Monohydrido-bridged Platinum(II)–Gold(I) Complexes. *X*-Ray Crystal Structure of $[(Ph_3P)_2(C_6Cl_5)Pt(\mu\text{-}H)Au(PPh_3)]ClO_4{\cdot}2Et_2O$ †

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The compounds $[(Ph_3P)_2RPt(\mu\text{-}H)Au(PPh_3)]ClO_4$ (R = C_6Cl_5, $C_6H_3Cl_2$-2,5, or C_6H_4Cl-*p*) have been obtained by reaction of the corresponding complex *trans*-$[PtH(R)(PPh_3)_2]$ with $[Au(thf)(PPh_3)]ClO_4$ and they have been characterized by ^1H and ^{31}P n.m.r. spectroscopy. The molecular structure of $[(Ph_3P)_2(C_6Cl_5)Pt(\mu\text{-}H)Au(PPh_3)]ClO_4$ has been determined by a single-crystal *X*-ray structural analysis. The crystals are triclinic, space group $P\bar{1}$, with a = 22.866(7), b = 13.844(5), c = 11.392(4) Å, α = 110.79(3), β = 85.13(2), γ = 96.95(2) °, and Z = 2.

The current interest in heterobimetallic hydrido-bridged complexes results from the search for new, or more selective, hydrogen-transfer reactions and from their catalytic activity.

The formation of both homo- and hetero-nuclear hydrido-bridged complexes can be rationalized on the basis of the formal 'donor–acceptor' scheme proposed by Venanzi,[1] in which a mononuclear hydrido complex acts as a ligand, binding through one or more of its hydrogen atoms to a co-ordinatively unsaturated complex, which acts as an acceptor [equation (1)].

$$L_nMH_x + L'_mM'S \longrightarrow L_nM(\mu\text{-}H)_xM'L'_m \qquad (1)$$

Several examples of homobinuclear complexes of this type have been reported for platinum,[2] and examples of heterobinuclear complexes include $[(Et_3P)_2(C_6Cl_5)Pt(\mu\text{-}H)Au(PEt_3)]^+$ and $[(Ph_3P)_3H_2Ir(\mu\text{-}H)Au(PPh_3)]^+$,[3a] and the more recently prepared $[(Et_3P)_2(C_6Cl_5)Pt(\mu\text{-}H)HgR]^+$ [3b] which are only stable in solution at low temperature.

The stability of both types of compounds, homo- and hetero-binuclear, depends on both the steric and electronic effects of the ligands, and thus a better understanding of these factors will help to evaluate the scope of this synthetic method.

We have recently prepared the compounds *trans*-$[PtH(R)(PPh_3)_2]$ (R = C_6Cl_5 or different σ-bonded aryl groups).[4] In this paper we report their behaviour in the reaction with cationic platinum or gold species, in order to study how the nature of the PPh_3 group, less basic and bulkier than the more studied PEt_3, affects the hydrido-donating ability of the compounds *trans*-$[PtH(R)L_2]$ and the stability of the resulting binuclear monohydrido complexes.

During the preparation of this paper, Venanzi and co-workers[5] reported the *X*-ray crystal structure of the compound $[(Et_3P)_2(C_6F_5)Pt(\mu\text{-}H)Au(PPh_3)][CF_3SO_3]$ and the synthesis of analogous compounds with the moiety Pt–H–Ag.

Results and Discussion

The reaction of the hydrido complexes of platinum with gold cationic species leads to binuclear complexes, similar to the reported complexes containing PEt_3 [equation (2) (R = C_6Cl_5, $C_6H_3Cl_2$-2, 5, or C_6H_4Cl-*p*)].[2b]

$$trans\text{-}[PtH(R)(PPh_3)_2] + [Au(thf)(PPh_3)]ClO_4 \longrightarrow \underset{(1)}{[(Ph_3P)_2RPt(\mu\text{-}H)Au(PPh_3)]ClO_4} \qquad (2)$$

On the other hand, the reactions between *trans*-$[PtH(R)(PPh_3)_2]$ and $[Pt(MeOH)R(PPh_3)_2]^+$ do not give the binuclear complexes, even when R is a small *para*-substituted group (R = C_6H_4Cl-*p* or C_6H_4Me-*p*).

