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REACTIONS OF *trans*-[Pt(H_2){P(C_6H_{11})$_3$}$_2$] WITH HETEROCUMULENES. THE CRYSTAL AND MOLECULAR STRUCTURE OF *trans*-[Pt{P(C_6H_{11})$_3$}$_2$(H){OCH=C(C_6H_5)$_2$}]

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Summary

Trans-$PtH_2(PCy_3)_2$ (**1**) reacts with phenylisocyanate (**2**) and with diphenylketene (**3**) to yield the formamido complex (**4**) and the vinyloxo complex (**5**), respectively. The structure of **5** has been determined by X-ray diffraction.

Introduction

The reactions of heterocumulenes with transition metal complexes attracts much interest [1]. We have previously reported that *trans*-$PtH_2(PCy_3)_2$ (**1**) reacts with CO_2 and CS_2 to yield products in which the hydrido hydrogen has been transferred to the carbon atom [2,3]. A similar reaction has been observed with ketoesters [4]. We describe here the reaction of **1** with phenylisocyanate (**2**) and diphenylketene (**3**). Insertion of organic isocyanates into the metal–hydrogen bond produces either formamido or carboxamido complexes [5]. In the former case hydrogen migrates to the carbon atom and a metal–oxygen bond is formed. Conversely, carboxamido complexes are formed through migration of hydrogen to the nitrogen atom.

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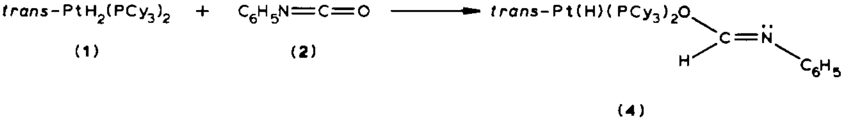
Results and discussion

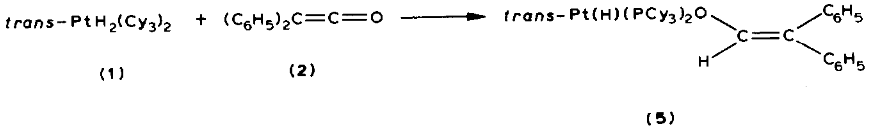
We have found that **1** reacts smoothly at room temperature with **2** to yield the formamido complex **4** (eq. 1).



(1)

The structure of **4** is based on the NMR data (Table 1). Migration of hydrogen to the carbon atom was revealed by the ^1H NMR spectrum, which showed a very low field resonance (δ 9.95) typical of formamido ligands [5,6]. Since, furthermore, no absorption, attributable to an N–H stretching vibration, was observed in the 3400 cm^{-1} region of the IR spectrum, we feel confident that **4** is a formamido complex. The *E* stereochemistry around the C–N double bond was established by difference nuclear Overhauser effect experiments. Irradiation of the *ortho*-aryl proton of **4** produced a 10% enhancement of the integrated area of the CH= resonance. In a confirmatory experiment, irradiation of the signal of the CH= proton at δ 9.95 belonging to molecules containing platinum with zero spin produced a NOE enhancement of the *ortho*-aryl proton. These NMR results suggest that the hydrido hydrogen migration is stereospecific, with the C–H bond *trans* to the lone pair of the nitrogen.

Diphenylketene (**3**) reacts at room temperature with **1** to yield the vinyloxo complex **5** (eq. 2).



(2)

The structure assigned to **5** is consistent with the NMR data (Table 2) and has been fully revealed by a single crystal X-ray diffraction study. The isomeric acyl complex was not observed in solution *.

TABLE 1

NMR DATA [a] FOR *trans*-[Pt(PCy$_3$)$_2$(H)(OCH=NC$_6$H$_5$)] (4) (δ(ppm), J(Hz))

^1H [b]

δ(Pt–H)	^2J(Pt–H)	^2J(P–H)	^4J(H–H)	δ(CH=)	^3J(Pt–H)	δ(*o*-H)	δ(*m*-H)	δ(*p*-H)
−17.25	925	15	3	9.95	42	7.87	7.47	7.12

^{31}P

δ(P)	^2J(Pt–P)
37.7	2876

[a] In C$_6$D$_6$. [b] 300 MHz.

