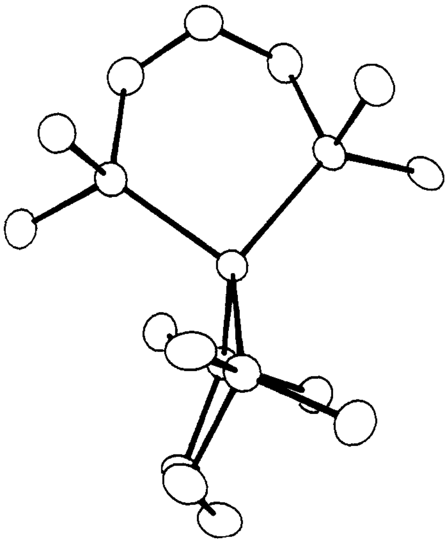

Figure 2. View of the conformation of the $\{PtP_2C_3\}$ chelate rings in $[Pt(dppp)_2]$, with the phenyl rings removed for clarity.

Table III. Crystal Data for $[Pt(dppp)_2]$

	this work	Gray and co-workers[2]
a/nm	1.8245 (3)	1.8306 (3)
b/nm	1.3277 (3)	1.3322 (2)
c/nm	2.0053 (4)	1.0067 (3)
α/deg	90	90
β/deg	109.27 (2)	109.28 (2)
γ/deg	90	90
Z	4	2
U/nm^3	4.585	2.317
space group	$C2/c$	$C2/m$

The molecular structure of the complex $[Pt(dppp)_2]$ is shown in Figure 1. The molecule lies on a crystallographic 2-fold rotation axis. The bond lengths and angles in the complex appear normal (Table II). The Pt-P bond lengths (0.2286 nm) are similar to those observed for four-coordinate platinum(0) in $[Pt(triphos)_2]$[4] (0.2275-0.2295 nm) but longer than those found for three-coordinate platinum(0) in $[Pt(PPh_3)_3]$[3] (0.2262-0.2271 nm), $[(dbpp)Pt{=}Pt(dbpp)]$[6] (0.2268-0.2272 nm), and $[Pt_2(dppm)_3]$[5] (0.2255-0.2272 nm) and for two-coordinate platinum(0) in $[Pt\{PPh(CMe_3)_2\}_2]$[13] (0.2252 nm) and $[Pt\{P(Cy)_3\}_2]$[14] (0.2231 nm). This is as expected since, all other factors being equal, r(ML) should decease in the order $ML_4 > ML_3 > ML_2$. The $\{PtP_2C_3\}$ chelate rings (see Figure 2) display a chair conformation. The dihedral angle between the $\{PtP(1)P(2)\}$ and $\{PtP(1')P(2')\}$ planes is 87.20 (2)°, close to the ideal value of 90°.

After the determination of this structure was complete, Gray and co-workers[2] independently published the crystal structure of $[Pt(dppp)_2]$. Their results suggested that the complex had a distorted tetrahedral coordination about the platinum atom with Pt-P bond lengths of 0.2267 (1) and 0.2317 (1) nm. The longer Pt-P bond length was attributed to the internal strain imposed by the ring system. A comparison of their crystal data with ours (Table III) shows that their results are based on an incorrect unit cell and space group. Our results show space group $C2/c$, with the platinum atom close to $y = 0$: this means that all reflections with l odd tend to be weak. It appears that Gray and co-workers[2] missed the weak reflections entirely, thus producing a unit cell of half the c-axis length. This results in overlapping images of the two c glide related molecules, to give an apparently disordered structure of mirror symmetry, which was refined in space group $C2/m$, although it was clear that the authors[2] were not happy with their assignment, which involved a mirror disorder for 29 out of its 30 heavy atoms. The demonstrable improvement of the geometry of the $\{PtP_4\}$ core in the present study (see Table III) is convincing evidence that the larger unit cell and space group $C2/c$ are correct.[15] Moreover, the published interpretation of the luminescent properties of $[Pt(dppp)_2]$[2] assume a tetrahedral $\{PtP_4\}$ coordination sphere, which is more in accord with the true C_{2v} structure.

Acknowledgment. We are indebted to the SERC for the award of a studentship (R.P.M.) and the Iraqi Government for a research scholarship (K.A.A.). We are particularly grateful to Profs. H. B. Gray and W. P. Schaefer for their supportive comments on the data presented here, prior to its publication.

Registry No. $Pt(dppp)_2$, 54206-19-8.

Supplementary Material Available: Tables listing hydrogen positions, thermal parameters, complete intramolecular bond distances and angles, and torsional angles (8 pages); a table of calculated and observed structure factors (7 pages). Ordering information is given on any current masthead page.