The ability of the species *trans*-$[PtH(R)(PR'_3)_2]$ to form hydrido-bridged complexes is related to the size of the PR'_3 group. Thus, for the small PMe_3 group a homonuclear hydrido-bridged complex of the type $[(R'_3P)_2RPt(\mu\text{-}H)PtR(PR'_3)_2]^+$ is obtained even for R = C_6Cl_5,[5] while for PEt_3 these compounds are only obtained when R has just one substituent in the *ortho* position (*e.g.* R = $C_6H_3Me_2$-2,4).[2b]

However, in reactions with the small linear gold species the complexes *trans*-$[PtH(R)(PPh_3)_2]$, with bulky ligands, behave as hydrido donors. The similar stability of the complexes (**1**) and the analogous PEt_3-containing complexes, in spite of the unfavourable steric effects of (**1**) may be due to the smaller basicity of PPh_3, since a greater electron density on the hydrido favours reduction to metallic gold.

The ^1H and ^{31}P n.m.r. spectra show unambiguously the bimetallic nature of the complexes with the hydrido bonded to both metals (see Table 1). The hydride is coupled to the phosphorus atoms bonded to platinum and to gold; in addition, platinum satellites are observed. The hydrido resonance is shifted (*ca.* 4 p.p.m.) towards lower fields and the *J*(Pt–H) coupling constant values decrease (*ca.* 20%) when compared to the corresponding mononuclear complexes.[4] The changes in the δ and *J* values are in the same range as for the analogous PEt_3 compounds.[5] The ^{31}P n.m.r. spectra show a *trans* configuration of the phosphines bound to platinum, and platinum satellites for both types of phosphorus.

The molecular structure of $[(Ph_3P)_2(C_6Cl_5)Pt(\mu\text{-}H)Au(PPh_3)]ClO_4$ is shown in the Figure. Selected bond lengths and angles are listed in Table 2. Although the position of the hydrido ligand has not been detected its presence has been unambiguously verified by n.m.r. spectroscopy. The Pt–Au distance, 2.792(1) Å, is slightly longer than for $[(Et_3P)_2(C_6F_5)Pt(\mu\text{-}H)Au(PPh_3)][CF_3SO_3]$, 2.714(1) Å,[5] in agreement with the smaller donor character of *trans*-$[PtH(C_6Cl_5)(PPh_3)_2]$

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† μ-Hydrido-2-pentachlorophenyl-1,2,2-tris(triphenylphosphine)gold platinum (*Au–Pt*) perchlorate–diethyl ether (1/2).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Proton and ^{31}P-(^1H) n.m.r. data[a] for the compounds $[(Ph_3P)_2RPt(\mu\text{-}H)Au(PPh_3)]ClO_4$

R	$\delta(P_a)$[b]	$J(P_aPt)$	$\delta(P_b)$	$J(P_bPt)$	$\delta(H)$[c]	$J(HPt)$	$J(HP_a)$	$J(HP_b)$
C_6Cl_5	−125.6	2 574	−100.0	240	−3.8	538	11.0	77.0
$C_6H_3Cl_2$-2,5	−122.6	2 648	−100.0	212	−2.7	505	10.5	84.0
C_6H_4Cl-*p*	−120.1	2 698	−100.5	199	−1.8	487	10.0	89.5

[a] ^1H N.m.r. in $CDCl_3$, referenced to $SiMe_4$; ^{31}P-{^1H} n.m.r. in CH_2Cl_2 at 213 K, referenced to $P(OMe)_3$; δ in p.p.m.; *J* in Hz. [b] P_a, P bound to Pt; P_b, P bound to Au. [c] Hydrido resonance.

