Zerovalent Platinum Chemistry. Part 12.[1] Unexpected Reactivity of $[Pt(PPh_3)_2(O_2)]$ towards *ortho* and *para* Quinones and the Structures of 1:1 Adducts with *p*-Benzoquinone and 1,4-Naphthoquinone†

Maddalena Pizzotti,*[a] Sergio Cenini,[a] Renato Ugo[a] and Francesco Demartin[b]

[a] *Dipartimento di Chimica Inorganica e Metallorganica, Universita' di Milano and Centro C.N.R., Via Venezian 21, 20133 Milano, Italy*

[b] *Istituto di Chimica Strutturistica Inorganica, Universita' di Milano and Centro C.N.R., Via Venezian 21, 20133 Milano, Italy*

The reaction of $[Pt(PPh_3)_2(O_2)]$ with both *o*- and *p*-benzoquinones produces only 1:1 adducts characterised by a pseudo-ozonide metallacycle involving one carbonyl group with a spiranic steric arrangement. Strangely the second carbonyl group of the quinone does not react with an excess of $[Pt(PPh_3)_2(O_2)]$. The X-ray structures of the adducts with *p*-benzoquinone and 1,4-naphthoquinone show a skew conformation of the metallacycle with the quinone moiety still planar. Reaction with $[Pt(PPh_3)_2(O_2)]$ produces only a slight perturbation of the π-electronic conjugated structure of the quinone, since the C=O bond length of the free carbonyl group does not change. Molecular models suggest the absence of steric hindrance for a second pseudo-ozonide metallacycle involving the *para* carbonyl group. It is suggested that the lack of reactivity could be of kinetic origin.

The reaction of $[Pt(PPh_3)_2(O_2)]$ with some organic carbonyl groups was first carried out in our laboratory[2] many years ago and was subsequently extended to a variety of suitable substrates.[3,4] Some carbonyl groups, *e.g.* those of amides and esters, do not react,[2] but other unsaturated groups like activated olefins,[5] acetylenic bonds,[6] and dicarbonyl compounds[7] do.

We recently investigated the reactivity of a non-traditional carbonyl group, the quinone, which forms part of a conjugated π system in a ring. A reaction between $[Pt(PPh_3)_2(O_2)]$ and quinones is expected, because this kind of conjugation produces a slight perturbation of the C=O bond length; the length of the C=O bond in *p*-benzoquinone is similar to that in ketones.[8] Furthermore the reaction of a quinone with two molecules of $[Pt(PPh_3)_2(O_2)]$ should form two metallo pseudo-ozonide rings. Thus the two platinum atoms could be linked electronically. Such a linkage can be considered an extended system of conjugation and has the potential to transmit electronic effects from one platinum atom to another. This hypothesis prompted us to attempt the reaction of both the carbonyl groups; the results are now described.

Results

The carbonyl groups of both *para* and *ortho* quinones, although part of a cyclic unsaturated structure, react with $[Pt(PPh_3)_2(O_2)]$ to produce adducts which, based on IR spectroscopic and analytical characterisation (Table 1), are the products of a reaction involving only one carbonyl group. This gives one pseudo-ozonide ring incorporating a platinum atom even under different reaction conditions. The lack of reactivity of the second carbonyl group could be explained for the *ortho* quinones by steric effects, although *ortho* quinones are basically α-diketones which are known to react with both carbonyl groups to give two pseudo-ozonide metallacycles or to break down into acid anhydrides.[7] The lack of double reactivity of the *para* quinones is totally unexpected.

† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii

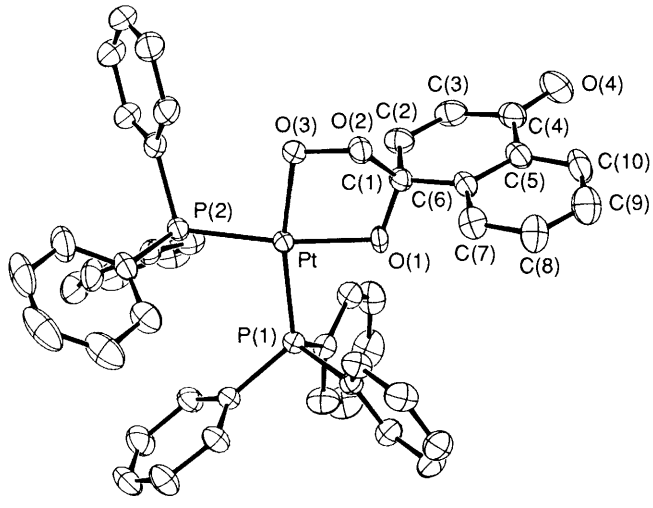
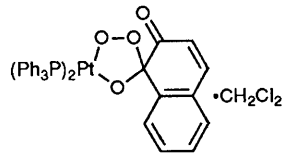
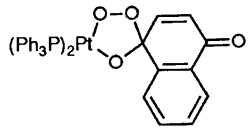
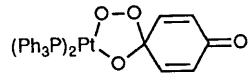
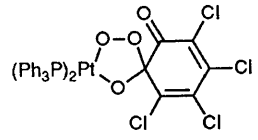


Fig. 1 ORTEP drawing of complex **2**. Thermal ellipsoids are drawn at 30% probability.

We carried out an X-ray investigation of the 1:1 *p*-benzoquinone and 1,4-naphthoquinone adducts with the aim of discovering why the second carbonyl group does not react. One reason could be a strong perturbation of the π-electronic structure of the organic moiety but this would be reflected in the ring conformation and bond lengths. That the lack of reactivity could be of steric origin and due to the presence of bulky phosphines cannot be completely rejected. The reaction is much more complex when a highly substituted quinone such as tetramethyl-*p*-benzoquinone is used. In this case not even the expected 1:1 adduct is formed, the reaction producing only an unknown product whose nature is at present under investigation.[9]

Molecular Structures.—Perspective views of adducts **2** and **3** (Table 1) are shown in Figs. 1 and 2, respectively. Selected bond distances and angles are compared in Table 2. The

Table 1 Analytical and IR data

Compound	Analysis (%)*		IR (Nujol, cm^{-1})		
	C	H	ν(C=O)	ν(C–O)	ν(O–O) or δ(C–O)
1 	57.0 (56.8)	3.8 (3.8)	1680	1025	925–850
2 	61.6 (60.8)	4.0 (4.0)	1650	1030	—
3 	57.5 (58.6)	3.8 (4.0)	1663	1065	991–854
4 	49.9 (50.4)	2.7 (3.0)	1680	1090	800

* Calculated values in parentheses.

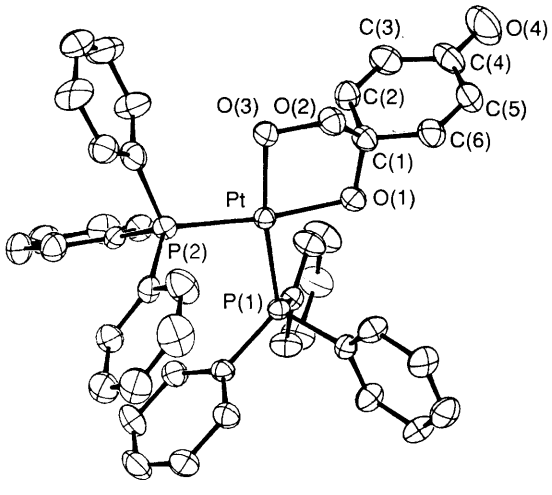


Fig. 2 ORTEP drawing of complex **3**. Thermal ellipsoids are drawn at 30% probability.