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* Thermal isomerization of vinyloxo complexes to acyl compounds have been reported for tri-osmium clusters [7].

TABLE 2

NMR DATA[a] FOR *trans*-[Pt(PCy$_3$)$_2$(H){OCH=C(C$_6$H$_5$)$_2$}] 5 (δ (ppm), J(Hz))

^{1}H[b]		
δ(Pt–H)	^2J(Pt–H)	^2J(P–H)
−22.84	14	1114
^{31}P		
δ(P)	^2J(Pt–P)	
40.56	2886	

[a] C$_6$D$_6$. [b] 80 MHz, CH= and C$_6$H$_5$ at δ 7.0 and 8.5 ppm.

Table 3 shows selected interatomic distances and angles for the molecules and Table 4 lists the best planes through groups of atoms. The crystal structure of Pt(H)(PCy$_3$)$_2$OC$_{14}$H$_{13}$ (5) involves packing of the monomeric species shown in Fig. 1. There was intermolecular distance below the sum of the commonly accepted Van der Waals radii. Two phosphine ligands, the vinyloxo residue, which is completely disordered (see below), and the hydrido hydrogen atom are coordinated to Pt to form a square-planar complex. The mean square displacement of the PtP(1)P(2)O plane is 0.03 Å. The average Pt–P distance 2.286(4) Å, is close to that in other Pt–PCy$_3$ complexes [2–4,8]. The cyclohexyl groups have a chair conformation and, as expected, are staggered with respect to one another. The P(1)–Pt–P(2) angle

TABLE 3

SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN THE MOLECULE (with e.s.d.'s in parentheses)

Pt–P(1)	2.286(4)	C(1A)–O(A)	1.34(3)
Pt–P(2)	2.286(4)	C(1B)–O(B)	1.33(3)
P–C$^a_{av}$	1.848(13)	C(2A)–C(1A)	1.37(4)
C–C$^b_{av}$	1.550(21)	C(2B)–C(1B)	1.40(4)
C–C$^c_{av}$ (A)	1.41(6)	C(3A)–C(2A)	1.41(3)
C–C$^d_{av}$ (B)	1.41(6)	C(3B)–C(2B)	1.53(3)
Pt–O(A)	2.124(18)		
Pt–O(B)	2.168(18)		
P(1)–Pt–P(2)	167.9(2)	O(A)–C(1A)–C(2A)	125.8(17)
C–C–C$^d_{av}$	109.9(13)	O(B)–C(1B)–C(2B)	124.2(18)
C–C–C$^e_{av}$ (A)	120.0(30)	C(1A)–C(2A)–C(3A)	113.2(21)
C–C–C$^e_{av}$ (B)	120.0(35)	C(1B)–C(2B)–C(3B)	121.4(18)
Pt–O(A)–C(1A)	121.6(13)		
Pt–O(B)–C(1B)	121.3(13)		
P(1)–Pt–O(A)	92.1(7)		
P(1)–Pt–O(B)	97.8(7)		
P(2)–Pt–O(A)	98.6(7)		
P(2)–Pt–O(B)	94.3(7)		

[a] The average value based on 6 P–C distances. [b] The average value for 36 C–C cyclohexyl distances. [c] The average value obtained from 12 C–C phenyl enolate residue distances for A and B molecules (see text). [d] Average value for 36 C–C–C cyclohexyl angles. [e] Average value for 12 C–C–C phenyl enolate residue angles for A and B molecules (see text).