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Contribution from the Research School of Chemistry,
Australian National University, Canberra, ACT 2601, Australia,
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Formation of Trinuclear Clusters by Addition of $[Au(PPh_3)]^+$ to Dinuclear Platinum(I) Complexes Containing Bridging Cyclometalated Arylphosphines. X-ray Structure of $[(Ph_3P)AuPt_2\{C_6H_4P(Ph)CH_2CH_2CH_2PPh_2\}_2]BF_4$

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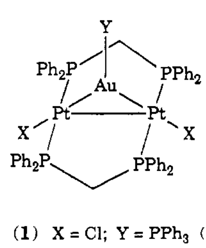
and Kathryn A. Beveridge[‡]

Received October 30, 1989

A variety of platinum-gold clusters have been made by addition of gold(I) complexes to mononuclear or polynuclear platinum compounds.[1-6] The A-frame complex **1** containing a Pt_2Au triangle has been isolated from the reaction of $[Au(PPh_3)]^+$ with $Pt_2Cl_2(\mu\text{-dppm})_2$, and the similar complexes **2** and **3** have been made from the reaction of AuC≡C-t-Bu with $Pt_2(\mu\text{-dppm})_3$[4] [dppm = bis(diphenylphosphino)methane].



(**1**) X = Cl; Y = PPh_3 (mono-cation)

(**2**) X = Y = C_2-t-Bu

(**3**) X = C_2-t-Bu; Y = I

The platinum(I)-platinum(I) dimers **4-6** containing two bridging ortho-metalated phenylphosphine ligands[7,8] react with electrophiles, such as iodine,[8] methyl iodide,[9] and acids containing poorly coordinating anions,[10] to give cationic platinum(II) A-frame adducts in which the ligand I, CH_3, or H bridges the two platinum

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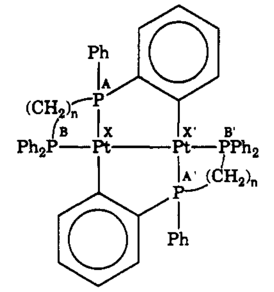
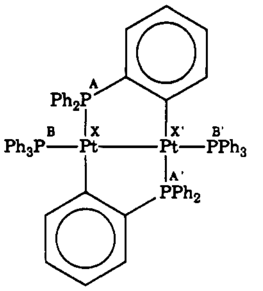


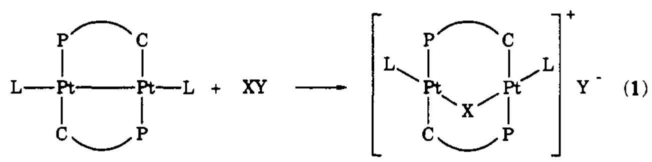
(**4**) n = 2

(**5**) n = 3



(**6**)

atoms (eq 1). It seemed reasonable to expect that the isolobal



$X = Y = I$

$X = CH_3$; $Y = I$

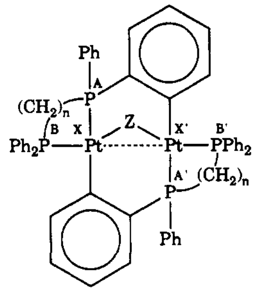
$X = H$; $Y = CF_3SO_3, BF_4$

electrophile $[Au(PPh_3)]^+$ would behave similarly and generate a triangular Pt_2Au cluster. We report here on this reaction.

Experimental Section

Starting Materials. All reactions were carried out in a nitrogen atmosphere. Before being used, solvents were distilled under nitrogen from appropriate drying agents. The platinum(I) dimers $Pt_2\{o\text{-}C_6H_4P(Ph)CH_2CH_2PPh_2\}_2$ (**4**)[7] and $Pt_2(o\text{-}C_6H_4PPh_2)_2(PPh_3)_2$ (**6**)[8] were prepared as described previously; $Pt_2\{o\text{-}C_6H_4P(Ph)CH_2CH_2CH_2PPh_2\}_2$ (**5**) was prepared similarly to **4** from $PtCl(CH_3)(Ph_2PCH_2CH_2CH_2PPh_2)$.

NMR spectra were measured in $CDCl_3$ at 30 °C on a Bruker WM250 spectrometer at 101.3 MHz (^{31}P) and 53.6 MHz (^{195}Pt). Chemical shifts (δ) are quoted in ppm relative to external H_3PO_4 (^{31}P) or to 21.4 MHz (^{195}Pt). The latter have also been converted into chemical shifts relative to aqueous Na_2PtCl_6 by use of the equation $\delta(PtCl_6^{2-}) = \delta$ (frequency scale) − 4522.[11] The coupling constants, which are given in Table I, were calculated on an IBM 3083 computer by means of a simulation program based on the UEAITR[12] and NMRPLOT programs[13] constructed by K. R. Dixon (University of Victoria). The nuclei are labeled as shown in the structural diagrams for complexes **4**–**12**.