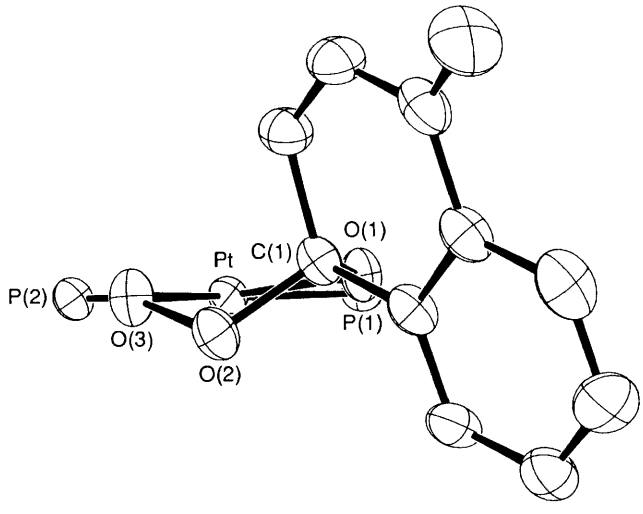


Fig. 3 ORTEP partial view of complex **2**, showing the conformational arrangement of the pseudo-ozonide moiety

intermolecular contacts in both compounds are normal van der Waals interactions, the shortest distances between refined atoms being C ··· C 3.68 and C ··· O 3.34 Å for **3** and C ··· C 3.45 and C ··· O 3.33 Å for **2**. The two square-planar complexes contain a puckered five-membered metallacycle of skew conformation, the result of the quinone insertion into the platinum–oxygen bond. The conformational parameters of this part are very similar in both compounds, as can be appreciated in Figs. 3 and 4 where perspective views almost parallel to the co-ordination plane are reported. The displacements of the C(1) and O(2) atoms from the Pt, O(1), O(3) plane are as follows: compound **3**, C(1) −0.193(8), O(2) +0.529(5); **2**, C(1) −0.131(4), O(2) +0.563(3) Å. The plane of the C(1)–C(6) ring makes a dihedral angle of 75.8° in **3** and 76.0° in **2** with the co-ordination plane. The pattern of bond distances within the metallacycles indicates residual partial double-bond character for the C(1)–O(1) interaction whereas C(1)–O(2) and O(2)–O(3) display lengths typical of single bonds. The asymmetry of the O(1)–C(1)–O(2) bond system has already been observed in the structure of the adduct formed between $[Pt(PPh_3)_2(O_2)]$ and acetone.[2]

To the best of our knowledge only two other examples of

Table 2 Selected bond distances (Å) and angles (°) for compounds **2** and **3**

	3	**2**	*p*-Benzoquinone[8]	1,4-Naphthoquinone[10]
Pt–P(1)	2.257(2)	2.268(1)		
Pt–P(2)	2.215(2)	2.243(1)		
Pt–O(1)	2.024(4)	2.033(3)		
Pt–O(3)	2.011(4)	2.015(3)		
O(1)–C(1)	1.381(7)	1.369(5)	1.222(8)	1.224(3)
C(1)–O(2)	1.446(8)	1.430(5)		
O(2)–O(3)	1.485(6)	1.500(4)		
C(1)–C(2)	1.508(10)	1.515(6)	1.477(6)	1.466(4)
C(1)–C(6)	1.473(9)	1.509(6)	1.477(6)	1.481(3)
C(2)–C(3)	1.321(10)	1.356(7)	1.322(8)	1.321(4)
C(3)–C(4)	1.442(12)	1.466(8)	1.477(6)	1.468(4)
C(4)–O(4)	1.222(9)	1.204(6)	1.222(8)	1.221(3)
C(4)–C(5)	1.437(12)	1.478(7)	1.477(6)	1.483(4)
C(5)–C(6)	1.302(10)	1.404(6)	1.322(8)	1.401(3)
C(5)–C(10)		1.421(7)		1.389(3)
C(6)–C(7)		1.365(7)		1.385(5)
C(7)–C(8)		1.398(7)		1.374(4)
C(8)–C(9)		1.357(8)		1.383(4)
C(9)–C(10)		1.355(8)		1.370(4)
P(1)–C(111)	1.830(6)	1.828(4)		
P(1)–C(121)	1.829(6)	1.820(4)		
P(1)–C(131)	1.818(6)	1.822(4)		
P(2)–C(211)	1.823(7)	1.823(5)		
P(2)–C(221)	1.815(8)	1.842(5)		
P(2)–C(231)	1.819(6)	1.805(4)		
P(1)–Pt–P(2)	98.97(7)	100.76(4)		
P(1)–Pt–O(1)	88.18(13)	85.94(8)		
P(2)–Pt–O(3)	89.81(14)	91.17(9)		
O(1)–Pt–O(3)	83.04(18)	81.17(11)		
P(1)–Pt–O(3)	171.21(14)	168.06(9)		
P(2)–Pt–O(1)	171.85(12)	171.04(9)		
Pt–O(1)–C(1)	108.5(4)	110.0(2)		
O(1)–C(1)–O(2)	110.0(5)	110.4(3)		
C(1)–O(2)–O(3)	105.6(4)	106.2(3)		
O(2)–O(3)–Pt	105.0(3)	104.9(2)		
C(2)–C(1)–O(2)	102.5(6)	109.1(4)		
C(2)–C(1)–C(6)	113.3(6)	115.2(4)	117.48(37)	118.0(2)
O(1)–C(1)–C(6)	114.3(6)	108.5(4)	121.06(27)	121.8(3)
C(1)–C(2)–C(3)	121.2(7)	122.3(5)	121.06(27)	122.3(3)
C(2)–C(3)–C(4)	122.5(8)	122.5(5)	121.06(27)	121.8(3)
C(3)–C(4)–C(5)	117.1(7)	117.2(4)	117.48(37)	118.0(2)
C(3)–C(4)–O(4)	121.7(9)	121.4(5)	121.06(27)	120.4(3)
C(5)–C(4)–O(4)	121.1(9)	121.4(6)	121.06(27)	121.6(3)
C(4)–C(5)–C(6)	121.7(8)	121.6(5)	121.06(27)	120.1(2)
C(5)–C(6)–C(1)	123.9(7)	120.9(4)	121.06(27)	119.8(3)
C(5)–C(6)–C(7)		119.7(5)		119.4(2)
C(6)–C(7)–C(8)		121.4(5)		120.5(3)
C(7)–C(8)–C(9)		118.8(5)		120.2(3)
C(8)–C(9)–C(10)		121.8(5)		120.1(3)
C(9)–C(10)–C(5)		120.3(5)		120.5(3)
C(4)–C(5)–C(10)		120.5(5)		120.6(4)

