Å and N(4)–H(of C(35)) = 3.00 Å; (c) Cl(2)–H(of C(6)R1C) = 3.01 Å, N(1)–H(of C(6)R1A) = 2.74 Å; (d) has the olefinic moiety disordered [9]; (e) unpublished coordinates [12]; (f) C(3)–H(40) = 2.66 Å, C(4)–H(40) = 2.74 Å. C(3) and C(4) belong to the CN groups, we estimate C(of CN)–H van der Waals distance similar than the N–H one (2.70 Å) [19]; (g) F(1)–H(of C(4)1C) = 2.59 Å, F(2)–H(of C(6)1C) = 2.34 Å, being the van der Waals distance = 1.35 (F) + 1.20 (H) = 2.55 Å [19]; (h) O(3)–H(of C(2)A) = 2.54 Å, H(1)(of C(1))–H(of C(2)F) = 2.39 Å, with related van der Waals distances of 2.60 (O–H) and 2.40 (H–H) Å [19]. The compound (h) shows a P–Pt–P bond angle much higher (109.5°) than the other *trans*-olefin complexes of this group. It has been reported that the two p-$NO_2C_6H_4$ groups are almost perpendicular [14] to the Pt–C(1)–C(2) plane (87°). In other words these aromatic rings lie in a plane that resembles the original (non-coordinated) olefin plane. This arrangement allows a minimum contact between the substituents of the olefin and the phenyls of the phosphines, therefore the PPh_3 groups can be closer to the olefin opening up the P–Pt–P angle.

To give an estimate of intramolecular repulsions for the ethylene derivative, positions of $CH_2{=}CH_2$ hydrogens were calculated assuming planarity. This gave H(phenyl)–H(ethylene) contacts = 2.47 and 2.56 Å (van der Waals distance being 2.40 Å [19]). As in coordinated ethylene the CH bonds are bent away from the metal, the actual H–H distances are longer than those calculated for the planar olefin. So the repulsions in the ethylene complex can be considered missing. We conclude that planarity of the C_2H_4 complex is a pure electronic requirement.

TABLE 4. Selected geometrical parameters in $Pt(PPh_3)_2$(olefin) complexes

Olefin (acyclic)	P–Pt–P	Pt–P(1)	Pt–P(2)	C–Pt–C[a]	C–C[b]	Pt–C(1)	Pt–C(2)	D.A.[c]	Reference
$CCl_2=CCl_2$	100.6(2)	2.278(8)	2.292(7)	47.1(1)	1.62(3)	2.02(2)	2.05(3)	12.3	9 (a)
$C(CN)_2=C(CN)_2$	101.4(3)	2.288(8)	2.291(9)	41(1)	1.49(5)	2.10(3)	2.12(3)	8.3	10 (b)
$C(CN)_2=CCl_2$	102.0(2)	2.260(6)	2.339(6)	40.6(9)	1.42(3)	2.00(2)	2.10(2)	1.9	11 (c)
$CCl_2=CF_2$	103.4(2)	2.303(6)	2.314(5)						9 (d)
t-C(CN)Ph=C(CN)Ph	103.51(9)	2.295(2)	2.289(2)	41.7(3)	1.50(1)	2.10(1)	2.11(1)	8.9	12 (e)
t-C(CN)H=C(CN)H	104.4(2)	2.277(5)	2.296(4)	43(1)	1.53(4)	2.05(2)	2.16(2)	5.2	13 (f)
$C(COOCH_3)_2=CH(COOCH_3)$	105.3(1)	2.283(4)	2.286(3)	39.9(6)	1.44(2)	2.10(1)	2.13(2)	13.2	this work
t-$C(CF_3)H=C(CF_3)H$	105.9(1)	2.302(3)	2.322(3)	41.0(4)	1.43(1)	2.03(1)	2.05(1)	10.8	3a (g)
t-CHZ=CHZ[d]	109.5(1)	2.298(4)	2.261(4)	38.8(4)	1.42(1)	2.09(1)	2.16(1)	8.9	14 (h)
$CH_2=CH_2$	111.6(1)	2.265(2)	2.270(2)	39.7(4)	1.43(1)	2.11(1)	2.12(1)	1.6	15 (i)
Olefin (cyclic)									
	103.90(3)	2.284(1)	2.301(1)	42.3(1)	1.504(4)	2.08(1)	2.09(1)	2.4	12 (j)
	103.9(2)	2.271(4)	2.309(4)	43.5(7)	1.53(4)	2.00(2)	2.12(2)	22.1	3b (k)
	105.5(1)	2.278(4)	2.288(4)	41.6(4)	1.50(1)	2.11(1)	2.12(1)	1	16 (l)
	107.0(1)	2.289(3)	2.278(3)	42.2(5)	1.52(2)	2.07(1)	2.14(2)	3.2	17 (m)
	108.3(4)	2.26(2)	2.26(1)	42(2)	1.50	1.98(5)	2.21(5)	16	16 (n)

