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Structure and Properties of the Hydride-Containing Cluster Ion $Pt(H)(PPh_3)(AuPPh_3)_7{}^{2+}$

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The title cluster ion can be prepared by the reaction of H_2 with $Au(PPh_3)^+$ and $Pt(PPh_3)_3$ as well as by the reaction of $Pt(AuPPh_3)_8{}^{2+}$ with PPh_3 and an acid. Mössbauer spectra show that the central atom is Pt. The structure was determined by X-ray diffraction of $Pt(H)(PPh_3)(AuPPh_3)_7(PF_6)_2\cdot{}^1/_2CH_2Cl_2$ (triclinic, $P\bar{1}$, a = 17.085 (6) Å, b = 17.301 (8) Å, c = 29.401 (12) Å, α = 94.62 (10)°, β = 96.26 (5)°, γ = 118.24 (5)°, V = 7523.2 Å^3, Z = 2, R = 0.085 and R_w = 0.115 for 15921 unique reflections and 596 variables, Cu Kα radiation). In the metal cluster the central Pt is surrounded by seven Au atoms and one PPh_3 in a distorted cubic geometry, each Au being attached to a PPh_3. The H is close to Pt and at least two Au atoms, as can be concluded from deformations in the metal frame and from Orpen calculations. Detailed ^{31}P, ^{195}Pt, and ^1H NMR spectra are presented. The different Au-*P*Ph$_3$ sites, present in the crystal, are equilibrated in solution at room temperature.

Introduction

Recently we reported the structure[1] and properties[2] of $Pt(AuPPh_3)_8{}^{2+}$ (PPh_3 = triphenylphosphine), which is a cluster compound with a central Pt surrounded by eight Au atoms and is isoelectronic with the homonuclear $Au(AuPPh_3)_8{}^{3+}$. In the conversions of homonuclear Au cluster compounds the reactions (1) and (2) are of great importance.[3]

$$Au(AuPPh_3)_8{}^{3+} \rightleftarrows Au(AuPPh_3)_7{}^{2+} + AuPPh_3{}^+ \qquad (1)$$

$$Au(AuPPh_3)_7{}^{2+} + PPh_3 \rightleftarrows Au(PPh_3)(AuPPh_3)_7{}^{2+} \qquad (2)$$

Here we report that these reactions in the case of $Pt(AuPPh_3)_8{}^{3+}$ yield $Pt(H)(PPh_3)(AuPPh_3)_7{}^{2+}$, the protonated analogue of $Au(PPh_3)(AuPPh_3)_7{}^{2+}$. In the crystal structure determination, we could neither distinguish between Pt and Au nor detect the proton in the cluster. ^{195}Pt, ^{31}P and, ^1H NMR spectra and ^{197}Au Mössbauer spectra, however, contribute to a more complete picture of the structure.

Experimental Section

Measurements. C, H, and N analyses were carried out in the microanalytical department of the University of Nijmegen, and the other analyses, by Dr. A. Bernhardt, Elbach über Engelskirchen, FRG. $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker WM 200 spectrometer at 81.02 MHz by using CD_2Cl_2 solutions and TMP in CD_2Cl_2 as reference, ^{195}Pt NMR spectra were recorded at 43.02 MHz by using CD_2Cl_2 solutions and $PtCl_6{}^{2-}$ in D_2O as reference, and ^1H NMR spectra were recorded at 200.13 MHz by using CD_2Cl_2 solutions and TMS in CD_2Cl_2 as reference. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer. Mössbauer spectra were measured in Kamerlingh Onnes Laboratorium of Leiden University with a spectrometer described elsewhere.[4] Fast atom bombardment mass spectrometry (FABMS) measurements were carried out with a VG Analytical Ltd. 7070 E-HF high-resolution double-focusing mass spectrometer at the University of Minnesota. A *m*-nitrobenzyl alcohol matrix was used, and mass calibration was achieved with reference spectra of CsI clusters. Calibration was checked before and after acquisition of data with a maximum error of 0.3 Da. Details of the experimental procedure can be found elsewhere.[5]

Preparations. $AuPPh_3NO_3$,[6] $Pt(AuPPh_3)_8(NO_3)_2$,[1] and $Pt(PPh_3)_3$[7] were prepared according to literature methods. The other reagents were obtained from commercial sources and used without further purification.