structures of pseudo-ozonide metallacycles have been reported, *i.e.* two rhodium peroxocarbonates of general formula Rh[OOC(O)O]R(L).[11,12] Such peroxocarbonates differ from our system by having a sp^2-hybridised carbon atom in the five-membered ring. Although their molecular parameters are not so accurate and are affected by high estimated standard deviations (e.s.d.s), the asymmetry of the O–C–O system is again detectable. It is of interest that such a feature is also evident in some organic ozonides like *endo*-1-methyl-3-phenylindene ozonide and *exo*-1-methyl-2,3-diphenylindene ozonide.[13]

Upon insertion into the platinum–oxygen bond the C(1) atom of the quinonic moiety changes its hybridisation and it can therefore be expected that the most relevant variations in the geometry of the benzoquinone or naphthoquinone will involve C(1) and its neighbours. There is a slight lengthening of the C(1)–C(2) and C(1)–C(6) bonds with respect to those of C(4)–C(3) and C(4)–C(5) and a closure of the C(2)–C(1)–C(6) angle towards the ideal sp^3 value. No significant deviation from planarity (more than six times its e.s.d.s) occurs for the six-membered ring C(1)–C(6). The C(5)–C(10) ring in complex **2** is rigorously planar. The C(4)–O(4) bond lengths can be compared with the value of 1.222(13) Å reported by Allen *et al.*[14] as an average of 86 observations on free quinones. In particular, the C=O bond lengths of the free carbonyl group in compounds **2** and **3** are not so different (see Table 2) from those in free *p*-benzoquinone[8] [1.222(9) in **3** against 1.222(8) Å] and free 1,4-naphthoquinone[10] [1.204(6) in **2** against 1.221(3) or 1.224(3) Å]. The Pt–O and Pt–P bond lengths are within the usual range. Nevertheless, it is worth noting that the great variability of the Pt–P bond length in the present compounds [from 2.215(2) to 2.268(1) Å] is not the result of a different *trans* influence, but only of packing effects.