Table 2. Selected bond lengths (Å) and angles (°) for $[(Ph_3P)_2(C_6Cl_5)Pt(\mu\text{-}H)Au(PPh_3)]ClO_4$

Au–Pt	2.792(1)	C(221)–P(2)	1.791(10)	O(1)–Cl(6)	1.285(17)
P(2)–Pt	2.312(7)	C(301)–P(3)	1.765(10)	O(2)–Cl(6)	1.407(21)
P(3)–Pt	2.334(7)	C(311)–P(3)	1.798(9)	O(3)–Cl(6)	1.259(15)
C(1)–Pt	2.099(12)	C(321)–P(3)	1.798(11)	O(4)–Cl(6)	1.487(15)
P(1)–Au	2.293(8)	C(2)–Cl(1)	1.768(18)	C(2)–C(1)	1.395(24)
C(101)–P(1)	1.713(19)	C(3)–Cl(2)	1.721(19)	C(6)–C(1)	1.395(25)
C(111)–P(1)	1.855(20)	C(4)–Cl(3)	1.682(13)	C(3)–C(2)	1.395(16)
C(121)–P(1)	1.785(15)	C(5)–Cl(4)	1.700(20)	C(4)–C(3)	1.395(25)
C(201)–P(2)	1.922(9)	C(6)–Cl(5)	1.686(19)	C(5)–C(4)	1.395(24)
C(211)–P(2)	1.784(10)			C(6)–C(5)	1.395(16)
P(2)–Pt–Au	86.5(1)	C(321)–P(3)–C(301)	105.0(6)	C(6)–C(5)–C(4)	120.0(16)
P(3)–Pt–Au	93.7(1)	C(321)–P(3)–C(311)	108.2(4)	C(1)–C(6)–Cl(5)	125.7(10)
P(3)–Pt–P(2)	176.3(2)	O(2)–Cl(6)–O(1)	103.7(11)	C(5)–C(6)–Cl(5)	114.3(14)
C(1)–Pt–Au	157.3(5)	O(3)–Cl(6)–O(1)	124.4(13)	C(5)–C(6)–C(1)	120.0(16)
C(1)–Pt–P(2)	89.7(6)	O(3)–Cl(6)–O(2)	104.9(12)	C(102)–C(101)–P(1)	114.2(11)
C(1)–Pt–P(3)	91.5(6)	O(4)–Cl(6)–O(1)	108.2(10)	C(106)–C(101)–P(1)	125.3(16)
P(1)–Au–Pt	160.9(2)	O(4)–Cl(6)–O(2)	101.1(11)	C(112)–C(111)–P(1)	119.9(16)
C(101)–P(1)–Au	111.6(8)	O(4)–Cl(6)–O(3)	111.6(9)	C(116)–C(111)–P(1)	120.1(11)
C(111)–P(1)–Au	110.6(6)	C(2)–C(1)–Pt	123.6(11)	C(122)–C(121)–P(1)	119.3(13)
C(111)–P(1)–C(101)	103.8(8)	C(6)–C(1)–Pt	116.3(12)	C(126)–C(121)–P(1)	120.7(13)
C(121)–P(1)–Au	116.1(6)	C(6)–C(1)–C(2)	120.0(11)	C(202)–C(201)–P(2)	118.2(7)
C(121)–P(1)–C(101)	107.3(9)	C(1)–C(2)–Cl(1)	116.0(9)	C(206)–C(201)–P(2)	121.8(6)
C(121)–P(1)–C(111)	106.6(10)	C(3)–C(2)–Cl(1)	123.3(13)	C(212)–C(211)–P(2)	124.3(6)
C(201)–P(2)–Pt	112.3(4)	C(3)–C(2)–C(1)	120.0(16)	C(216)–C(211)–P(2)	115.5(6)
C(211)–P(2)–Pt	112.6(4)	C(2)–C(3)–Cl(2)	115.8(14)	C(222)–C(221)–P(2)	119.4(8)
C(211)–P(2)–C(201)	104.3(4)	C(4)–C(3)–Cl(2)	124.1(10)	C(226)–C(221)–P(2)	120.6(6)
C(221)–P(2)–Pt	114.9(4)	C(4)–C(3)–C(2)	120.0(16)	C(302)–C(301)–P(3)	109.7(9)
C(221)–P(2)–C(201)	104.0(4)	C(3)–C(4)–Cl(3)	113.6(12)	C(306)–C(301)–P(3)	130.3(6)
C(221)–P(2)–C(211)	108.0(6)	C(5)–C(4)–Cl(3)	126.4(13)	C(312)–C(311)–P(3)	122.3(6)
C(301)–P(3)–Pt	117.3(4)	C(5)–C(4)–C(3)	120.0(11)	C(316)–C(311)–P(3)	117.7(6)
C(311)–P(3)–Pt	109.9(5)	C(4)–C(5)–Cl(4)	115.5(10)	C(322)–C(321)–P(3)	121.7(5)
C(311)–P(3)–C(301)	108.0(5)	C(6)–C(5)–Cl(4)	124.5(14)	C(326)–C(321)–P(3)	118.2(6)
C(321)–P(3)–Pt	108.1(4)				