$Pt(H)(PPh_3)(AuPPh_3)_7(NO_3)_2$. A 637-mg (1.22-mmol) sample of $AuPPh_3NO_3$ and 200 mg (0.204 mmol) of $Pt(PPh_3)_3$ were dissolved in 30 mL of THF. H_2 was bubbled through the solution for 2 h at room temperature and atmospheric pressure, and a red product began to precipitate. After the mixture was allowed to stand overnight, the product was filtered off, recrystallized by slow diffusion of diethyl ether in a dichloromethane solution of the product, and dried in vacuo; yield 350 mg (0.1 mmol). Anal. Calcd for $PtAu_7P_8C_{144}H_{121}N_2O_6$: C, 45.54; H, 3.12; N, 0.74. Found: C, 45.22; H, 3.20; N, 0.73.

$Pt(H)(PPh_3)(AuPPh_3)_7(PF_6)_2$. A 380-mg (0.1-mmol) sample of $Pt(H)(PPh_3)(AuPPh_3)_7(NO_3)_2$ was dissolved in 50 mL of methanol, and then 80 mg (0.5 mmol) of NH_4PF_6 was added. The precipitated product was purified by the same procedure as described for the nitrate compound; yield 90%. Anal. Calcd for $PtAu_7P_{10}C_{144}H_{121}F_{12}$: Au, 34.80; Pt, 4.92. Found: Au, 35.00; Pt, 4.93.

Table I. Crystal Data for $Pt(H)(PPh_3)(AuPPh_3)_7(PF_6)_2\cdot{}^1/_2CH_2Cl_2$

formula	$C_{144}H_{121}Au_7F_{12}P_{10}Pt\cdot C_{1/2}HCl$	γ	118.24 (5)°
fw	4089	V	7523.2 Å^3
cryst syst	triclinic	Z	2
space group	$P\bar{1}$	ρ(calcd)	1.641 g/cm^3
temp	193 K	radiation	Cu Kα (λ = 1.54184 Å)
a	17.085 (6) Å	μ(Cu Kα)	162.4 cm^{-1}
b	17.301 (8) Å	transmissn coeff	0.09-0.45
c	29.401 (12) Å	R	0.085
α	94.62 (10)°	$R_w{}^a$	0.115
β	96.26 (5)°		

[a] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

A crystal suitable for X-ray diffraction study was obtained by slow diffusion of diethyl ether into a dichloromethane solution of $Pt(H)(PPh_3)(AuPPh_3)_7(PF_6)_2$. The precipitated crystals contained half of a molecule of CH_2Cl_2 per cluster, as could be detected in the X-ray structure determination.

Infrared spectra show absorptions of the triphenylphosphine and of the uncoordinated negative ion ($NO_3{}^-$ or $PF_6{}^-$); no metal-hydride absorption could be detected. $^{31}P\{^1H\}$ NMR: AuP (doublet) δ = 47.5 ppm, ^2J(PtP) = 414 Hz, 3J(PP) = 34 Hz; PtP (octet) δ = 61.0 ppm, ^1J(PtP) = 2300 Hz, 3J(PP) = 34 Hz. When the ^1H decoupling was limited to the area of the phenyl protons, the doublet of the AuP was further split with J(HP) = 14 Hz; the PtP octet was broadened, but no J(HP) could be determined. ^{195}Pt NMR: δ = −5425 ppm (multiplet), J(PtH) = 537 Hz, ^2J(PtP) = 413 Hz, ^1J(PtP) = 2287 Hz. ^1H NMR (hydride): δ = 2.26 ppm (multiplet), ^1J(HPt) = 537 Hz, 2J(HPtP) = 6.6 Hz, J(HAuP) = 16.6 Hz.