The formation of the pseudo-ozonide ring does not induce a relevant perturbation of the π-electronic system located in the

Table 3 Crystallographic data for compounds **2** and **3**[a]

	3	**2**
Formula	$C_{42}H_{34}O_4P_2Pt$	$C_{46}H_{36}O_4P_2Pt$
M	859.77	909.84
Space group	$P2_1/c$	$P2_1/n$
a/Å	15.374(6)	14.412(3)
b/Å	10.835(3)	18.338(2)
c/Å	21.452(6)	15.101(2)
β/°	93.34(2)	102.55(1)
U/Å^3	3567(3)	3896(2)
D_c/g cm^{-3}	1.601	1.551
F(000)	1704	1808
μ(Mo-Kα)/cm^{-1}	41.02	37.61
Crystal dimensions/mm	0.08 × 0.15 × 0.25	0.10 × 0.15 × 0.30
Minimum transmission factor	0.67	0.79
Scan width/°	1.50 + 0.35 tan θ	1.20 + 0.35 tan θ
Measured reflections	6314	6825
Unique observed reflections with $I > 3\sigma(I)$	3931	5101
Final R and R' [b]	0.034, 0.041	0.024, 0.033
No. of variables, N_v	442	478
E.s.d.[c]	1.428	1.256

[a] Details in common: monoclinic; $Z = 4$; scan mode ω; θ range 3–25°; octants explored $\pm h, +k, +l$. [b] $R = [\Sigma(F_o - k\|F_c\|)/\Sigma F_o]$, $R' = [\Sigma(F_o - k\|F_c\|)^2/\Sigma w F_o^2]^{\frac{1}{2}}$. [c] E.s.d. $= [\Sigma w(F_o - k\|F_c\|)^2/(N_o - N_v)]^{\frac{1}{2}}$, $w = 1/[\sigma(F_o)]^2$, $\sigma(F_o) = [\sigma^2(I) + (0.04I)^2]^{\frac{1}{2}}/2F_oL_p$, L_p = Lorentz polarisation.

Table 4 Positional parameters and their e.s.d.s for compound **3**

Atom	x	y	z	Atom	x	y	z
Pt	0.766 90(2)	0.871 09(3)	0.976 03(1)	C(131)	0.842 8(5)	1.115 0(7)	0.900 4(3)
P(1)	0.753 7(1)	1.004 6(2)	0.895 25(8)	C(132)	0.916 6(5)	1.092 9(8)	0.938 3(4)
P(2)	0.750 7(1)	0.695 8(2)	0.923 45(8)	C(133)	0.986 2(5)	1.173 3(9)	0.938 7(4)
O(1)	0.782 7(3)	1.018 1(5)	1.033 8(2)	C(134)	0.984 5(5)	1.272 7(9)	0.900 8(4)
O(2)	0.828 0(4)	0.860 5(5)	1.101 1(2)	C(135)	0.910 9(6)	1.296 7(8)	0.863 1(4)
O(3)	0.781 8(4)	0.775 2(5)	1.056 2(2)	C(136)	0.840 9(5)	1.218 2(8)	0.862 5(4)
O(4)	0.692 4(6)	1.164 9(8)	1.243 9(3)	C(211)	0.646 8(5)	0.678 0(7)	0.878 9(3)
C(1)	0.782 2(5)	0.976 8(8)	1.094 7(3)	C(212)	0.628 2(5)	0.576 7(9)	0.841 0(4)
C(2)	0.839 2(5)	1.062 3(9)	1.134 6(4)	C(213)	0.545 3(6)	0.563(1)	0.812 5(4)
C(3)	0.807 9(7)	1.124 4(9)	1.181 4(4)	C(214)	0.481 8(6)	0.646(1)	0.822 6(4)
C(4)	0.720 0(7)	1.108 0(9)	1.200 0(4)	C(215)	0.498 0(5)	0.746(1)	0.861 1(4)
C(5)	0.666 3(6)	1.020 5(9)	1.165 3(4)	C(216)	0.580 6(5)	0.761 1(8)	0.889 2(4)
C(6)	0.694 4(5)	0.961 1(8)	1.117 7(4)	C(221)	0.745 1(6)	0.565 0(8)	0.975 9(4)
C(111)	0.757 0(5)	0.953 4(7)	0.814 1(3)	C(222)	0.674 9(7)	0.558 5(9)	1.013 6(4)
C(112)	0.682 4(5)	0.914 6(8)	0.779 7(4)	C(223)	0.662 9(8)	0.456(1)	1.050 5(5)
C(113)	0.688 8(6)	0.874 7(9)	0.718 8(4)	C(224)	0.718 8(9)	0.360 6(9)	1.051 3(5)
C(114)	0.765 3(7)	0.875 5(9)	0.691 0(4)	C(225)	0.785 5(7)	0.363 1(8)	1.011 8(5)
C(115)	0.839 0(6)	0.914 1(9)	0.724 4(4)	C(226)	0.799 3(6)	0.465 3(9)	0.976 5(4)
C(116)	0.835 3(5)	0.950 9(8)	0.785 7(3)	C(231)	0.839 2(5)	0.667 0(7)	0.872 7(3)
C(121)	0.653 4(4)	1.095 2(7)	0.896 7(3)	C(232)	0.828 3(5)	0.647 5(8)	0.809 4(4)
C(122)	0.620 1(5)	1.157 4(8)	0.844 8(4)	C(233)	0.901 2(6)	0.635 1(9)	0.773 6(4)
C(123)	0.545 5(6)	1.227 7(9)	0.848 6(4)	C(234)	0.982 0(6)	0.638 6(9)	0.801 1(5)
C(124)	0.504 9(6)	1.238 5(9)	0.903 4(4)	C(235)	0.994 9(6)	0.655(1)	0.864 3(6)
C(125)	0.537 8(6)	1.177(1)	0.954 4(4)	C(236)	0.922 3(6)	0.671(1)	0.900 5(4)
C(126)	0.611 7(6)	1.103 0(9)	0.951 5(4)				