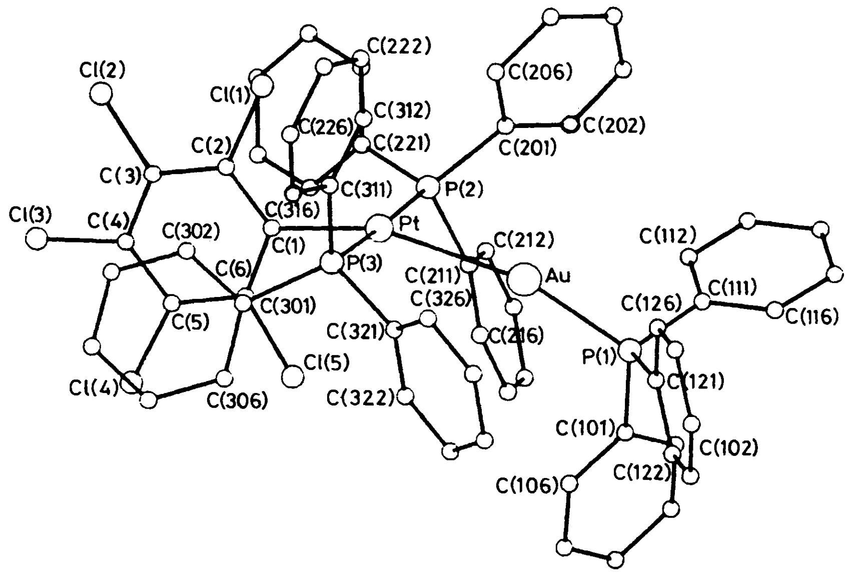

Figure. Molecular structure of $[(Ph_3P)_2(C_6Cl_5)Pt(\mu\text{-}H)Au(PPh_3)]^+$

Table 3. Positional parameters ($\times 10^4$) (Pt, Au, P, and Cl, $\times 10^5$) with estimated standard deviations in parentheses