Structure Determination of $Pt(H)(PPh_3)(AuPPh_3)_7(PF_6)_2\cdot{}^1/_2CH_2Cl_2$

Collection of X-ray Data. A single crystal was obtained by slow diffusion of diethyl ether into a dichloromethane solution of the compound. To avoid decomposition, due to loss of solvent, the data were collected at 193 K. The unit cell dimensions were calculated from the

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Table II. Selected Fractional Positional and Thermal Parameters ($Å^2$) with Esd's

atom	x	y	z	10^2U_{eq}
Pt	0.00891 (5)	0.50664 (4)	0.29068 (3)	3.95 (3)
Au2	−0.05109 (6)	0.34386 (5)	0.24257 (3)	5.08 (3)
Au3	0.11785 (6)	0.43524 (5)	0.30429 (3)	5.33 (4)
Au4	0.17194 (6)	0.59409 (6)	0.26590 (4)	6.81 (4)
Au5	0.08369 (7)	0.68571 (5)	0.31738 (3)	6.37 (4)
Au6	−0.16965 (6)	0.38975 (7)	0.28189 (4)	6.60 (4)
Au7	0.00638 (6)	0.50379 (5)	0.19971 (3)	4.95 (3)
Au8	−0.07450 (8)	0.59014 (9)	0.25000 (4)	7.78 (6)
P1	0.0064 (3)	0.5017 (3)	0.3698 (2)	4.0 (2)
P2	−0.1161 (4)	0.2024 (3)	0.2012 (2)	5.8 (2)
P3	0.2082 (4)	0.3774 (4)	0.3290 (2)	5.9 (2)
P4	0.3106 (4)	0.6714 (4)	0.2438 (2)	6.7 (2)
P5	0.1490 (5)	0.8306 (3)	0.3537 (2)	7.3 (3)
P6	−0.3181 (3)	0.3065 (4)	0.2883 (2)	6.6 (2)
P7	0.0038 (4)	0.5037 (4)	0.1208 (2)	5.8 (2)
P8	−0.1501 (5)	0.6557 (4)	0.2161 (2)	7.1 (3)

Table III. Selected Bond Lengths (Å) and Bond Angles (deg) with Esd's

Pt–Au2	2.700 (1)	Au4–Au7	2.890 (1)
Pt–Au3	2.691 (1)	Au5–Au8	2.835 (1)
Pt–Au4	2.685 (1)	Au6–Au8	3.326 (2)
Pt–Au5	2.737 (1)	Au7–Au8	2.893 (1)
Pt–Au6	2.714 (1)	Pt–P1	2.340 (5)
Pt–Au7	2.666 (1)	Au2–P2	2.315 (5)
Pt–Au8	2.721 (1)	Au3–P3	2.290 (5)
Au2–Au3	2.864 (1)	Au4–P4	2.303 (6)
Au2–Au6	2.820 (1)	Au5–P5	2.308 (5)
Au2–Au7	2.910 (1)	Au6–P6	2.287 (5)
Au3–Au4	2.829 (1)	Au7–P7	2.316 (6)
Au4–Au5	3.074 (2)	Au8–P8	2.288 (6)
Au3–Au2–Au6	106.5 (1)	Au2–Pt–P1	111.7 (1)
Au3–Au2–Au7	87.5 (1)	Au3–Pt–P1	83.0 (1)
Au6–Au2–Au7	86.8 (1)	Au4–Pt–P1	116.5 (1)
Au2–Au3–Au4	93.1 (1)	Au5–Pt–P1	83.5 (1)
Au3–Au4–Au5	103.2 (1)	Au6–Pt–P1	83.8 (1)
Au3–Au4–Au7	88.5 (1)	Au7–Pt–P1	177.2 (1)
Au5–Au4–Au7	87.2 (1)	Au8–Pt–P1	116.0 (1)
Au4–Au5–Au8	89.2 (1)	Pt–Au2–P2	174.6 (1)
Au2–Au6–Au8	92.5 (1)	Pt–Au3–P3	170.1 (2)
Au2–Au7–Au4	90.8 (1)	Pt–Au4–P4	178.5 (2)
Au2–Au7–Au8	100.3 (1)	Pt–Au5–P5	169.3 (2)
Au4–Au7–Au8	91.8 (1)	Pt–Au6–P6	168.6 (1)
Au5–Au8–Au6	102.6 (1)	Pt–Au7–P7	178.9 (1)
Au5–Au8–Au7	91.8 (1)	Pt–Au8–P8	177.7 (2)
Au6–Au8–Au7	78.2 (1)		

setting angles of 25 reflections with 32° < 2θ < 66°. The crystal data are listed in Table I. A profile analysis was performed on all reflections.[8,9] After correction for Lorentz and polarization effects and after an empirical absorption correction,[10] the equivalent reflections were averaged ($R_{av} = \sum||F| - |\bar{F}||/\sum|F|$) = 0.057, including all reflections). No extinction correction was applied.