C(2)–C(3), C(3)–C(4) and C(4)–O(4) bonds. The most relevant deformation occurs in compound **2**,[10] the C(2)–C(3) bond distance increasing from 1.321 to 1.356(7) Å and C(4)–O(4) decreasing from 1.221(3) or 1.224(3) to 1.204(6) Å. In addition a sensible perturbation of the π system occurs in the aromatic ring C(5)–C(10) (see Table 2).

Discussion and Conclusion

Our investigation has shown that only one carbonyl group of quinones (both *ortho* and *para*) reacts with $[Pt(PPh_3)_2(O_2)]$ to give a pseudo-ozonide metallacycle structure. X-Ray investigation has shown that in two cases (even with the rather rigid structure of 1,4-naphthoquinone) the pseudo-ozonide structure produces no significant deformation of the quinone ring plane nor a large perturbation of its π delocalisation.

Molecular models show that there is room for another pseudo-ozonide metallacycle, the two $Pt(PPh_3)_2(O_2)$ moieties being far enough apart, thus the hypothesis of purely steric hindrance as the reason for the lack of further reactivity can be rejected. The lack of reactivity could be of kinetic origin. The insertion reaction of ketones into the Pt–O bond of $[Pt(PPh_3)_2(O_2)]$ is characterised by two reaction pathways.[15] The major pathway involves nucleophilic attack of the metal-co-ordinated peroxide anion at the carbon atom of the carbonyl group co-ordinated to the same metal centre, a transition state occurring in which the platinum atom is five-co-ordinated.[15] The insertion is kinetically very dependent on steric effects; whereas acetone reacts easily, a more hindered ketone such as methyl *tert*-butyl ketone does not react at all. It therefore follows that steric hindrance in the five-co-ordinated transition state could occur in the reaction of the 1:1 adducts between $[Pt(PPh_3)_2(O_2)]$ and quinones with *ortho* and *para* structures and excess of $[Pt(PPh_3)_2(O_2)]$.