TABLE 4

SELECTED BEST PLANES THROUGH GROUPS OF ATOMS IN THE MOLECULE

Plane	Equations	δ^a
Pt–P(1)–P(2)–O(A)	$0.7335x - 0.3744y + 0.5405z - 2.8017 = 0$	0.043
Pt–P(1)–P(2)–O(B)	$0.6672x - 0.6653y + 0.3350z - 1.6448 = 0$	0.008
Pt–O(A)–C(1A)–C(2A)	$-0.3092x - 0.4527y + 0.8364z + 3.2750 = 0$	0.005
Pt–O(B)–C(1B)–C(2B)	$-0.4424x - 0.3982y + 0.8036z + 3.8707 = 0$	0.070

[a] δ is the mean square displacement in Å.

(167.9(3)°) is slightly bent towards the hydrido hydrogen because of the steric requirements of the disordered vinyloxo group. The Pt–O distance (2.15(3) Å) is quite comparable to those observed in similar complexes, namely *trans*-$[Pt(PCy_3)_2(H)\{OC{=}CHC(Me)(COOEt)OCO\}]$ [4] (6) (2.11(2) Å) and *trans*-$[Pt(PCy_3)_2(H)(O_2COMe)]$ [3] (2.13(1) Å). However, it is noteworthy that all the above Pt–O distances are longer than the sum of covalent radii (2.01 Å) [4], and refer to complexes containing H atoms *trans* with the respect to O atom, reflecting a marked *trans* effect of the H atom. In Pt complexes having no coordinated hydrogen atom, Pt–O distances close to 2.01 Å were observed (e.g. in $(PPh_3)_2PtON(Ph)C(CO_2Me){=}C(CO_2Me))$, (2.01(1) Å) [9] and in $Pt(NH_2CH_2CH_2O)_2 \cdot 2H_2O$, (2.002(4) Å) [10].

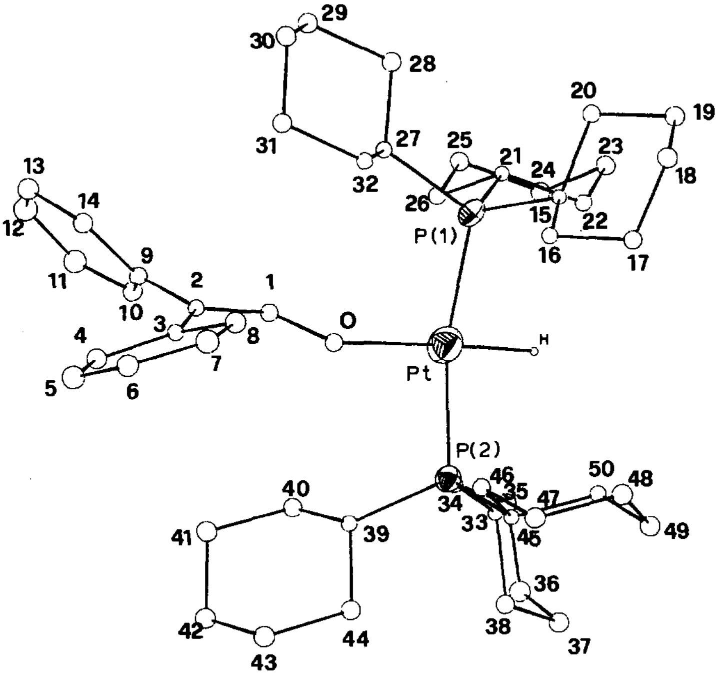

Fig. 1. The ORTEP drawing of the molecule viewed perpendicular to the coordination plane. The calculated position of the hydrido atom is indicated. For the sake of clarity only one of the two orientations of enolate residue (see text) is shown.