Solution and Refinement of the Structure. The positions of the heavy atoms (Au, Pt, and P) were found automatically by PATSYS,[11] which combines the Patterson part of SHELXS-86[12] and DIRDIF.[13] The remaining phenyl carbons were positioned from four successive difference Fourier maps. The phenyl rings were treated as rigid groups with ideal geometry. The electron density peaks found at positions between the cluster ions (at distances more than 3.5 Å from any atom) could be interpreted as three disordered PF_6 ions and a CH_2Cl molecule, which were included in the refinement as rigid groups. Refinement of the occupation factors leads to a total of two PF_6 ions and half of a CH_2Cl_2 molecule per cluster unit. The structure was refined by full-matrix least squares on F values by using SHELX.[14] Scattering factors were taken from ref 15. Isotropic refinement converged to R = 0.164. At this stage an additional empirical absorption correction was applied,[16] resulting in a further decrease of R to 0.138. During the final stage of the refinement the anisotropic vibration parameters of the gold, platinum, and phosphorus atoms were refined. The hydrogen atoms were given fixed isotropic temperature factors of 0.08 $Å^2$. Selected positional and thermal parameters are given in Table II, and selected bond distances and angles, in Table III. Experimental details, calculated and observed structure factors, and all positional parameters of the light atoms are available as supplementary material.

Table IV. Positive-Ion FABMS Data for $Pt(H)(PPh_3)(AuPPh_3)_7(NO_3)_2$ ($M = PtAu_7H(PPh_3)_8$)

mass	rel abund	assgnt
3472	16	$(M - PPh_3 + NO_3)^+$
3410	24	$(M - PPh_3)^+$
3211	29	$(M - 2PPh_3 + NO_3)^+$
3148	53	$(M - 2PPh_3)^+$
2951	100	$(M - 2PPh_3 - Au)^+$
2689	42	$(M - 3PPh_3 - Au)^+$

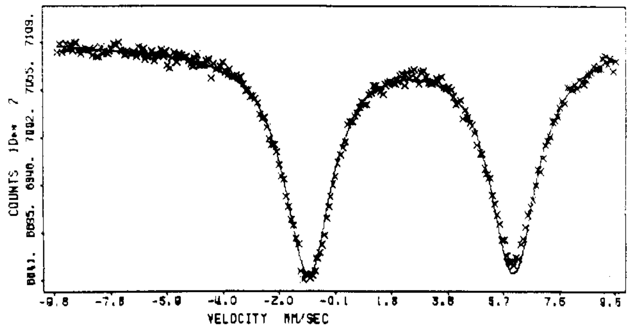

Figure 1. ^{197}Au Mössbauer spectrum of $Pt(H)(PPh_3)(AuPPh_3)_7(NO_3)_2$.

Results

Synthesis and Composition. The red compound can be prepared in good yield by the reaction of H_2 at room temperature and atmospheric pressure with a solution of $AuPPh_3NO_3$ and $Pt(PPh_3)_3$ (molar ratio 6:1). Elemental analysis shows a cluster composition of $PtAu_7(PPh_3)_8$ and two negative ions (NO_3^- or PF_6^-). As no paramagnetism is present, the cluster should either be a dimer or contain an uneven number of protons. The ^{195}Pt NMR spectrum shows a doublet due to Pt–H coupling (δ = −5425 ppm; J(PtH) = 537 Hz), so one H is present per Pt. The molecular composition $PtHAu_7(PPh_3)_8(NO_3)_2$ was confirmed by FABMS. This has been shown to be a successful technique for the determination of the correct molecular composition of cationic cluster compounds.[5] The positive-ion FABMS spectrum in the 1000–4000 mass range has a great number of peaks; those with the highest mass are given in Table IV. Each peak consists of a complex envelope due to the various isotopic combinations for a given molecular formula. A complete simulation of isotopic combinations gave a distribution pattern that closely matched the observed pattern. This provides strong evidence that the formula of M is correct and one hydride per Pt is present in $Pt(H)(PPh_3)(AuPPh_3)_7^{2+}$.