[a] Bond angle C(1)–Pt–C(2). [b] C–C is C(1)–C(2) bond distance. [c] D.A. = dihedral angle between the planes P(1)–Pt–P(2) and C(1)–Pt–C(2). [d] Z = p-$NO_2C_6H_4$.

In $Pt(PPh_3)_2[C(COOCH_3)_2=CH(COOCH_3)]$ O(2)–H(of C(38)) = 2.76 Å and O(5)–H(of C(20)) = 2.67 Å, being the van der Waals distance 1.40 (O) + 1.20 (H) = 2.60 Å [19]; this is in line with the behaviour observed for the other complexes.

Contacts between H (of phenyls) and substituents of the olefin seem also important for cyclic olefins and have been reported for (j) [12], (k) [3b] and (m) [17]. In the case of the complex (k) the asymmetry of the Pt–olefin bond has been related to intramolecular contacts [3b]. For (l) H(of C(2a))–H(of C(2C)) = 2.55 Å; in addition C(1)–H(of C(2F)) = 2.80 Å may indicate some approach between H(of C(2F)) and H(of C(1)). The structure of (n) is affected by high standard deviations [16], therefore no calculations were made.

We can consider $Pt(PPh_3)_2(C_2H_4)$ as a non-strained species. If we increase substitution on the olefin the steric strain also increases. This can be alleviated as follows:

(i) by pushing back the phosphines, e.g. closening up the P–Pt–P bond angle (this value is 111.6(1)° for the ethylene complex);

(ii) by rotating around the axis mp-Pt, e.g. increasing the dihedral angle between the planes P–Pt–P and Pt–C(1)–C(2) (this D.A. is almost 0° for the ethylene complex);

(iii) by rotating around an axis that passes the olefin midpoint and is approximately normal to the P–Pt–P plane. In other words providing asymmetry of Pt–olefin bonds, Pt–C(1) and Pt–C(2) lengths (these values are equal for the ethylene complex, e.g. 2.11(1) and 2.12(1) Å).

Looking at Table 4 we can see that:

1. The P–Pt–P bond angle ranges from 100.6 to 111.6°. In addition, for acyclic olefins, it increases in the order $CX_2=CX_2 < CX_2=CY_2 <$ *trans*-CHX=CHX $< C_2H_4$.

2. The dihedral angle (D.A.) ranges from 1.6 to 22.1°. The maximum value is found for 1-methyl-2-phenylcyclobutendione, a very crowded olefin [3b]. It seems that effects (i) and (ii) are not correlated;

3. The asymmetry of Pt–olefin bonds seems to correlate with effect (ii) so that lower D.A. are associated with higher Pt–olefin asymmetry (C_2H_4 and (h) complexes excepted). This explains the trend for the complexes $CCl_2=CCl_2$, $C(CN)_2=C(CN)_2$ and $CCl_2=C(CN)_2$ (D.A. = 12.3, 8.3 and 1.9°, respectively, and Pt–C(1), Pt–C(2) = 2.02(3) and 2.05(3) Å; 2.10(3) and 2.12(3) Å; 2.00(2) and 2.10(2) Å, respectively).

Therefore we can conclude that, besides effect (i), olefins of the type $CX_2=CX_2$ alleviate the strain mainly through (ii) and $CX_2=CY_2$ through (iii). The large value of D.A. for $Pt(PPh_3)_2[C(COOCH_3)_2=CH(COOCH_3)]$ indicates that this complex uses the set (ii) and thus also in this respect it behaves like the derivatives of symmetric olefins.

On the other hand one may expect that olefins of the type $CX_2=CH_2$ prefer the latter type of rotation by which the X groups can move further from the phosphines, H atoms being closer to the metal than normally. We are also planning to study this type of complex by diffraction methods.