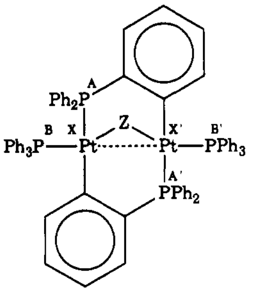


(**7**) n = 2; Z = Au(P^KPh_3)

(**8**) n = 3; Z = Au(P^KPh_3)

(**10**) n = 2; Z = I

(**11**) n = 3; Z = I



(**9**) Z = Au(P^KPh_3)

(**12**) Z = I

Preparation of Complexes. 1. $[Pt_2\{o\text{-}C_6H_4P(Ph)CH_2CH_2PPh_2\}_2Au(PPh_3)]BF_4$ (7a). A mixture of $AuCl(PPh_3)$ (0.225 g, 0.45 mmol) and $AgBF_4$ (0.088g, 0.45 mmol) was stirred in benzene (25 mL) to generate in situ $[Au(PPh_3)]BF_4$.[14] The precipitated AgCl was removed by decantation, and the solution was added to a solution of **4** (0.538 g, 0.45 mmol) in benzene (30 mL). A yellow solid precipitated immediately. After 10 min of stirring at room temperature, the supernatant liquid was decanted and the precipitate was washed with benzene (4 × 10 mL) to give 0.210 g (0.12 mmol, 27%) of **7a**, identified by its NMR spectra. More product is present in the supernatant liquid, as shown by its NMR spectra, but the yield has not been optimized. NMR ($CDCl_3$): $\delta(P)$ 32.7 (A), 64.7 (B), 26.9 (K); $\delta(Pt)$ 666.9 (relative to 21.4 MHz), Ξ = 21.414271 MHz, δ −3855 (Na_2PtCl_6).

2. $[Pt_2\{C_6H_4P(Ph)CH_2CH_2PPh_2\}_2Au(PPh_3)]BPh_4$ (7b). A solution of $AuCl(PPh_3)$ (0.057 g, 0.12 mmol) in benzene (5 mL) and dichloromethane (5 mL) was added to a solution of **4** (0.137 g, 0.11 mmol) in benzene (10 mL). After the mixture was stirred for 2 h, solvents were removed under reduced pressure. The $^{31}P\{^1H\}$ NMR spectrum of the residue, dissolved in CH_2Cl_2, was identical with that of **7a**. A solution of $NaBPh_4$ (0.04 g, 0.12 mmol) in dichloromethane (10 mL) was added, and the mixture was stirred for 5 h at room temperature and then filtered. The product was precipitated from the filtrate by addition of ether (5 mL) and recrystallized by slow addition of hexane to a chlorobenzene solution. The yield was 0.087 g (0.044 mmol, 48%). Anal. Calcd for $C_{94}H_{81}AuBP_5Pt_2$: C, 57.50; H, 4.16. Found: C, 57.72; H, 4.63.

3. $[Pt_2\{o\text{-}C_6H_4P(Ph)CH_2CH_2CH_2PPh_2\}_2Au(PPh_3)]BF_4$ (8). A solution of $[Au(PPh_3)]BF_4$, prepared as in method 1 from $AuCl(PPh_3)$ (0.060 g, 0.12 mmol) and $AgBF_4$ (0.023 g, 0.11 mmol) in benzene (15 mL), was added to a suspension of **5** (0.142 g, 0.12 mmol) in benzene (15 mL). A green-yellow precipitate formed immediately. After being stirred for 1 h at room temperature, the mixture was evaporated to dryness under reduced pressure. The solid was extracted with tetrahydrofuran (3 × 10 mL), leaving a black residue, and the solution was filtered through charcoal. Slow diffusion of hexane into this solution at −18 °C gave yellow needles of **8** (0.027 g, 13%). NMR ($CDCl_3$): $\delta(P)$ −0.2 (A), 28.0 (B), 30.4 (K); $\delta(Pt)$ 711.8 (relative to 21.4 MHz), Ξ = 21.415233 MHz, δ −3810 (Na_2PtCl_6). Anal. Calcd for $C_{72}H_{65}AuBF_4P_5Pt_2$: C, 49.16; H, 3.72. Found: C, 48.76; H, 4.05.

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Table I. Coupling Constants for Dinuclear Platinum Complexes Obtained by Analysis of Their ^{31}P NMR Spectra

	AA′	AB	AB′	BB′	AX	AX′	BX	BX′
4	66	19	−1	223	1809	−148	2010	1039
7[a]	62	0	0	132	1666	−130	2840	511
10	35	6	0	0	1618	51	4638	130
5	63	20	10	214	1858	−143	1725	1064
8[b]	59	26	0	150	1771	−126	2586	538
11[c]					1664	0	3719	73
6	55	10	10	227	1933	−141	1865	1157
9[d]	52	14	1	151	1897	−124	2815	617
12	29	20	0	0	1677	0	5065	123

[a] $J_{AK} = 0, J_{BK} = 45, J_{KX} = 619$. [b] $J_{AK} = 0, J_{BK} = 36, J_{KX} = 620$. [c] Data obtained from $^{195}Pt\{^1H\}$ NMR spectrum. The ^{31}P spectrum could not be analyzed because of the similarity of the chemical shifts. [d] $J_{AK} = 0, J_{BK} = 41, J_{KX} = 605$.