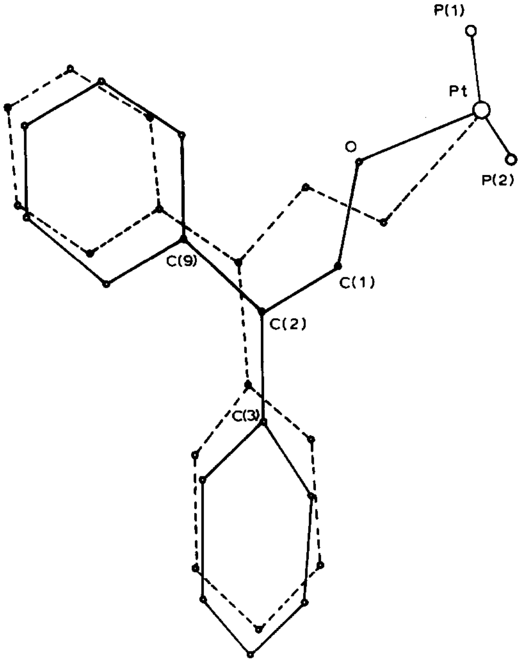

Fig. 2. The two orientations of the enolate residue, viewed perpendicular to the P(1)–Pt–P(2) plane.

The angle between metal coordination plane and the Pt enolate plane (73°) is close to that in **6**. All these geometrical features are indicative of a weak influence of the bulky phosphine ligands on the coordination geometry.

The vinyloxo group was found to display a dynamic and/or static disorder. Attempts to refine this entity using anisotropic thermal parameters gave results insignificant by the Hamilton test [11], and were abandoned. The lowest disagreement factor in the refinement was achieved with isotropic thermal parameters and the introduction of two different orientations of the enolate residue having occupation factors close to 0.5.

As depicted in Fig. 2, the A and B orientations do not differ significantly in geometrical features (see also Tables 3 and 4). They are related to each other by an approximate two fold axis, passing through the platinum atom and the middle point of O–C(1) bond, giving rise to a solid cone well positioned among the bulky phosphines. The intermolecular contacts involving these groups are comparable for both A and B conformations, and are not particularly severe.

The distances between Pt–C(1)_{av} and Pt–C(2)_{av} (3.06 and 4.39 Å respectively) are too long for any significant direct interactions. The C(1)–C(2)_{av} distance (1.39(4) Å) is probably longer than that in some titanium enolate complexes (1.306(5) Å) [12]. In conclusion, as can be seen from Table 3, the bond distances and angles of the enolate group, averaged over the two orientations, have no unusual values.

Experimental

^{1}H NMR spectra were recorded on Bruker WP80SY and CPX300 instruments, and ^{31}P spectra were recorded on the former instrument at 32.38 MHz.

Elemental analysis were carried out at the Istituto di Chimica Organica, Università di Milano.

Trans-$PtH_2(PCy_3)_2$ was prepared by a published procedure [13]. The preparations of the complexes were carried out under dinitrogen purified by passage through BASF catalyst R3-11. Solvents were dried and degassed before use.

[*trans*-$Pt(PCy_3)_2(H)(OCH{=}NC_6H_5)$] (4)

Phenylisocyanate (0.127 g, 1.066 mmol) was added to a toluene solution (3.5 ml) of *trans*-$PtH_2(PCy_3)_2$ (0.710 mg, 0.937 mmol). Upon standing at room temperature white microcrystalline material separated. Further material separated out at −15°C. The microcrystalline solid was filtered off, washed with cold toluene, and dried (0.716 g, 87% yield).

Analysis. Found: C, 58.88; H, 8.16; N, 1.59. $C_{43}H_{73}NOP_2Pt$ calcd.: C, 58.92; H, 8.54; N, 1.64%. IR (Nujol, cm^{-1}): 2180 (Pt–H).

[*trans*-$Pt(PCy_3)_2(H)\{OCH{=}C(C_6H_5)_2\}$] (5)

Diphenylketene (0.150 g, 0.773 mmol) was added to a toluene solution (2 ml) of *trans*-$PtH_2(PCy_3)_2$ (0.405 g, 0.535 mmol). After 2 h at room temperature heptane (4 ml) was added. The solution was kept at 4°C, and white prismatic crystals separated. The crystals were filtered off, washed with heptane, and dried (0.503 g, 70% yield).

Analysis. Found: C, 62.87; H, 8.42. $C_{50}H_{78}OP_2Pt$ calcd.: C, 63.07; H, 8.26%. IR (Nujol, cm^{-1}) 2200 (Pt–H).