^{13}C NMR spectra

^{13}C NMR parameters of phosphine carbons for the $Pt(PPh_3)_2$[olefin] compounds are reported in Table 5.

ortho Carbons

In the symmetric compounds these carbons originate the multiplets expected for the X part of an AA'X system. In the asymmetric compounds their spectral patterns are interpreted as the overlap of the multiplets expected for the X and Y parts of an ABX and an ABY system, the ^4J[C,P] being negligible; the chemical shift difference of the *ortho* carbons of the non-equivalent phosphines is large enough to give separate resonances, except for methylacrylate and $C(CN)_2=C(CH_3)_2$ derivatives. ^{195}Pt satellites are always well detectable.

As for other metal complexes [20, 21] the complexation shift is small (this recalls the weak changes observed on going from PPh_3 to PPh_4^+ [22]) and just slightly affected by olefin substitution, being of about 0.45 ppm, apart from $C(COOCH_3)_2=CH(COOCH_3)$, in which it is significantly larger: 0.7 ppm.

^2J[C,P] values, presumably positive (about 12–13 Hz except for the monosubstituted olefin derivatives where they are smaller), are lower than in the free ligand, like in other metal complexes [21].

meta Carbons

In the symmetric compounds the phosphine *meta* carbons originate the multiplets expected for the X parts of AA'X systems. From these spectra AA' scalar coupling could be estimated for $CH(CN)=CH(CN)$ and $C(CN)_2=C(CN)_2$ derivatives. In the asymmetric compounds these carbons give rise to spectral patterns pertinent to one ABX system for each phosphine, although the internal chemical shifts difference can be detected only for the $C(COOCH_3)_2=CH(COOCH_3)$ derivative. ^4J[C,Pt] and ^5J[C,P] have no appreciable effect at our resolution.

In line with what has been observed for many other triphenylphosphine derivatives, the complexation shift of *meta* carbons is relatively small. In the cyano substituted compounds the shielding shows a slow almost linear decrease with increasing number of substituents (Fig. 2), while in the carbomethoxy derivatives it is almost unaffected by the number of substituents (Fig. 3).

The ^3J[C,P] values are assumed positive and are between free phosphine (7 Hz) and phosphonium salts (12–13 Hz) [22], as is usual for metal phosphine complexes.

TABLE 5. ^{13}C data of triphenylphosphine in $Pt(PPh_3)_2$(olefin)[a]

Olefin	C *ortho*			C *meta*		C *para*
	δ	^2J[P,C][b]	$\lvert ^3J[Pt,C] \rvert$	δ	^3J[P,C][b]	δ[c]
$CH(CN)=CH_2$	134.0	9	29	128.4	12	130.0
	134.3	8	29			
$CH(CN)=CH(CN)$	134.2	13	20	128.7	10	130.7
$C(CN)_2=C(CH_3)_2$	134.2	12	26	128.5	10	130.3
$C(CN)_2=CH(CN)$	134.1	12	19	128.9	12	131.2
	134.0	12	19			
$C(CN)_2=C(CN)_2$	134.2	12	19	129.2	11	131.7
$CH(COOCH_3)=CH_2$	134.2	10	25	128.3	9	129.6
$CH(COOCH_3)=CH(COOCH_3)$	134.2	13	21	128.4	11	130.0
$C(COOCH_3)_2=CH(COOCH_3)$	134.3	12	21	128.2	10	130.0
	134.4	13	20	128.3	10	
$C(COOCH_3)_2=C(COOCH_3)_2$	134.4	12		127.9	10	129.8

[a] δ values are in ppm from TMS, calculated from the frequencies relative to CD_2Cl_2 assumed to resonate at $\delta=53.73$. J values are in Hz. [b] ^4J[P,C] and ^5J[P,C], which result negligible in asymmetric compounds, are assumed to be 0 in all these compounds. [c] Average values are reported for *para* carbons.