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pt	19 067(1)	28 539(1)	22 895(2)
Au	30 672(1)	23 324(2)	18 295(2)
P(1)	38 608(5)	13 884(11)	10 635(13)
P(2)	19 531(3)	28 580(8)	2 585(10)
P(3)	18 779(4)	29 741(9)	43 866(10)
Cl(1)	9 833(5)	46 871(9)	29 424(13)
Cl(2)	−3 923(6)	42 462(14)	29 145(18)
Cl(3)	−9 817(6)	20 663(20)	24 328(24)
Cl(4)	−2 340(7)	1 826(13)	18 269(19)
Cl(5)	11 055(6)	5 493(9)	17 038(13)
Cl(6)	34 165(6)	80 904(12)	39 843(19)
C(1)	981(1)	2 625(2)	2 233(2)
C(2)	613(1)	3 413(2)	2 466(2)
C(3)	2(1)	3 188(2)	2 525(2)
C(4)	−241(1)	2 175(2)	2 349(2)
C(5)	127(1)	1 387(2)	2 116(2)
C(6)	738(1)	1 612(2)	2 057(2)
C(101)	4 315(1)	1 883(3)	139(3)
C(102)	4 037(1)	2 163(3)	−720(3)
C(103)	4 373(1)	2 466(3)	−1 635(3)
C(104)	4 986(1)	2 488(3)	−1 690(3)
C(105)	5 263(1)	2 207(3)	−830(3)
C(106)	4 928(1)	1 905(3)	84(3)
C(111)	4 326(1)	1 461(2)	2 363(3)
C(112)	4 475(1)	2 427(2)	3 275(3)
C(113)	4 810(1)	2 499(2)	4 277(3)
C(114)	4 994(1)	1 605(2)	4 367(3)
C(115)	4 845(1)	639(2)	3 456(3)
C(116)	4 511(1)	567(2)	2 454(3)
C(121)	3 696(1)	35(2)	201(3)
C(122)	3 324(1)	−568(2)	763(3)
C(123)	3 181(1)	−1 621(2)	100(3)
C(124)	3 410(1)	−2 070(2)	−1 125(3)
C(125)	3 782(1)	−1 467(2)	−1 687(3)
C(126)	3 925(1)	−415(2)	−1 024(3)
C(201)	2 111(1)	1 522(2)	−967(2)
C(202)	2 026(1)	1 338(2)	−2 229(2)
C(203)	2 121(1)	375(2)	−3 135(2)
C(204)	2 300(1)	−406(2)	−2 779(2)
C(205)	2 385(1)	−222(2)	−1 516(2)
C(206)	2 290(1)	741(2)	−610(2)
C(211)	2 546(1)	3 727(2)	−26(2)
C(212)	2 898(1)	3 525(2)	−1 132(2)
C(213)	3 316(1)	4 296(2)	−1 292(2)
C(214)	3 382(1)	5 269(2)	−346(2)
C(215)	3 030(1)	5 471(2)	761(2)
C(216)	2 612(1)	4 700(2)	921(2)
C(221)	1 290(1)	3 118(2)	−235(3)
C(222)	815(1)	2 352(2)	−531(3)
C(223)	295(1)	2 552(2)	−920(3)
C(224)	249(1)	3 518(2)	−1 013(3)
C(225)	724(1)	4 284(2)	−717(3)
C(226)	1 244(1)	4 084(2)	−328(3)
C(301)	1 227(1)	2 423(3)	4 963(3)
C(302)	788(1)	3 100(3)	5 257(3)
C(303)	235(1)	2 822(3)	5 723(3)
C(304)	120(1)	1 867(3)	5 895(3)
C(305)	559(1)	1 190(3)	5 601(3)
C(306)	1 113(1)	1 468(3)	5 135(3)
C(311)	2 004(1)	4 299(2)	5 388(2)
C(312)	2 187(1)	5 092(2)	4 912(2)
C(313)	2 289(1)	6 114(2)	5 731(2)
C(314)	2 207(1)	6 343(2)	7 025(2)
C(315)	2 024(1)	5 551(2)	7 501(2)
C(316)	1 922(1)	4 529(2)	6 682(2)
C(321)	2 457(1)	2 276(2)	4 577(3)
C(322)	2 892(1)	2 764(2)	5 442(3)
C(323)	3 319(1)	2 193(2)	5 612(3)
C(324)	3 313(1)	1 135(2)	4 917(3)
C(325)	2 878(1)	648(2)	4 052(3)
C(326)	2 451(1)	1 218(2)	3 881(3)
O(1)	3 723(2)	7 317(4)	3 602(5)
O(2)	3 345(3)	8 276(4)	2 857(5)
O(3)	2 905(2)	8 076(4)	4 469(5)
O(4)	3 805(2)	9 034(4)	4 692(5)
C(71)	4 882(3)	4 692(5)	1 724(6)
C(72)	4 282(3)	4 982(5)	2 488(6)
O(73)	4 349(3)	4 947(5)	3 681(6)
C(74)	3 803(3)	5 056(5)	4 347(6)
C(75)	3 912(3)	5 323(5)	5 792(6)
C(81)	1 897(5)	6 645(9)	558(6)
O(82)	1 457(5)	7 167(9)	1 676(6)
C(83)	1 528(5)	7 582(9)	2 988(6)
C(84)	1 541(5)	8 283(9)	2 225(6)
C(85)	1 802(5)	8 656(9)	3 732(6)