TABLE 5

CRYSTAL DATA AND INTENSITY COLLECTION

Molecular formula	$PtP_2OC_{50}H_{78}$
$F(000)$	1968 e $cell^{-1}$
Molecular weight	952.2
Density (calculated)	1.337 g cm^{-3}
Molecules in the unit cell	4
Cell constants	a 19.928(9), b 16.383(8), c 15.428(6) Å β 110.3(2)°
Cell volume	4725.3 $Å^3$
Space group	$P2_1/n$
Absorption coefficient	32.26 cm^{-1}
Scan mode	θ–2θ
Scan speed	2.4° min^{-1}
Scan width	0.8°
θ range (d_{min})	2–23° (0.909 Å)
Background time	2×5 s
Reciprocal space explored	$k, l \geqslant 0$
Measured reflections	6484
Observed reflections ($I > 3.0\ \sigma$) (σ^2 = peak counts + total background counts)	4388
Wavelength (graphite-monochromated Mo-K_α radiation)	0.71069 Å
Power used	50 kV × 30 mA
Approximate crystal size	0.15 × 0.20 × 0.13 mm^3

TABLE 6

ATOMIC FRACTIONAL COORDINATES OF **5** (with e.s.d.'s in parentheses) ISOTROPIC THERMAL PARAMETERS FOR C ATOMS

Atom	x/a	y/b	z/c	B_{iso}
Pt	28371(3)	15810(3)	9130(4)	
P(1)	36813(17)	20903(19)	3648(22)	
P(2)	21006(17)	12572(19)	17154(23)	
O(A)	2799(9)	450(11)	224(12)	50(4)
O(B)	2398(9)	659(11)	−140(12)	50(4)
C(1A)	2206(14)	203(17)	−452(18)	49(6)
C(1B)	2748(14)	−28(17)	−146(18)	50(6)
C(2A)	2127(14)	−519(14)	−928(18)	40(5)
C(2B)	2449(14)	−703(16)	−696(17)	45(5)
C(3A)	1448(15)	−607(17)	−1618(19)	50(6)
C(3B)	1688(15)	−681(17)	−1393(19)	50(6)
C(4A)	1121(16)	−1384(19)	−1726(21)	60(7)
C(4B)	1290(16)	−1446(20)	−1597(21)	64(7)
C(5A)	418(17)	−1453(21)	−2402(22)	67(7)
C(5B)	581(17)	−1478(21)	−2247(22)	67(7)
C(6A)	95(21)	−827(25)	−2948(27)	89(9)
C(6B)	222(19)	−805(22)	−2770(24)	74(8)
C(7A)	414(20)	−112(24)	−2870(26)	79(9)
C(7B)	624(20)	−24(24)	−2541(26)	84(9)
C(8A)	1039(16)	28(19)	−2224(21)	57(7)
C(8B)	1344(18)	27(21)	−1891(23)	65(8)
C(9A)	2708(13)	−1190(16)	−733(17)	41(5)
C(9B)	2907(15)	−1424(18)	−537(19)	55(6)
C(10A)	3209(18)	−1340(21)	221(23)	67(8)
C(10B)	3365(18)	−1639(24)	306(24)	76(8)
C(11A)	3672(21)	−2005(24)	321(26)	83(9)
C(11B)	3776(20)	−2333(24)	407(26)	80(9)
C(12A)	3674(19)	−2549(23)	−410(25)	75(9)
C(12B)	3782(21)	−2763(25)	−303(27)	90(9)
C(13A)	3224(20)	−2393(23)	−1311(26)	81(9)
C(13B)	3319(20)	−2519(24)	−1182(26)	83(9)
C(14A)	2708(16)	−1705(20)	−1480(21)	63(7)
C(14B)	2894(17)	−1851(20)	−1343(22)	63(7)
C(15)	3527(7)	3186(8)	135(9)	34(3)
C(16)	2770(7)	3378(11)	−555(11)	49(3)
C(17)	2642(9)	4324(11)	−564(12)	57(4)
C(18)	3194(11)	4791(13)	−864(14)	69(5)
C(19)	3961(10)	4581(12)	−193(13)	62(4)
C(20)	4097(9)	3638(11)	−198(12)	55(4)
C(21)	4584(8)	2046(9)	1242(10)	38(3)
C(22)	4653(8)	2585(9)	2081(10)	43(3)
C(23)	5405(10)	2534(12)	2804(13)	62(4)
C(24)	5585(10)	1635(13)	3138(13)	66(4)
C(25)	5526(11)	1087(12)	2310(14)	67(5)
C(26)	4774(9)	1136(10)	1555(11)	49(3)
C(27)	3749(7)	1516(10)	−633(10)	41(3)
C(28)	4430(9)	1679(12)	−864(12)	59(4)
C(29)	4457(11)	1060(12)	−1645(14)	68(5)
C(30)	3768(10)	1115(12)	−2491(13)	64(4)
C(31)	3093(10)	968(12)	−2239(13)	63(4)
C(32)	3070(9)	1606(11)	−1489(11)	55(4)
C(33)	2653(7)	1271(8)	2960(9)	33(3)