Table 5 Positional parameters and their e.s.d.s for compound **2**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Pt	−0.121 76(1)	−0.165 19(1)	0.134 05(1)	C(125)	−0.483 7(4)	−0.291 2(3)	0.050 0(4)
P(1)	−0.277 50(7)	−0.134 53(7)	0.113 19(7)	C(126)	−0.411 7(3)	−0.246 8(3)	0.096 9(3)
P(2)	−0.133 22(8)	−0.285 57(7)	0.107 64(8)	C(131)	−0.315 1(3)	−0.115 4(3)	0.218 5(3)
O(1)	−0.094 3(2)	−0.060 1(2)	0.174 4(2)	C(132)	−0.248 1(4)	−0.106 5(3)	0.298 2(3)
O(2)	0.052 6(2)	−0.092 8(2)	0.151 1(2)	C(133)	−0.276 3(5)	−0.094 2(3)	0.379 5(3)
O(3)	0.021 2(2)	−0.170 2(2)	0.158 2(2)	C(134)	−0.369 1(4)	−0.090 0(4)	0.382 8(3)
O(4)	0.143 6(3)	0.084 9(3)	0.410 6(3)	C(135)	−0.437 9(4)	−0.097 3(4)	0.302 4(4)
C(1)	0.001 6(3)	−0.050 2(3)	0.204 0(3)	C(136)	−0.410 2(4)	−0.109 9(4)	0.222 2(4)
C(2)	0.030 1(4)	−0.073 9(3)	0.302 3(3)	C(211)	−0.170 0(1)	−0.318 2(3)	−0.008 7(3)
C(3)	0.073 3(4)	−0.028 1(3)	0.369 2(3)	C(212)	−0.219 2(4)	−0.274 1(3)	−0.074 7(3)
C(4)	0.099 7(4)	0.046 8(3)	0.351 1(3)	C(213)	−0.253 5(5)	−0.299 1(5)	−0.162 6(4)
C(5)	0.068 6(3)	0.074 0(3)	0.257 2(3)	C(214)	−0.233 8(5)	−0.368 1(4)	−0.183 8(4)
C(6)	0.025 1(3)	0.027 9(3)	0.186 0(3)	C(215)	−0.180 8(5)	−0.412 5(4)	−0.119 4(4)
C(7)	−0.003 3(4)	0.055 4(3)	0.100 3(3)	C(216)	−0.149 7(4)	−0.389 0(3)	−0.030 7(4)
C(8)	0.010 0(4)	0.128 8(3)	0.081 7(4)	C(221)	−0.018 6(3)	−0.331 9(3)	0.148 4(3)
C(9)	0.050 1(4)	0.173 6(3)	0.151 0(4)	C(222)	0.056 5(4)	−0.314 1(3)	0.107 8(4)
C(10)	0.081 2(4)	0.148 4(3)	0.236 7(4)	C(223)	0.143 8(4)	−0.347 7(3)	0.137 0(5)
C(111)	−0.294 1(3)	−0.050 1(3)	0.047 3(3)	C(224)	0.155 6(4)	−0.398 2(3)	0.207 5(5)
C(112)	−0.363 6(3)	−0.000 0(3)	0.054 6(3)	C(225)	0.082 1(4)	−0.416 3(3)	0.245 5(4)
C(113)	−0.374 8(4)	0.062 6(3)	−0.000 4(4)	C(226)	−0.005 5(4)	−0.383 0(3)	0.216 1(4)
C(114)	−0.316 2(4)	0.075 2(3)	−0.058 8(4)	C(231)	−0.208 4(3)	−0.328 7(2)	0.173 5(3)
C(115)	−0.248 3(4)	0.026 9(3)	−0.065 2(4)	C(232)	−0.208 3(3)	−0.298 8(3)	0.257 6(3)
C(116)	−0.236 3(3)	−0.036 7(3)	−0.013 4(3)	C(233)	−0.259 7(4)	−0.331 2(3)	0.315 4(4)
C(121)	−0.372 7(3)	−0.192 6(3)	0.052 3(3)	C(234)	−0.310 1(4)	−0.393 7(4)	0.287 7(4)
C(122)	−0.407 1(4)	−0.184 3(3)	−0.040 2(3)	C(235)	−0.314 1(4)	−0.422 8(3)	0.204 2(5)
C(123)	−0.478 1(4)	−0.229 6(3)	−0.087 6(3)	C(236)	−0.261 6(4)	−0.390 8(3)	0.146 3(4)
C(124)	−0.517 3(4)	−0.282 0(3)	−0.041 6(4)				