Mössbauer Spectrum. The ^{197}Au Mössbauer spectrum is shown in Figure 1. It has two asymmetric resonance bands, which are too broad to be interpreted as one quadrupole pair. The best fit for the experimental curve is obtained with a simulation of two quadrupole pairs with isomer shifts of 1.95 and 2.17 mm·s^{-1} and quadrupole splittings of 5.96 and 7.33 mm·s^{-1}, respectively, and

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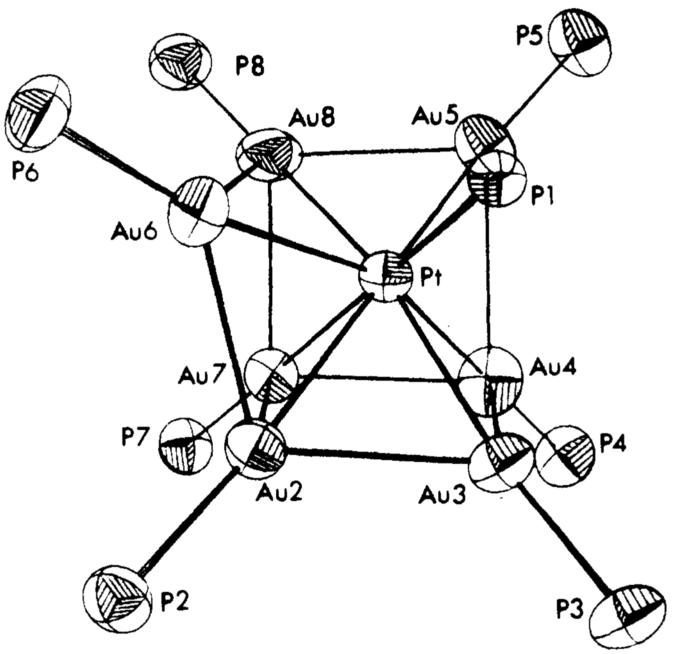

Figure 2. Molecular structure, determined by X-ray analysis of $[Pt(H)(PPh_3)(AuPPh_3)_7](PF_6)_2 \cdot {}^1/_2CH_2Cl_2$.

with an intensity ratio of 2:5. The most significant feature of the spectrum is the absence of a singlet at an isomer shift of about 3 $mm \cdot s^{-1}$. Such a singlet is always found in gold clusters with a central Au atom and a $(S^{\sigma})^2(P^{\sigma})^6$ cluster-electron configuration, like $Au_8(PPh_3)_8^{2+}$, $Au_9(PPh_3)_8^{+}$, $Au_{11}(PPh_3)_7X_3$ (X = CN, I, SCN), and $Au_{11}(dppp)_5^{3+}$. When the cluster-electron configuration is $(S^{\sigma})^2(P^{*})^4$, the central Au atom has a quadrupole pair that often is hidden under the quadrupole pairs of the peripheral Au atoms. The absence of a singlet in the $(S^{\sigma})^2(P^{\sigma})^6$ $Pt(H)(PPh_3)(AuPPh_3)_7^{2+}$ spectrum proves that the central atom, which the X-ray crystal structure determination has detected, is a Pt atom. The two quadrupole pairs are from the seven peripheral Au atoms. The Mössbauer parameters of these atoms are very close to those of peripheral Au sites in $Au(PPh_3)(AuPPh_3)_7^{2+}$ (isomer shift 1.9 $mm \cdot s^{-1}$; quadrupole splitting 6.7 $mm \cdot s^{-1}$). The peripheral Au atoms are all bonded to a phosphine, but their geometrical positions are different (see Figure 2). However, such geometrical differences have not caused significantly different Mössbauer parameters in the polynuclear gold clusters studies to date.[17] We think that the H in $Pt(H)(PPh_3)(AuPPh_3)_7^{2+}$ is close to two Au atoms (vide infra), and this might be the reason that two slightly different quadrupole pairs appear in the Mössbauer spectrum.