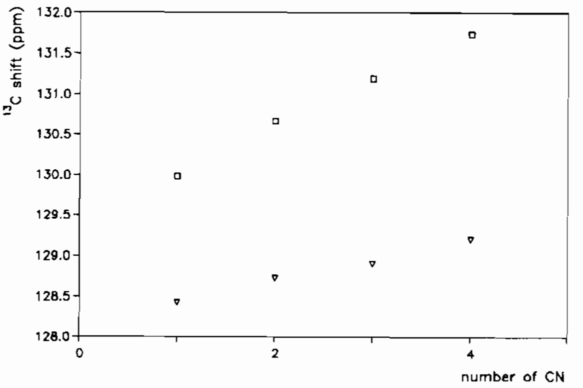


Fig. 2. ^{13}C shift: □ average $\delta_{(C_{para})}$ and ▽ average $\delta_{(C_{meta})}$ of triphenylphosphine in $Pt(PPh_3)_2(C_2H_{4-n}(CN)_n)$, $n = 1$–4.

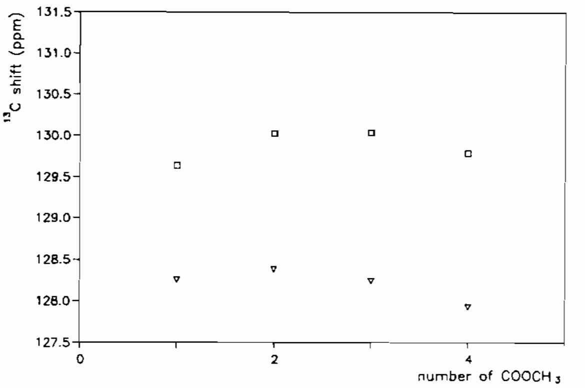


Fig. 3. ^{13}C shift: □ average $\delta_{(C_{para})}$ and ▽ average $\delta_{(C_{meta})}$ of triphenylphosphine in $Pt(PPh_3)_2(C_2H_{4-n}(COOCH_3)_n)$, $n = 1$–4.

para Carbons

Coupling with phosphorus affects the *para* carbon resonances for all the compounds. In $CH_2{=}CH(CN)$, $CH_2{=}CH(COOCH_3)$, $CH(CN){=}CH(CN)$, *trans*-$CH(COOCH_3){=}CH(COOCH_3)$ and $C(CN)_2{=}C(CN)_2$ complexes the signal is broadened. In $C(COOCH_3)_2{=}CH(COOCH_3)$, $C(CN)_2{=}CH(CN)$ and $C(CN)_2{=}C(CH_3)_2$ derivatives there are evidences of splitting, due also to the lack of equivalence of the *para* carbons of the two phosphines. This is an expected behaviour, ^4J[C,P] being 0.3 Hz in free PPh_3, usually higher in metal complexes, and 3 Hz in RPh_3P^+ salts [22].

Due to the introduction of a CN group the average $\delta_{(C_{para})}$ increases significantly; the difference in effect on the two phosphines is difficult to appreciate because of its smallness and the concomitant coupling with phosphorus. Thus in CN derivatives the complexation shift of *para* carbons increases almost linearly on increasing the number of substituents from 1.4 ppm in $Pt(PPh_3)_2[CH(CN){=}CH_2]$ to 3.1 ppm in $Pt(PPh_3)_2[C(CN)_2{=}C(CN)_2]$ (Fig. 2). The latter value is close to the one of $(PPh_3)_2\overline{PtC(CN)_2CH_2C}(CN)_2$ [23], which is usually described as a Pt(II) complex.

It is generally agreed that in substituted phenyls changes in screening constants of *para* carbons reflect changes in their electron density [24], even if a distinction between total and π electron charge seems not achievable through NMR [25]. The $\delta_{(C_{para})}$ of triphenylphosphine were already assumed as indicators of electron density withdrawal in metal complexes [20, 21]. Interestingly the quaternarization of triphenylphosphine to give RPh_3P^+ is followed by a strong deshielding of *para* carbons (≈ 7 ppm). Thus it can be concluded that in cyano substituted derivatives the electron density at *para* carbons is lower than in the free ligand and decreases almost linearly with increasing substitution.