Table II. Crystallographic Data for $[Pt_2\{C_6H_4P(Ph)CH_2CH_2CH_2PPh_2\}_2AuPPh_3]BF_4$

formula	$C_{72}H_{65}BF_4P_5AuPt_2$	space group	$P\bar{1}$ (No. 2)
mol wt	1759.13	T	20 °C
a	15.278 (5) Å	λ	0.71069 Å
b	19.118 (5) Å	ρ_{obsd}	1.642 g cm^{-3}
c	13.251 (4) Å	ρ_{calcd}	1.629 g cm^{-3}
α	88.20 (3)°	μ	69.33 cm^{-1}
β	111.95 (3)°	transm coeff	0.322–0.473
γ	88.50 (3)°	$R(F_o)$	0.064
V	3585 (2) Å^3	$R_w(F_o)$	0.067
Z	2		

4. $[Pt_2(o\text{-}C_6H_4PPh_2)_2(PPh_3)_2Au(PPh_3)]BF_4$ (9). This was prepared similarly to **8** from $AuCl(PPh_3)$ (0.046 g, 0.09 mmol), $AgBF_4$ (0.018 g, 0.09 mmol), and **6** (0.133 g, 0.09 mmol). Recrystallization of the precipitate from tetrahydrofuran/hexane at −18 °C gave yellow crystals of **9** (0.020 g, 11%). NMR ($CDCl_3$): δ(P) −24.2 (A), 11.3 (B), 29.9 (K). Anal. Calcd for $C_{90}H_{73}AuBF_4P_5Pt_2$: C, 54.50; H, 3.71. Found: C, 54.43; H, 3.80.

5. $[Pt_2(\mu\text{-}I)\{o\text{-}C_6H_4P(Ph)CH_2CH_2CH_2PPh_2\}_2]I$ (11). A Schlenk tube was charged with **4** (0.150 g, 0.12 mmol) and iodine (0.030 g, 0.12 mmol), and dichloromethane (10 mL) was added. The dark red solution was stirred at room temperature for 2 h, during which time the color lightened. The mixture was evaporated to dryness under reduced pressure, and the product was recrystallized from tetrahydrofuran/hexane. The yield of pale yellow, crystalline **11** was 0.088 g (0.060 mmol, 49%). ^{31}P NMR (CH_2Cl_2, external C_6D_6): δ −9.8 (A), −9.4 (B). ^{195}Pt NMR ($CDCl_3$): δ −155.1 (relative to 21.4 MHz), Ξ = 21.396680 MHz, δ −4677 (Na_2PtCl_6).

Data for **10** will be reported in a full paper on the chemistry of **4**.[15]

Collection and Reduction of X-ray Data. A needle of **8** with approximate dimensions 0.37 × 0.17 × 0.12 mm was mounted approximately along the *a* axis. Crystal data are summarized in Table II.

Preliminary photographic work was carried out with Weissenberg and precession cameras using Cu Kα radiation. Data were collected on a Picker four-circle diffractometer automated with a PDP11/10 computer, using Mo Kα radiation with a zirconium filter. Lattice parameters were determined at 293 K by using 22 pairs of reflections ($16° \le |2\theta| \le 40°$). The $\theta/2\theta$ scan mode was used in 160 steps of 0.01° in 2θ counting for 0.25 s/step. Background measurements were for 20 s at each end of the scan. A total of 9368 reflections were collected ($0 \le h \le 16$; $-20 \le k \le 20$; $-13 \le l \le 13$; $0° < 2\theta < 45°$) and corrected for Lorentz, polarization, and absorption effects with a Gaussian grid (16 × 8 × 8). No deterioration of the crystal was observed during the data acquisition. A total of 6684 reflections ($I > 3\sigma(I)$) were used in the structure refinement.

Structure Solution and Refinement. The structure was solved by direct methods using the SHELX-76[16] program package, and illustrations were drawn by using ORTEP.[17] Refinement was completed by standard Fourier synthesis procedures with use of difference maps and by the method of least squares; the function minimized was $\sum w\Delta^2$ where $\Delta = ||F_o| - |F_c||$. The weights were obtained from counting statistics using $w = 1/(\sigma^2(F) + 0.001F^2)$. The refinement converged, and the residuals were $R = 0.064$ and $R_w = 0.067$ after employing anisotropic thermal parameters for all non-hydrogen atoms except carbon atoms of terminal phenyl groups (isotropic). Atomic parameters for all atoms are given in Table III, and selected bond distances and angles are given in Table IV.