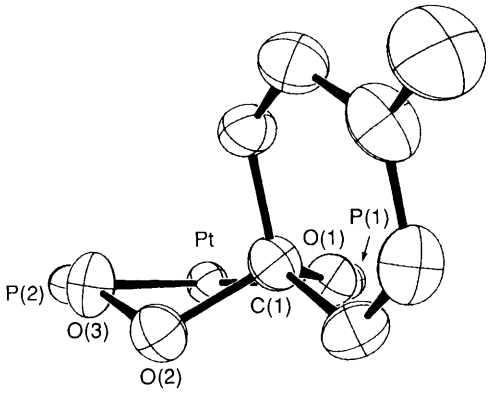


Fig. 4 ORTEP partial view of complex **3**, showing the conformational arrangement of the pseudo-ozonide moiety

However this latter point cannot be confirmed with molecular models due to the poor knowledge of the real geometry of the five-co-ordinated transition state.[15] Furthermore the lack of reactivity could be due to a weak interaction with the platinum atom, a decrease in basicity of the free carbonyl group occurring after the insertion of the first carbonyl into the platinum–dioxygen bond. Esters, being less basic than ketones or aldehydes, do not react,[2] although the C=O bond distance is very similar to that observed in ketones or aldehydes.[14]

Experimental

The complex $[Pt(PPh_3)_2(O_2)]$ was obtained as previously reported.[16] All the quinones were purchased from Aldrich and were used without further purification.

Infrared spectra were recorded on a Beckman 4210 spectrophotometer; elemental analyses (Table 1) were carried out in the Analytical Laboratory of the Chemistry Departments of Milan University.

Reaction between $[Pt(PPh_3)_2(O_2)]$ *and* para *or* ortho *Quinones.*—The reaction was performed at room temperature in benzene as solvent with a 1:2 molar ratio between the quinone and $[Pt(PPh_3)_2(O_2)]$ with *p*-benzoquinone and 1,4- and 1,2-naphthoquinone, and 2:1 with tetrachloro-*o*-benzoquinone (Table 1). After 1 h a yellow or yellow-brown precipitate separated; it was filtered off, washed with benzene and dried under vacuum. It can be crystallised by addition of n-hexane to a solution in dichloromethane.

Analytical data and IR spectra (Table 1) both suggest the formation of 1:1 adducts with a platinum pseudo-ozonide ring. Crystals of compounds **2** and **3**, suitable for X-ray analysis, were obtained by very slow diffusion of hexane into dichloromethane solutions of the compounds.

Reaction between $[Pt(PPh_3)_2(O_2)]$ *and the Platinum Adducts* **1**–**4**.—The reaction was performed in dichloromethane (room temperature or under reflux) by adding the platinum adducts in Table 1 (in a 1:1 molar ratio) to $[Pt(PPh_3)_2(O_2)]$. In all cases the starting platinum complexes were recovered unchanged. Under reflux some decomposition occurred.

X-Ray Data Collection and Structure Determination.—Crystal data for compounds **2** and **3**, together with other experimental details, are summarised in Table 3. The diffraction experiments were carried out on an Enraf-Nonius CAD-4 diffractometer at room temperature with Mo-Kα radiation (λ = 0.710 73 Å). The diffracted intensities were corrected for Lorentz, polarisation and absorption (empirical correction)[17] but not for extinction. Scattering factors and anomalous dispersion corrections for non-hydrogen atoms were taken from ref. 18. Both structures were solved by Patterson and Fourier methods and refined by full-matrix least squares, minimising the function $\Sigma w(F_o - k|F_c|)^2$.

All the calculations were performed on a PDP11/73 computer using the SDP-Plus structure determination package.[19] Anisotropic thermal parameters were refined for all the non-hydrogen atoms. The hydrogen atoms were introduced in the models at calculated positions (C–H 0.95 Å) but not refined.

The final Fourier difference syntheses showed maximum residuals of 0.5 e $Å^{-3}$ for compound **3** and 0.3 e $Å^{-3}$ for **2**. The atomic coordinates are listed in Tables 4 and 5 respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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