The X-ray-Determined Structure of $Pt(H)(PPh_3)(AuPPh_3)_7^{2+}$. The molecular structure is shown in Figure 2, and some relevant bond lengths and angles are listed in Table III. The geometry of the $PtAu_7$ frame is that of a distorted cube with Pt in the center and seven vertices occupied by Au. The P of the phosphine ligand bonded to Pt is close to the eighth vertex of the cube. The bond lengths between Pt and Au atoms 2, 3, 4, and 7 are between 2.67 and 2.70 Å, which is about the same as in $Pt(PPh_3)(C_2{}^tBu)(AuPPh_3)_6^{+}$ (2.67–2.69 Å)[18] and in $Pt(CO)(AuPPh_3)_8^{2+}$ (2.65–2.70 Å)[2] but longer than in $Pt(AuPPh_3)_8^{2+}$ (2.63–2.64 Å).[1] The distance between the central metal and the Au atom trans to the phosphine attached to the central metal (Pt–Au(7)) is the smallest, just as in $Au(PPh_3)(AuPPh_3)_7^{2+}$. The bond lengths between Pt and Au atoms 6, 8, and 5 are significantly longer: 2.71, 2.72, and 2.74 Å, respectively. The nearest Au–Au distances in the periphery are nearly all between 2.82 and 2.91 Å, which is about the same as in $Pt(AuPPh_3)_8^{2+}$ and in $Au(PPh_3)(AuPPh_3)_7^{2+}$. However, the Au(4)–Au(5) and Au(6)–Au(8) distances are much longer, 3.07 and 3.33 Å, respectively. Radial and peripheral bond lengths are much longer around Au(5), Au(6), and Au(8), which is probably caused by the proximity of H (vide infra).

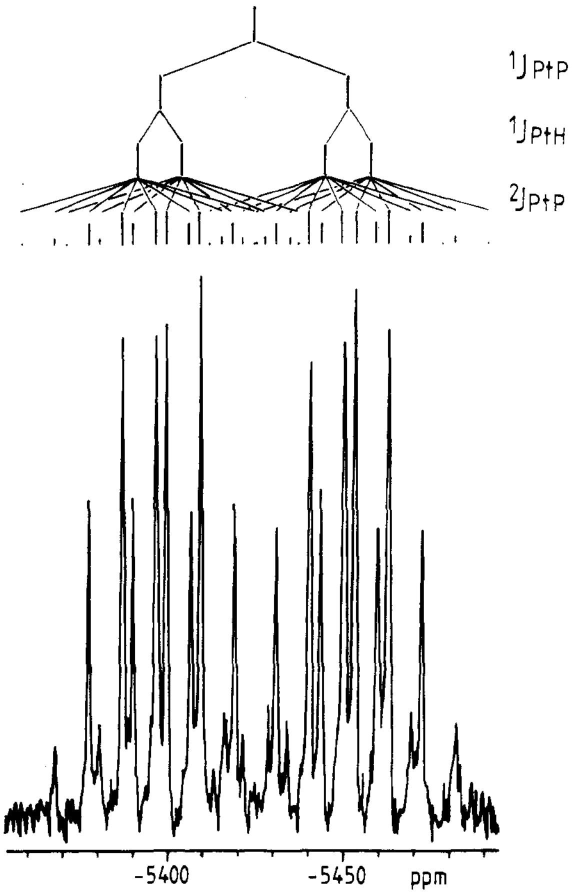

Figure 3. ^{195}Pt NMR spectrum of $Pt(H)(PPh_3)(AuPPh_3)_7^{2+}$, showing the coupling with H and the two different P sites.