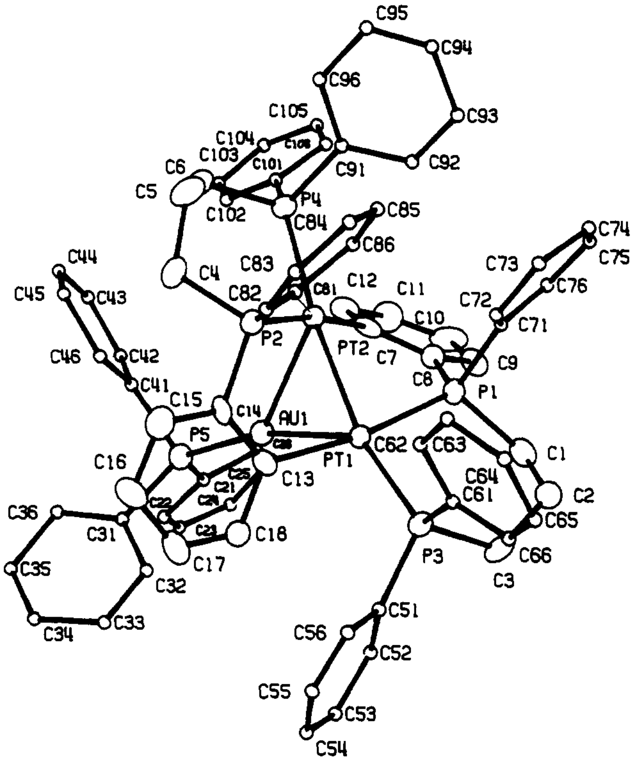

Figure 1. ORTEP plot of cation **8** in its BF_4 salt.

Results and Discussion

When 1 equiv of $[Au(PPh_3)]BF_4$, generated in situ from $AuCl(PPh_3)$ and $AgBF_4$ in benzene,[14] was added separately to suspensions of the dimers **4**–**6** at room temperature under nitrogen, green-yellow precipitates of the 1:1 adducts **7**–**9** formed immediately. Although ^{31}P NMR spectroscopy suggested that there were no major byproducts, the yields after recrystallization were poor and undoubtedly could be improved.

The structures of **7**–**9** follow from the NMR spectra (^{31}P, ^{195}Pt). The basic patterns are similar to those of **4**–**6** and of the corresponding μ-iodo cations **10**–**12** formed by addition of iodine to **4**–**6**; hence the diplatinum cyclometalated framework is retained. When both platinum atoms are spin inactive, the spin system is AA′KBB′, where (A,A′), (B,B′), and K refer to the ^{31}P nuclei that are respectively off-axis, axial, and attached to gold (see diagrams). The presence of one and two ^{195}Pt isotopes (natural abundance 33.8%) generates subspectra of the types AA′BB′KX (relative intensity 44%) and AA′BB′KXX′ (relative intensity 11%).[18] Analysis of these spectra gave the coupling constants for complexes **4**–**12** in Table I, which are discussed briefly below. The fact that the ^{31}P nucleus K attached to gold shows appreciable coupling to ^{195}Pt (ca. 600 Hz) and to the axial ^{31}P nuclei B and B′ (ca. 40 Hz) is consistent with the formulation of **7**–**9** as triangular Pt_2Au clusters, and this has been confirmed by single-crystal X-ray analysis of cation **8** as its BF_4 salt.

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(18) Note that the labeling of X and X′ is opposite to that in refs 7–9.

Table III. Fractional Atomic Coordinates and Temperature Parameters[a]