when compared to *trans*-[PtH(C_6F_5)(PEt_3)$_2$]; according to the statement of Venanzi and co-workers[5] that the M–M′ interaction in these systems is related to the electron-donor capacity of the neutral MHL_n group. However, steric effects cannot be excluded as the increased size of PPh_3 would also lead to an increase in the Pt–Au distance.

The platinum atom displays a puckered square co-ordination with Au–Pt–C(1) angles equal to 157.3(5)° and deviations from atom to mean plane equal to Pt 0.147(1), Au −0.257(1), P(2) 0.243(7), P(3) 0.212(7), and C(1) −0.345(12) Å.

As expected for an aryl-platinum(II) complex, the C_6Cl_5 ligand is nearly perpendicular to the mean platinum co-ordination plane; the dihedral angle being 81.2(6)°. The Pt–C and Pt–P bond lengths compare well with those of similar compounds. The torsion angles Au–Pt–P(3)–C(321) −19.0(6)° and Au–Pt–P(2)–C(211) −56.68(6)° indicate a different conformation of triphenylphosphine ligands in marked contrast with their usual eclipsed form.[4]

Experimental

Chemical analyses were carried out at the 'Institut de Química Bio-Orgànica de Barcelona (CSIC)'. The ^1H and $^{31}P-\{^1H\}$ n.m.r. spectra were obtained on a Bruker FT-80 SY spectrometer.

X-*Ray Crystal-structure Determination.—Crystal data.* $C_{60}H_{46}AuCl_6O_4P_3Pt{\cdot}2C_4H_{10}O$, $M = 1\,677.0$, triclinic, $a = 22.866(7)$, $b = 13.844(5)$, $c = 11.392(4)$ Å, $\alpha = 110.79(3)$, $\beta = 85.13(2)$, $\gamma = 96.95(2)$°, $U = 3\,343(2)$ Å^3, space group $P\bar{1}$, $D_c = 1.665$ g cm^{-3}, $Z = 2$, $F(000) = 1\,652$, λ(Mo-K_α) = 0.710 69 Å, μ(Mo-K_α) = 48.18 cm^{-1}, $T = 288$ K.

Data collection. A prismatic crystal (0.1 × 0.1 × 0.15 mm) was selected and mounted on a Philips PW-1100 four-circle diffractometer. Unit-cell parameters were determined from 25 reflections ($4 \leqslant \theta \leqslant 12$°) and refined by the least-squares method. Intensities were collected with graphite-monochromatized Mo-K_α radiation, using the ω-scan technique with scan width 0.8° and scan speed 0.03° s^{-1}. 9 327 Reflections were measured in the range $2 \leqslant \theta \leqslant 25$°, 4 477 of which were assumed as observed applying the condition $I \geqslant 2.5\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity control; significant intensity decay was not observed. Lorentz polarization and absorption corrections were made. An empirical method was used for absorption correction (maximum and minimum transmission factors were 0.95 and 0.87).