The effect of increasing the number of $COOCH_3$ is not so straightforward (Fig. 3). In methylacrylate and dimethylfumarate derivatives the $COOCH_3$ causes electronwithdrawal from the phosphines. In this respect $COOCH_3$ is less efficient than CN; this parallels the β effects being smaller for the former than for the latter in free olefins [5]. However introduction of more substituents to give $C_2H(COOCH_3)_3$ and $C_2(COOCH_3)_4$ derivatives is not followed by further electron withdrawal from the phosphines. The above reported X-ray structure of $Pt(PPh_3)_2[C(COOCH_3)_2{=}CH(COOCH_3)]$ shows that only the two *trans* CO groups can conjugate with the complexed olefin; it is likely that the same thing holds for the tetrasubstituted derivative. Thus the trend of $\delta_{(C_{para})}$ in the $COOCH_3$ series can be explained considering that non-conjugating CO are associated with much weaker withdrawal.

The dependence of the average *para* carbon chemical shift on the sum of Hammett substituent constants [26] ($\Sigma\sigma_p$) shown in Fig. 4 is consistent with the above explanation.

^{31}P and ^{195}Pt NMR spectra

For $Pt(PPh_3)_2[C(CN)_2{=}C(CH_3)_2]$ only the four more intense signals could be detected on the ^{195}Pt spectrum (X part of an ABX system). The ^{31}P spectrum consists of an AB quartet within the two smaller quartets from molecules with ^{195}Pt (AB part of an ABX spectrum). Spectral parameters are: δ_{Pt} −505, δ_{P1} 24.5, δ_{P2} 22.7 ppm; ^1J[Pt,P1] 4512, ^1J[Pt,P2] 2925, ^2J[P1,P2] 26 Hz. The platinum chemical shift is close to the value found in $Pt(PPh_3)_2$[*trans*-$CH(CN){=}CH(CN)$] [4].

For $Pt(PPh_3)_2[CH(OCH_3){=}C(CN)_2]$ the ^{31}P spectrum can be described as above, spectral parameters being: δ_{P1} 24.4, δ_{P2} 23.5 ppm; ^1J[Pt,P1] 3078, ^1J[Pt,P2] 4480, ^2J[P1,P2] 25 Hz.

Within platinum compounds direct Pt–P coupling constants cover a huge range. Small values are found

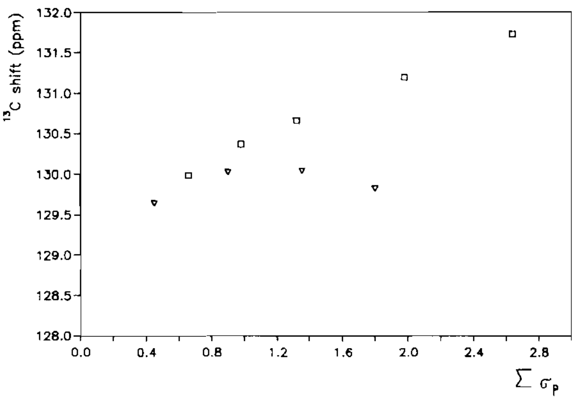


Fig. 4. ^{13}C shift: average $\delta_{(C_{para})}$ of triphenylphosphine. $\Sigma\sigma_p$: sum of the Hammett constants [22] for all the substituents on an olefin. □ $Pt(PPh_3)_2[C_2H_{4-n}(CN)_n]$, $n = 1$–4, $Pt(PPh_3)_2[C(CN)_2{=}C(CH_3)_2]$; ▽ $Pt(PPh_3)_2[C_2H_{4-n}(COOCH_3)_n]$, $n = 1$–4.

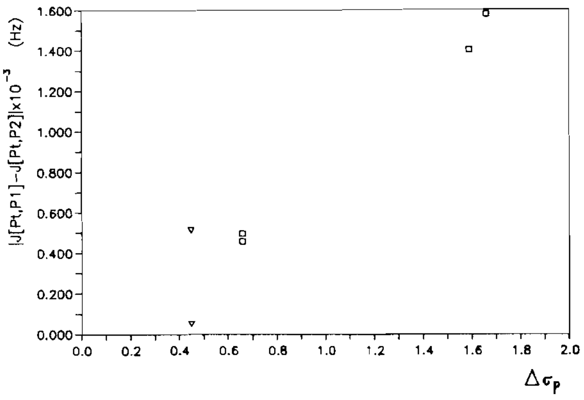


Fig. 5. $|J[Pt,P1]-J[Pt,P2]|$: internal difference of direct $J[Pt, P]$ values. $\Delta\sigma_p$: $\Sigma\sigma_p$ of substituents on C(1) − $\Sigma\sigma_p$ of substituents on C(2). □ $Pt(PPh_3)_2[C_2H_{4-n}(CN)_n]$, $n = 1, 3$, $Pt(PPh_3)_2[C(CN)_2{=}C(CH_3)_2]$, $Pt(PPh_3)_2[C(CN)_2{=}CH(OCH_3)]$; ▽ $Pt(PPh_3)_2[C_2H_{4-n}(COOCH_3)_n]$, $n = 1, 3$.