atom	x/a	y/b	z/c	U_{eq}, Å^2	atom	x/a	y/b	z/c	U_{eq}, Å^2
Au(1)	−26626 (7)	13713 (5)	61754 (7)	473 (4)	C(46)	−9 (2)	132 (1)	762 (2)	75 (8)′
Pt(1)	−39257 (6)	18024 (4)	41697 (7)	377 (3)	C(51)	−510 (2)	34 (1)	272 (2)	58 (6)′
Pt(2)	−26614 (6)	26944 (4)	54074 (6)	367 (3)	C(52)	−527 (2)	−11 (1)	352 (2)	69 (7)′
P(1)	−4898 (4)	2659 (3)	4434 (5)	45 (2)	C(53)	−517 (3)	−82 (2)	349 (3)	113 (12)′
P(2)	−1920 (4)	2340 (3)	4270 (5)	43 (2)	C(54)	−487 (3)	−108 (2)	272 (3)	106 (11)′
P(3)	−5156 (4)	1291 (3)	2819 (5)	48 (2)	C(55)	−468 (2)	−65 (2)	193 (2)	88 (9)′
P(4)	−1642 (4)	3584 (3)	6087 (5)	45 (2)	C(56)	−480 (2)	2 (2)	192 (2)	83 (8)′
P(5)	−1722 (4)	745 (3)	7668 (5)	49 (2)	C(61)	−537 (2)	164 (1)	146 (2)	46 (5)′
C(1)	−615 (2)	243 (1)	414 (2)	65 (12)	C(62)	−464 (2)	200 (1)	127 (2)	57 (6)′
C(2)	−665 (2)	214 (1)	296 (2)	60 (11)	C(63)	−479 (2)	233 (1)	19 (2)	66 (7)′
C(3)	−632 (2)	143 (1)	290 (2)	74 (13)	C(64)	−566 (2)	223 (1)	−65 (2)	62 (6)′
C(4)	−66 (2)	243 (1)	475 (2)	58 (11)	C(65)	−636 (2)	185 (2)	−49 (3)	96 (10)′
C(5)	−37 (2)	323 (1)	504 (2)	72 (13)	C(66)	−623 (2)	158 (1)	61 (2)	67 (7)′
C(6)	−44 (2)	341 (1)	614 (2)	55 (10)	C(71)	−509 (2)	348 (1)	363 (2)	61 (6)′
C(7)	−343 (2)	288 (1)	636 (2)	47 (10)	C(72)	−493 (2)	351 (1)	264 (2)	67 (7)′
C(8)	−446 (2)	291 (1)	581 (2)	48 (10)	C(73)	−516 (2)	415 (2)	201 (3)	96 (10)′
C(9)	−508 (2)	307 (1)	636 (2)	58 (11)	C(74)	−561 (2)	471 (2)	224 (3)	89 (9)′
C(10)	−463 (2)	319 (1)	752 (2)	79 (16)	C(75)	−575 (2)	465 (2)	324 (3)	99 (10)′
C(11)	−367 (2)	311 (1)	805 (2)	67 (13)	C(76)	−548 (2)	408 (1)	394 (2)	61 (6)′
C(12)	−303 (2)	296 (1)	752 (2)	56 (10)	C(81)	−229 (2)	279 (1)	293 (2)	50 (6)′
C(13)	−287 (2)	113 (1)	409 (2)	49 (10)	C(82)	−205 (2)	249 (1)	209 (2)	72 (7)′
C(14)	−204 (2)	141 (1)	402 (2)	47 (9)	C(83)	−221 (2)	292 (2)	112 (2)	82 (8)′
C(15)	−135 (2)	102 (1)	386 (2)	66 (12)	C(84)	−259 (2)	358 (2)	101 (3)	88 (9)′
C(16)	−139 (2)	27 (1)	380 (2)	75 (14)	C(85)	−285 (2)	385 (2)	181 (3)	90 (9)′
C(17)	−223 (2)	−2 (1)	385 (2)	69 (13)	C(86)	−274 (2)	347 (1)	279 (2)	64 (7)′
C(18)	−293 (2)	37 (1)	399 (2)	50 (9)	C(91)	−204 (2)	439 (1)	527 (2)	54 (6)′
C(21)	−215 (2)	61 (1)	880 (2)	46 (5)′	C(92)	−304 (2)	457 (1)	480 (2)	60 (6)′
C(22)	−183 (2)	3 (1)	953 (2)	55 (6)′	C(93)	−335 (2)	519 (1)	422 (2)	71 (7)′
C(23)	−210 (2)	−2 (1)	1043 (2)	69 (7)′	C(94)	−263 (2)	566 (2)	408 (3)	89 (9)′
C(24)	−266 (2)	46 (1)	1058 (2)	77 (8)′	C(95)	−170 (2)	553 (2)	446 (3)	90 (9)′
C(25)	−296 (3)	112 (2)	986 (3)	106 (11)′	C(96)	−139 (2)	487 (2)	504 (2)	88 (9)′
C(26)	−271 (2)	115 (1)	891 (2)	72 (7)′	C(101)	−135 (2)	384 (1)	747 (2)	47 (5)′
C(31)	−133 (2)	−12 (1)	743 (2)	50 (6)′	C(102)	−79 (2)	343 (1)	831 (2)	78 (8)′
C(32)	−196 (2)	−46 (1)	655 (2)	66 (7)′	C(103)	−56 (2)	358 (2)	948 (2)	85 (9)′
C(33)	−171 (2)	−113 (1)	629 (2)	79 (8)′	C(104)	−93 (2)	419 (2)	965 (3)	93 (9)′
C(34)	−78 (2)	−143 (2)	696 (3)	87 (9)′	C(105)	−154 (2)	463 (2)	884 (3)	92 (9)′
C(35)	−16 (2)	−111 (2)	779 (2)	85 (9)′	C(106)	−179 (2)	444 (1)	767 (2)	75 (8)′
C(36)	−42 (2)	−37 (1)	805 (2)	66 (7)′	B(1)	223 (3)	235 (2)	623 (4)	95 (12)′
C(41)	−64 (2)	119 (1)	827 (2)	63 (7)′	F(1)	198 (2)	263 (1)	523 (2)	138 (8)′
C(42)	−28 (2)	141 (1)	935 (2)	61 (6)′	F(2)	181 (2)	285 (1)	677 (2)	123 (7)′
C(43)	52 (2)	182 (2)	977 (3)	89 (9)′	F(3)	176 (2)	180 (2)	618 (2)	190 (11)′
C(44)	102 (2)	193 (2)	909 (3)	101 (10)′	F(4)	308 (4)	262 (2)	671 (4)	308 (22)′
C(45)	76 (2)	174 (2)	809 (3)	86 (9)′					

[a] Estimated standard deviations are given in parentheses. Coordinates ×10^n where n = 5, 5, 4, 3, 3, 3 for Au, Pt, P, F, C, B, respectively. Temperature parameters ×10^n where n = 4, 4, 3, 3, 3, 3 for Au, Pt, P, F, C, B, respectively. U_{eq} = the equivalent isotropic temperature parameter. $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i{}^*a_j{}^*(a_ia_j)$. Primed values indicate that U_{iso} is given; $T = \exp[-8\pi^2U_{iso}(\sin^2\theta)/\lambda^2]$.