TABLE 6 (continued)

Atom	x/a	y/b	z/c	B_{iso}
C(34)	3335(8)	755(9)	3178(10)	41(3)
C(35)	3864(9)	981(11)	4156(11)	52(4)
C(36)	3501(10)	843(12)	4861(13)	63(4)
C(37)	2813(10)	1320(11)	4661(12)	60(4)
C(38)	2287(9)	1115(10)	3659(11)	49(4)
C(39)	1594(8)	283(10)	1335(10)	42(3)
C(40)	2110(8)	−458(9)	1608(10)	41(4)
C(41)	1699(10)	−1230(11)	1091(13)	59(4)
C(42)	1062(10)	−1385(12)	1389(13)	62(4)
C(43)	547(10)	−646(12)	1155(13)	61(4)
C(44)	965(9)	140(11)	1666(12)	57(4)
C(45)	1398(7)	2019(8)	1609(9)	33(3)
C(46)	973(8)	2150(10)	564(11)	46(3)
C(47)	361(9)	2768(11)	455(12)	54(4)
C(48)	653(9)	3587(11)	920(12)	57(4)
C(49)	1059(9)	3436(12)	1986(11)	54(4)
C(50)	1686(8)	2835(10)	2091(11)	45(3)

[a] The values are $\times 10^5$ for Pt and P atoms and $\times 10^4$ for other atoms. [b] All the values are $\times 10$.

X-ray diffraction experiments

Suitable crystals for X-ray analysis were obtained by low temperature crystallization from toluene/heptane.

Unit cell parameters and integrated intensities were determined by means of a computer-controlled four circle diffractometer Philips PW1100, with a randomly oriented crystal. Lattice parameters were refined by least-squares methods from accurate positioning of 50 strong reflections.

Crystal data and experimental details are shown in Table 5. Intensities were corrected for Lorentz and polarization effects, and an experimental absorption correction [14] was applied. The structure was solved by the heavy atom method and refined by least-squares in the block diagonal approximation, minimizing $\Sigma w(kF_0 - F_c)^2$, with unitary weight factors [15]. Atomic scattering factors were taken from ref. 16, and both the real and imaginary components of the anomalous dispersion were included for Pt and P atoms. Anisotropic thermal vibration parameters were used only for Pt and P atoms. Because of the total disorder in the enolate residue (see Results and Discussion), attempts to locate H atoms by Fourier difference map failed. The final shift did not exceed 0.3σ. In the last cycle the contribution of H atoms to the structure factors was included. The final R value was 0.053.

The calculations were performed on the Univac 1100/90 computer of the Consorzio Interuniversitario Lombardo per l'Elaborazione Automatica at Milan.

Table 6 lists the atomic fractional coordinates of the non-hydrogen atoms, (with their e.s.d.'s), and the isotropic thermal parameters for C atoms. Anisotropic thermal parameters for P and Pt atoms together with lists of experimental and calculated structure factors are available from the authors.

Acknowledgments

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