TABLE 6. Internal differences of direct platinum–phosphorus coupling constants in compounds with asymmetric olefins

Olefin	$\lvert J[Pt,P1]-J[Pt,P2]\rvert$ (Hz)
$CH(CN){=}CH_2$	497
$C(CN)_2{=}C(CH_3)_2$	1587
$C(CN)_2{=}CH(OCH_3)$	1402
$C(CN)_2{=}CH(CN)$	460
$CH(COOCH_3){=}CH_2$	514
$C(COOCH_3)_2{=}CH(COOCH_3)$	52

where Pt and P belong to three-membered rings [27]. Phosphine complexes have much larger constants. Even if these parameters are known for several Pt(0) derivatives [4, 28], a comprehensive understanding of their behaviour has not made much progress so far.

Inspection of previously reported data [4] shows that in ethene derivatives the introduction of a CN group on the complexed olefin increases one Pt–P coupling constant and decreases the other, in almost equivalent amounts, so that successive substitutions do not originate relevant changes in the average values, differently from the complexes with substituted acetylenes, where these values have a significant dependence on substitution [29]. For asymmetric olefins there are noticeable internal differences in $^1J[Pt,P]$ (Table 6). Spectra of the $C(CN)_2{=}C(CH_3)_2$ and $C(CN)_2{=}CH(OCH_3)$ complexes show that this difference becomes larger when the substituents on one carbon are far apart in electronic properties from those on the other carbon (Fig. 5). Differences of this magnitude are not usual in Pt(0) complexes where the metal interacts with double bonds even if this implies different atoms (N=O, P=C, S=C) [28], the differences being larger than 2000 Hz [28a] only for $Pt(\eta^2\text{-}S{=}CO)(PPh_3)_2$ and $Pt(\eta^2\text{-}S{=}CS)(PPh_3)_2$. The effect seems related to the shape of the delocalized π system of the unsaturate molecule.

Within our compounds $CH(COOCH_3){=}CH_2$ results as effective as $CH(CN){=}CH_2$ and $C(CN)_2{=}CH(CN)$ in differentiating the two platinum–phosphorus coupling constants, but $C(COOCH_3)_2{=}CH(COOCH_3)$ is much less effective. This is another feature explainable through the lack of conjugation of the third carbonyl: the delocalized π system of the tricarbomethoxyethylene moiety, resembling that of the dimethylfumarate derivative, influences almost equally the two phosphorus atoms, while methylacrylate, acrylonitrile and tricyanoethylene differentiate much stronger the two olefinic carbons and the two phosphorus atoms.

Except for $C(COOCH_3)_2{=}CH(COOCH_3)$ the introduction of CN or $COOCH_3$ on the complexed olefin increases the ^{31}P shieldings, even if by different amounts. For CN substituted complexes the average δ_P decreases almost linearly with increasing number of substituents (Fig. 6) and therefore with increasing $\delta_{(C_{para})}$ (Fig. 7). Also for $COOCH_3$ substituted derivatives the average δ_P decreases with increasing substitution, but the plot of shift values versus the number of substituents (Fig. 6) shows a variation in slope going from dimethylfumarate to tricarbomethoxyethylene derivatives. Once again we have evidence for a different behaviour of the third and fourth $COOCH_3$. Increasing the number of electron withdrawing substituents, the expected stronger interaction between PPh_3 and the Pt(olefin) moiety is reflected by the stronger perturbation of the PPh_3,

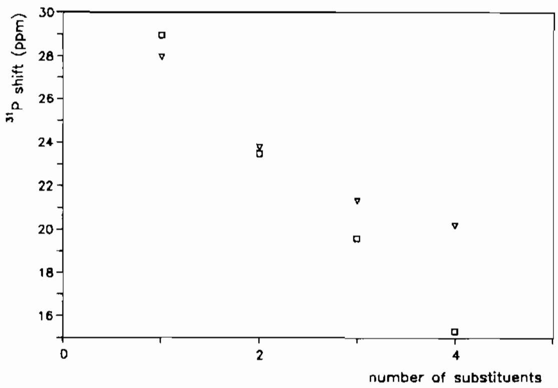


Fig. 6. ^{31}P shift: average δP values. ☐ $Pt(PPh_3)_2[C_2H_{4-n}(CN)_n]$, $n = 1–4$; ▽ $Pt(PPh_3)_2[C_2H_{4-n}(COOCH_3)_n]$, $n = 1–4$.