Table IV. Selected Bond Distances and Angles[a]

Bond Distances (Å)			
Pt(1)–Au(1)	2.722 (1)	Pt(2)–Au(1)	2.697 (1)
P(5)–Au(1)	2.247 (5)	Pt(2)–Pt(1)	2.703 (1)
P(1)–Pt(1)	2.303 (6)	P(3)–Pt(1)	2.320 (6)
P(4)–Pt(2)	2.305 (6)	P(2)–Pt(2)	2.306 (7)
C(13)–Pt(1)	2.07 (3)	C(7)–Pt(2)	2.05 (3)
Bond Angles (deg)			
Pt(2)–Au(1)–Pt(1)	59.8 (1)		
P(5)–Au(1)–Pt(2)	133.9 (2)	P(5)–Au(1)–Pt(1)	165.4 (2)
Pt(2)–Pt(1)–Au(1)	59.6 (1)	Pt(1)–Pt(2)–Au(1)	60.5 (1)
P(1)–Pt(1)–Au(1)	106.9 (1)	P(2)–Pt(2)–Au(1)	92.1 (1)
P(1)–Pt(1)–Pt(2)	78.2 (1)	P(2)–Pt(2)–Pt(1)	79.4 (1)
P(3)–Pt(1)–Au(1)	135.0 (2)	P(4)–Pt(2)–Au(1)	131.2 (1)
P(3)–Pt(1)–Pt(2)	165.3 (1)	P(4)–Pt(2)–Pt(1)	167.0 (2)
P(3)–Pt(1)–P(1)	93.5 (2)	P(4)–Pt(2)–P(2)	93.6 (2)
C(13)–Pt(1)–Au(1)	67.4 (6)	C(7)–Pt(2)–Au(1)	81.3 (5)
C(13)–Pt(1)–Pt(2)	92.1 (6)	C(7)–Pt(2)–Pt(1)	92.6 (6)
C(13)–Pt(1)–P(1)	170.3 (6)	C(7)–Pt(2)–P(2)	171.5 (6)
C(13)–Pt(1)–P(3)	96.0 (6)	C(7)–Pt(2)–P(4)	94.9 (6)

[a] Estimated standard deviations are given in parentheses.

The molecular structure of the cation, shown in Figure 1, consists of an approximately equilateral triangle formed by the gold atom and the two platinum atoms. This arrangement is similar to that found in the first example of a Pt_2Au species (**3**)[4a,c] and is consistent with the concept of a three-center, two-electron bond predicted by the isolobal analogy.[19] The platinum-gold distances [Pt(1)–Au = 2.722 (1) Å, Pt(2)–Au = 2.697 (1) Å] are significantly greater than the values of 2.656 (2) Å and 2.661 (2) Å found in **3**[4a,c] but fall in the wide range (ca. 2.57–3.03 Å) that has been observed in Pt–Au clusters.[1–6,20,21] The Pt–Pt distance [2.703 (1) Å] is significantly greater than those in the precursor complexes **4** [2.628 (1) Å][7] and **6** [2.630 (1) Å][8] but is much less than that in the μ-iodo complex **12** [2.931 (2) Å],[8] suggesting that Pt–Pt bonding is only slightly weakened as a result of addition of the $[Au(PPh_3)]^+$ unit. The phosphorus atom bound to gold is coplanar with the triangle of metal atoms, but the bond vector is slightly tilted so that it does not bisect the Pt–Au–Pt angle. The axial phosphorus atoms P(3) and P(4) also lie in the plane of the triangle, but in contrast to their arrangement in the precursor complexes **4** and **6**, they are no longer collinear with the Pt–Pt axis [angles P(3)–Pt(1)–Pt(2) and P(4)–Pt(2)–Pt(1) are 165.3 (1) and 167.0 (2)°]. This bending is presumably necessary to accommodate the bulky $[Au(PPh_3)]$ group. In **4** and **6** the Pt–P bonds trans to Pt–Pt are longer than the Pt–P bonds

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trans to the ortho-metalated carbon atoms; e.g. for **4** the distances are 2.270, 2.275 Å (trans to Pt–Pt) and 2.248, 2.230 Å (trans to C)[7]. In contrast, the Pt–P bond lengths in **8** are similar; the fact that the Pt(1)–P(3) bond length [2.320 Å] is slightly greater than the others [2.305 Å] may be because the $Au(PPh_3)$ fragment is tilted slightly toward Pt(2) rather than Pt(1).

The magnitudes of some of the coupling constants in Table I are sensitive to oxidative addition to the Pt–Pt center. The magnitude of J_{BX} (ca. 4500 Hz) in complexes **10–12** clearly shows the axial Pt–P bond to be trans to the bridging iodo group, which has a low trans influence. The coupling constants $J_{BX'}$ and $J_{BB'}$ decrease in the order [Pt···Pt] > [Pt···Au···Pt] > [Pt···I···Pt] for each series, e.g. $J_{BX'}$ = 1039 (**4**), 511 (**7**), and 130 Hz (**10**). The Pt–Pt distances increase in the same order, which suggests that these long-range coupling constants may be a rough guide to the strength of the Pt–Pt interaction. Similar correlations of $^2J_{PtP}$ with the Pt–Pt distance have been observed in closely related diplatinum complexes containing bridging dppm.[22] It would be of obvious interest to see whether $J_{XX'}$ correlates with the Pt–Pt distance in this series of complexes,[23] but unfortunately we have been unable to derive J_{PtPt} values from the spectra of complexes **7–12**.