Structure solution and refinement. The structure was solved by direct methods, using the MULTAN system of computer programs[6] and refined by full-matrix least squares, using the SHELX 76 program.[7] The function minimized was $\Sigma w[(F_o) - F_c]^2$, where $w = \sigma^{-2}(F_o)$. Scattering factors, f, f', and f'', were taken from ref. 8. Benzene rings were refined with planarity and geometry constrained to theoretical values. The diethyl ether molecules were refined with an overall isotropic thermal parameter and constrained bond lengths and angles. Hydrogen atoms were not located. The final R value was 0.032 for all observed reflections. Maximum shift/e.s.d. = 0.4 in z of C(75). Maximum peak in final difference synthesis was 0.4 e Å^{-3}. Final positional parameters are given in Table 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Preparation.—The synthesis of compounds (**1**) was carried out under nitrogen. To a solution of $[AuCl(PPh_3)]$[9] (0.095 g, 0.19 mmol) in thf (tetrahydrofuran, 5 cm^3), a solution of $Ag(ClO_4)$ (0.039 g, 0.19 mmol) in thf (5 cm^3) was added at room temperature. The AgCl was filtered off over Celite and the solution obtained was added to a solution of *trans*-$[PtH(R)(PPh_3)_2]$[4] (R = C_6Cl_5, $C_6H_3Cl_2$-2,5, or C_6H_4Cl-*p*) (0.19 mmol) in thf (10 cm^3) at −40 °C. The mixture was stirred at this temperature for 45—60 min and then concentrated to 5 cm^3 and filtered over Celite. On addition of diethyl ether (15 cm^3) white crystals were formed, filtered off, and dried *in vacuo*. Yield 50—60%.

R = C_6Cl_5. M.p. 150 °C (decomp.) (Found: C, 46.9; H, 3.3; Cl, 11.7. $C_{60}H_{46}AuCl_6O_4P_3Pt$ requires C, 47.1; H, 3.0; Cl, 11.6%).

R = $C_6H_3Cl_2$-2,5. M.p. 110 °C (decomp.) (Found: C, 50.5; H, 4.0; Cl, 5.2. $C_{60}H_{49}AuCl_3O_4P_3Pt$ requires C, 50.6; H, 3.5; Cl, 5.2%).

R = C_6H_4Cl-*p*. M.p. 105 °C (decomp.) (Found: C, 50.9; H, 3.7; Cl, 2.3. $C_{60}H_{50}AuCl_2O_4P_3Pt$ requires C, 51.8; H, 3.6; Cl, 2.5%).

References

1 L. M. Venanzi, *Coord. Chem. Rev.*, 1982, **43**, 251.

2 (*a*) G. Bracher, D. M. Grove, P. S. Pregosin, and L. M. Venanzi, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 155; (*b*) D. Carmona, R. Thouvenot, L. M. Venanzi, F. Bachechi, and L. Zambonelli, *J. Organomet. Chem.*, 1983, **250**, 589; (*c*) J. Terheijden, G. vanKoten, D. M. Grove, K. Vrieze, and A. L. Spek, *J. Chem. Soc., Dalton Trans.*, 1987, 1359.

3 (*a*) H. Lehner, D. Matt, P. S. Pregosin, L. M. Venanzi, and A. Albinati, *J. Am. Chem. Soc.*, 1982, **104**, 6825; (*b*) B. S. McGilligan, L. M. Venanzi, and M. Wolfer, *Organometallics*, 1987, **6**, 946.

4 M. Crespo, J. Sales, X. Solans, and M. Font Altaba, *J. Chem. Soc., Dalton Trans.*, 1988, 1617.

5 A. Albinati, H. Lehner, L. M. Venanzi, and M. Wolfer, *Inorg. Chem.*, 1987, **26**, 3933.

6 P. Main, S. E. Fiske, S. L. Hull, L. Lessinger, G. Germain, J. P. Declercq, and M. M. Woofson, MULTAN, an automatic system of computer programs for crystal structure determination from *X*-ray diffraction data, University of York and University of Louvain, Belgium, 1984.

7 G. M. Sheldrick, SHELX 76, A computer program for crystal structure determination, University of Cambridge, 1976.

8 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4, pp. 99—100, 149.

9 C. A. McAuliffe, R. V. Parish, and P. D. Randall, *J. Chem. Soc., Dalton Trans.*, 1979, 1730.

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