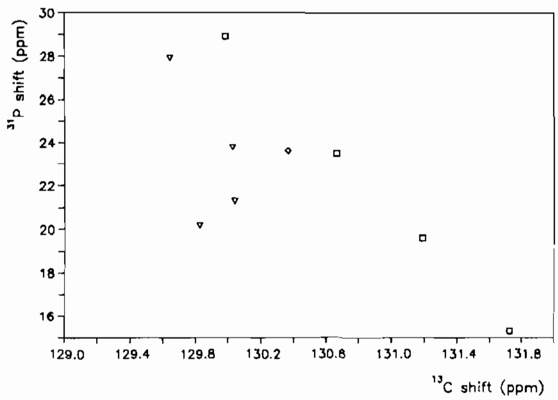


Fig. 7. ^{31}P shift: average δP values. ^{13}C shift: average $\delta_{(C\ para)}$ values. ☐ $Pt(PPh_3)_2[C_2H_{4-n}(CN)_n]$, $n = 1–4$; ◇ $Pt(PPh_3)_2[C(CN)_2{=}C(CH_3)_2]$; ▽ $Pt(PPh_3)_2[C_2H_{4-n}(COOCH_3)_n]$, $n = 1–4$.

as monitored by $\delta_{(C\ para)}$, while the ^{31}P frequencies move towards the free phosphine value. The charge released cannot be the only important factor determining the trend of ^{31}P chemical shifts in these compounds. This can be inferred also looking at Fig. 7.

Conclusions

As expected in $Pt(PPh_3)_2[C(COOCH_3)_2{=}CH(COOCH_3)]$ the olefin substituents are not coplanar. More remarkably only the two *trans* carbonyls can conjugate with the 'olefin' carbon–carbon bond. The P–Pt–P bond angle is 105.3(1)°, i.e. similar to those of *trans*-disubstituted olefin complexes and the geometry around platinum does not reflect the asymmetry of the alkene.

Structural analysis made on $Pt(0)(PPh_3)_2$(olefin) compounds so far studied by diffraction methods shows that finer variations in the geometry between the moieties $Pt(PPh_3)_2$ and olefin are governed mainly by steric factors.

From ^{13}C spectra it can be concluded that in bistriphenylphosphino platinum complexes with CN and $COOCH_3$ substituted olefins the electron densities at the phosphine *para* carbons are smaller than in the free ligand and that they decrease further by increasing the number of substituents, the magnitude of these variations being related to the conventional substituent effects. In $Pt(PPh_3)_2[C(COOCH_3)_2{=}CH(COOCH_3)]$ and $Pt(PPh_3)_2[C(COOCH_3)_2{=}C(COOCH_3)_2]$ electron withdrawal from phosphine *para* carbons is close to that of $Pt(PPh_3)_2$[*trans*-$CH(COOCH_3){=}CH(COOCH_3)$]; this provides further support to our description if one remembers that one carbonyl in the former compound and presumably two in the latter do not conjugate with the olefin π bonding and therefore the corresponding $COOCH_3$ groups lose their electron acceptor character.

For $Pt(0)(PPh_3)_2$(olefin) complexes electron withdrawal from the $Pt(PPh_3)_2$ fragment towards the complexed olefin was already inferred through interpretation of ESCA spectra [30], but the influence of electron acceptor substituents on the olefin was left undefined. The ^{13}C chemical shift [5] of the complexed alkene suggested that its carbons compensate the loss of electron density due to the substituents by subtracting electron charge from the $Pt(PPh_3)_2$ moiety.

When, because of substitution, the olefin carbons are not equivalent the NMR spectra reflect the inequivalence induced on the phosphines through differences in phosphorus chemical shifts and platinum–phosphorus coupling constants, the latter being specially strong, and through much smaller differences in carbon chemical shifts.

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