Acknowledgment. We thank Ms. V. J. Farina and Mr. C. van Huynh for preparing starting materials and Mrs. C. Greenwood for NMR service spectra.

Supplementary Material Available: Tables of all interatomic distances and angles, selected intermolecular distances, and anisotropic temperature parameters and an ORTEP view of the cation with all atoms represented by 25% probability thermal ellipsoids (9 pages); a table of structure factor amplitudes (28 pages). Ordering information is given on any current masthead page.

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High-Yield Synthesis of *cis*-Dihydrido-*trans*-bis(phosphite)dicarbonyliron Complexes $H_2Fe(CO)_2[P(OR)_3]_2$ (R = Me, Et, Ph)

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Received February 27, 1990

As part of our initiative in developing new applications for $[HFe(CO)_4]^-$ in organic synthesis,[1] catalysis,[2] and coordination chemistry, we have recently discovered an expedient synthesis of $Fe(CO)_3(PPh_3)_2$ in 82% yield by reaction of $K[HFe(CO)_4]$ with triphenylphosphine in ethanol at 70 °C, 24 h.[3,4] This procedure has been successfully applied to other phosphines.[5]

Table I. Synthesis of $H_2Fe(CO)_2[P(OR)_3]_2$ Complexes[a]

R	product (% yield)	formula	elem anal.
Me	**1** (90) colorless oil	$C_8H_{20}FeO_8P_2$	calcd: H, 5.57; C, 26.54 found: H, 5.60; C, 26.32
Et	**2** (91) colorless oil	$C_{14}H_{32}FeO_8P_2$	calcd: H, 7.23; C, 37.69 found: H, 7.41; C, 37.75
Ph	**3** (94) white crystals mp = 84–85 °C	$C_{38}H_{32}FeO_8P_2$	calcd: H, 4.39; C, 62.12 found: H, 4.31; C, 62.32

[a] See Experimental Section.

In a continuation of our study concerning the reactivity of $[HFe(CO)_4]^-$ with phosphorus compounds, we have now found that the reaction with phosphites follows a different course. We wish to report here a very simple and efficient synthesis of $H_2Fe(CO)_2[P(OR)_3]_2$ complexes (R = Me, Et, Ph).

Results

Addition of $P(OMe)_3$ (22 mmol) to a solution of $K[HFe(CO)_4]$ (11 mmol) in MeOH (60 mL) at room temperature under argon results in the evolution of 22 mmol of carbon monoxide (GC analysis) within 1 h with a simultaneous thickening of the reaction medium. Evaporation of the solvent, followed by a very simple, but careful, workup (vide infra), allows the isolation of the complex $H_2Fe(CO)_2[P(OMe)_3]_2$ (**1**) (75% yield) (eq 1), identified by comparison of its IR and NMR (^1H, ^{31}P) spectra with literature data,[6] by ^{13}C NMR spectroscopy, and by elemental analysis.

$$K[HFe(CO)_4] + 2P(OMe)_3 \xrightarrow{\text{MeOH, 25 °C, 1 h}} \underset{\mathbf{1}\ (75\%)}{H_2Fe(CO)_2[P(OMe)_3]_2} \quad (1)$$

As the reaction depicted in eq 1 appeared very expedient and easy to perform, it was further attempted to include other phosphites. Reaction of $P(OEt)_3$ with $K[HFe(CO)_4]$ under the conditions of eq 1 gives the previously unreported $H_2Fe(CO)_2[P(OEt)_3]_2$ (**2**) in 68% yield. When the reaction was attempted with $P(OPh)_3$ in methanol, a complex mixture resulted. This complex mixture is attributed to the partial exchange (as evidenced by ^1H NMR) of the phenoxy groups on the phosphorus atom by methoxy ones.[7] This observation led us to carry out these reactions in H_2O/THF solvent mixtures, which proved to be particularly convenient for the synthesis and isolation of $H_2Fe(CO)_2[P(OR)_3]_2$ complexes **1–3** (eq 2, Table I).

$$K[HFe(CO)_4] + 2P(OR)_3 \xrightarrow[\text{25 °C}]{\text{H}_2\text{O/THF}} \begin{array}{l} H_2Fe(CO)_2[P(OR)_3]_2 \\ \quad \mathbf{1},\ R = Me \\ \quad \mathbf{2},\ R = Et \\ \quad \mathbf{3},\ R = Ph \end{array} \quad (2)$$

Spectral characteristics for complexes **1–3** are reported in Table II. The IR and ^1H and ^{31}P NMR spectra of **1** and **3** are in full agreement with previously reported data for $H_2Fe(CO)_2[P(OR)_3]_2$ (R = Me, Ph), both having trans phosphites and cis hydride ligands.[6,8] The spectroscopic data unambiguously show that complex **2** has the same configuration. Finally, ^{13}C NMR data for complexes **1–3** are reported here for the first time.

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