The Au–P bond lengths (2.28–2.31 Å) are in the normal range found for gold–triphenylphosphine clusters. The Pt–P bond length is 2.34 Å, which is considerably longer than in mononuclear platinum–triphenylphosphine compounds (2.24 Å). There are two other compounds known where both triphenylphosphine and Au are bonded to Pt. In these compounds the Pt–P distances are also long: 2.31–2.32 Å in $Au_2Pt_2(PPh_3)_4(CN\text{-}2,6\text{-}Me_2C_6H_3)_4(PF_6)_2$[19] and 2.34–2.41 Å in $Pt_3Au(\mu_2\text{-}CO)_3(PPh_3)_5(NO_3)$.[20]

NMR Spectra. The $^{31}P\{^1H\}$ NMR spectrum shows a doublet (δ = 47.5 ppm; J(PtP) = 414 Hz) and an octet (δ = 61.0 ppm; J(PtP) = 2300 Hz) in an intensity ratio of 7:1, caused by the AuP and PtP sites, respectively. The different geometric sites for AuP in the crystalline state are apparently equilibrated in solution at room temperature by a fast fluxionality. The ^{195}Pt NMR spectrum is shown in Figure 3 (δ = −5425 ppm; $^1J(PtP)$ = 2287 Hz, $^2J(PtP)$ = 413 Hz, $^1J(PtH)$ = 537 Hz). The high Pt–H coupling constant indicates that H and Pt are directly bonded. In the ^1H NMR spectrum this H gives a signal at 2.26 ppm with Pt satellites and $^2J(HP)$ = 6.6 Hz and $^3J(HP)$ = 16.6 Hz. These assignments could be confirmed in the ^{31}P NMR spectrum with partial H decoupling. The low value for $^2J(HP)$ indicates that the P–Pt–H angle is rather sharp.

Discussion

$Pt(AuPPh_3)_8^{2+}$ and $Pt(H)(PPh_3)(AuPPh_3)_7^{2+}$ can be interconverted through reactions 3 and 4, which are similar to reactions 1 and 2. However, acid and base are needed in (3) and (4),

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Table V. Best Results of Orpen Calculations: Fractional Positions, Bond Lengths (Å), and Potential Energies (eV)

bond length					fractional position			
Pt-H	Au-H				*x*	*y*	*z*	energy
1.86	Au(5)	1.83	Au(8)	1.82	-0.0282	0.5879	0.3084	0.54
1.85	Au(4)	1.82	Au(5)	1.82	0.1204	0.6029	0.3157	1.01
1.86	Au(3)	1.82	Au(4)	1.82	0.1281	0.5447	0.3162	1.16
1.86	Au(2)	1.81	Au(6)	1.81	-0.0649	0.3887	0.2971	1.99
1.85	Au(2)	1.80	Au(3)	1.80	-0.0007	0.3986	0.3011	2.46

respectively, for a reasonable yield. Unprotonated $Pt(PPh_3)(AuPPh_3)_7^+$ could not be detected.

$$Pt(AuPPh_3)_8^{2+} + H^+ + 2PPh_3 \rightarrow Pt(H)(PPh_3)(AuPPh_3)_7^{2+} + Au(PPh_3)_2^+ \quad (3)$$

$$Pt(H)(PPh_3)(AuPPh_3)_7^{2+} + NEt_3 + 2AuPPh_3^+ \rightarrow Pt(AuPPh_3)_8^{2+} + HNEt_3^+ + Au(PPh_3)_2^+ \quad (4)$$

The presence of H in the Pt-Au cluster compound is firmly established by FABMS and NMR data. The asymmetric positions of the Au atoms around the central Pt give an indication where this H could be located. A method for the location of hydride ligands has been developed by Orpen.[21] On the basis of the X-ray-determined coordinates of the non-hydrogen atoms, the potential energy is minimized by varying the hydride position. For a large variety of clusters this method has proven to be useful in determining hydride positions.[22,23] For $Pt(H)(PPh_3)(AuPPh_3)_7^{2+}$ the best solutions are obtained if bonding interactions of H with Pt and two Au atoms (facial bridging μ_3-coordination) are allowed. The five best solutions are given in Table V. The lowest potential energy corresponds with H μ_3-bonded to Pt, Au(5), and Au(8), and this is in accord with the conclusions given above, concerning bonding lengths around Au(5) and Au(8), the high ^{195}Pt-H coupling constant, and the intensity ratio of 2:5 for the two quadrupole pairs in the Mössbauer spectrum. In a simple approximation of the HOMO of $Pt(PPh_3)(AuPPh_3)_7^+$, which lacks the H atom, using X-ray-determined coordinates and an EHMO calculation, the maximum electron density was found in a lobe pointing toward Au(6) and Au(8). This suggests that H should be bonded near that region. Although all these arguments do not give an accurate position of H, we can safely conclude that it is positioned within the area defined by Pt, Au(5), Au(6), and Au(8).

In the very few other known hydride complexes of gold, the hydride is μ_2-bridging between Au and Pt, Ir, Ru, Cr, or W.[23,24]

The Pt-P bonding distance is relatively large and suggests a loosely bonded phosphine. The reactivity caused by loosely bonded phosphine is well-known,[24] e.g. for $Au(PPh_3)(AuPPh_3)_7^{2+}$,[3] and is currently being explored for $Pt(H)(PPh_3)(AuPPh_3)_7^{2+}$.

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Supplementary Material Available: Tables of experimental details for the X-ray diffraction study, anisotropic temperature factors, fractional positional and thermal parameters of the phenyl atoms and dichloromethane atoms, and fractional positional and occupation parameters of the fluoride atoms (9 pages); a table of calculated and observed structure factors (81 pages). Ordering information is given on any current masthead page.

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Reactions of a Phosphoranide Platinum(II) Complex with Nucleophilic and Electrophilic Reagents and the X-ray Crystal Structures of (η^2-cyclenP)Pt[Co(CO)$_4$]PPh$_3$ and (η^2-cyclenP)Pt(I)PPh$_3$

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The reactions of the phosphoranide-containing complex (η^2-cyclenP)Pt(Cl)PPh$_3$ (**1**) with a variety of nucleophiles and electrophiles have been studied. These reactions demonstrate the remarkable range and selectivity of this complex. With the anionic nucleophiles $Co(CO)_4^-$, SMe^-, I^-, and Br^-, the corresponding chloride-substituted derivatives are formed, (η^2-cyclenP)PtLPPh$_3$, where L = Co(CO)$_4$ (**5**), SMe (**6**), I (**7**), and Br (**8**). The neutral, potentially bidentate, donor dppm leads to PPh$_3$ substitution to give (η^2-cyclenP)Pt(Cl)dppm (**9**), where only one of the phosphorus sites of dppm is bound to the platinum. The electrophiles MeI and *n*-BuBr also lead to **7** and **8**. However, the reaction of MeO_3SCF_3 with **1** led to [(η^2-MecyclenP)Pt(Cl)PPh$_3$]O$_3$SCF$_3$ (**10**), where the platinum-bound nitrogen is methylated and the P-N bond is cleaved. This suggests that the alkyl halide reactions may proceed through such an intermediate, rather than the usual oxidative-addition/reductive-elimination path. The reaction of **1** with HC≡CPh and NaBPh$_4$ leads to the σ-bonded alkyne complex [(η^2-HcyclenP)Pt(C≡CPh)PPh$_3$]BPh$_4$ (**11**), where both P-N bond cleavage and chloride substitution has occurred. Reaction of **5** and Me$_3$SiI leads to **7** and Me$_3$SiCo(CO)$_4$. The X-ray crystal structures of **5** and **7** were obtained and show extremely long Pt-Co and Pt-I bonds, respectively. X-ray data: $C_{30}H_{31}N_4O_4P_2CoPt$ (**5**), triclinic, space group $P\bar{1}$, $a = 10.374$ (4) Å, $b = 10.857$ (6) Å, $c = 16.086$ (9) Å, $\alpha = 78.93$ (4)°, $\beta = 83.31$ (4)°, $\gamma = 61.93$ (3)°, $Z = 2$, $R = 0.059$, $R_w = 0.060$; $C_{26}H_{31}N_4P_2IPt$ (**7**), monoclinic, space group $P2_1/c$, $a = 11.939$ (5) Å, $b = 14.446$ (5) Å, $c = 15.407$ (9) Å, $\beta = 92.80$ (4)°, $Z = 4$, $R = 0.053$, $R_w = 0.064$.

Reactions at square-planar platinum(II) centers are important due to their central role in catalysis, which include activation of C-H bonds and fundamental aspects of oxidative addition and reductive elimination.[1] In addition, metal complexes containing

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