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Chemistry of Phosphido-Bridged Group 8 Compounds. Molecular Structures of the Platinum Dimers $[\mathrm{PtCl(PPh_2)(PPh_2H)}]_2$ and $[\mathrm{Pt(Ph_2PCH_2CH_2PPh_2)(PPh_2)}]_2\mathrm{Cl_2}$

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Received July 31, 1981

The crystal structures of two phosphido-bridged platinum(II) dimers are reported. The compound $[\mathrm{PtCl(PPh_2)(PPh_2H)}]_2\cdot\mathrm{C_3H_6O}$ crystallizes from acetone in the monoclinic space group $P2_1/n$ (a nonstandard setting of $P2_1/c$) with a = 11.673 (3) Å, b = 15.708 (5) Å, c = 14.469 (4) Å, β = 100.38 (2)°, and V = 2610 (1) Å^3 with 2 molecules in the unit cell. The structure was refined with use of anisotropic thermal parameters for all nonhydrogen atoms to an R value of 0.036 on the basis of 2430 unique observed ($I \geq 3[\sigma(I)]$) reflections. In the dimeric molecule, two nonbonded platinum atoms (Pt···Pt′ = 3.585 (1) Å) are bridged by two phosphido groups. The Pt–P–Pt′ angle of 102.8 (0)° is one of the largest reported for a bis(phosphido)-bridged dimer. The second complex $[\mathrm{Pt(Ph_2PCH_2CH_2PPh_2)(PPh_2)}]_2\mathrm{Cl_2}\cdot 2.5\mathrm{C_2H_4Cl_2}$ crystallizes from dichloroethane in the triclinic space group $P\bar{1}$ with a = 12.679 (11) Å, b = 13.096 (6) Å, c = 13.740 (5) Å, α = 79.18 (3)°, β = 70.37 (6)°, and γ = 74.53 (5)°. With V = 2059 (1) Å^3 and 1 formula unit per unit cell the structure was refined by full-matrix least-squares methods to a final R value of 0.043 using a set of 4071 unique reflections. In the dimer the platinum–platinum distance is again nonbonding (Pt···Pt′ = 3.699 (1) Å). Each platinum atom is coordinated by the two phosphorus atoms of a chelating diphosphine and by the bridging phosphido groups. The Pt–P–Pt′ angle is 103.9 (0)°. These structural parameters are discussed in terms of ^{31}P NMR shifts for phosphido bridges between bonding and nonbonding metals.

Introduction

A recent resurgence of interest in the chemistry of phosphido- and arsenido-bridged complexes can be attributed largely to the realization that the $\mathrm{PR_2}$ bridging unit has several desirable structural characteristics of potential use in the design and exploitation of binuclear and cluster catalysts.[1,2] As a three-electron donor, the $\mathrm{PR_2}$ or $\mathrm{AsR_2}$ bridge is a stable yet highly flexible entity capable of supporting a wide range of bonding and nonbonding M–M distances with M–P–M′ (or M–As–M′) angles ranging from less than 70° through values close to the tetrahedral angle[4] and even beyond 120° in situations where a single bridge supports two noninteracting metal fragments.[5] A further important feature is the availability of a potentially useful spectroscopic probe, the ^{31}P chemical shift, for structural assignments. These considerations have recently led to the synthesis of a number of bi- and polynuclear phosphido-bridged carbonyl compounds with interesting chemical properties. Thus the dianion $[\mathrm{Fe_2(CO)_6(PPh_2)_2}]^{2-}$, lacking an Fe–Fe bond, obtained via a two-electron reduction of $[\mathrm{Fe_2(CO)_6(PPh_2)_2}]$, can be used to produce aldehydes quantitatively via reaction with alkyl halides and subsequent protonation.[6]

Vahrenkamp et al.[7] have synthesized numerous homo- and heteronuclear clusters with dimethylphosphido bridges that have unusual chemical and dynamic properties, while the arsenido-bridged complex $[\mathrm{Fe_2(CO)_6(NO)(AsMe_2)}]$ effectively catalyzes the dimerization of norbornadiene.[8] The open and closed triruthenium clusters $[\mathrm{Ru_3(CO)_9(C_2R)(PPh_2)}]$ and $[\mathrm{Ru_3(CO)_8(C_2R)(PPh_2)}]$ (R = *t*-Bu, *i*-Pr) are interconvertible via loss or gain of CO, closing and opening of a metal triangle, and $\mathrm{PR_2}$ bridge flexibility.[9] These few examples serve to illustrate the extreme versatility of $\mathrm{PR_2}$ groups as supporting ligands.

As part of a broad-based program of research on the chemistry of phosphido-bridged bi- and polynuclear complexes, we have determined the structures of two binuclear platinum complexes: $[\mathrm{PtCl(PPh_2)(PPh_2H)}]_2$ and $[\mathrm{Pt(PPh_2)(PPh_2CH_2CH_2PPh_2)}]_2\mathrm{Cl_2}$. These molecules, which are representative of a large class of palladium and platinum compounds first synthesized in the 1960s by Issleib and Wenschuk,[10] Hayter et al.,[11-13] and Chatt and Davidson[14] were of interest to us for several reasons. First, ^{31}P NMR studies on a wide variety of bi- and polynuclear phosphido-bridged iron group clusters[1,9,15] suggested that $\delta_{^{31}\mathrm{P}}(\mathrm{PPh_2})$ was exceedingly sensitive to changes in M–P–M bond angles, and the presence or absence of M···M bonding, with high-field ^{31}P shifts characteristic of large M–P–M angles and long M···M distances. For palladium and platinum complexes of the type $[\mathrm{M_2X_2(\mu\text{-}PPh_2)_2(PR_3)_2}]$ the reported ^{31}P NMR shifts were at very high field (270–320 ppm upfield of $\mathrm{(MeO)_3P}$[16,17]) compared to values for phosphido bridges in the palladium cluster cations $[\mathrm{Pd_3(\mu\text{-}X)(\mu\text{-}PPh_2)_2(PR_3)_3}]^+$ characterized by Dixon and co-workers[18] where strong Pd–Pd bonds are present. We were thus interested in obtaining structural data for the platinum dimers to confirm the presence of large Pt–P–Pt′ angles, and the absence of substantial Pt–Pt interactions inferred by the NMR data. The structures and spectroscopic properties of these dimers were also of interest in the context of our desire to more fully understand the nature of the ubiquitous "red platinum clusters" variously derived from the pyrolysis or fragmentation of zerovalent platinum species such as $\mathrm{Pt(PPh_3)_4}$.[19-24]

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0020-1669/82/1321-1349$01.25/0

Table I. Crystal and Intensity Data

	$[PtCl(PPh_2)(PPh_2H)]_2 \cdot C_3H_6O$	$[Pt(Ph_2PCH_2CH_2PPh_2)(PPh_2)]_2Cl_2 \cdot 2.5C_2H_4Cl_2$
space group	$P2_1/n$	$P\bar{1}$
unit cell	$a = 11.673$ (3) Å, $b = 15.708$ (5) Å, $c = 14.469$ (4) Å, $\beta = 100.38$ (2)°	$a = 12.679$ (11) Å, $b = 13.096$ (6) Å, $c = 13.740$ (5) Å, $\alpha = 79.18$ (3)°, $\beta = 70.37$ (6)°, $\gamma = 74.53$ (5)°
vol, Å^3	2610 (1)	2059 (1)
mol wt	1261.9	1875.74
Z	2	1
d_{obsd}, g cm^{-3}	1.58	1.49
d_{calcd}, g cm^{-3}	1.61	1.51
$F(000)$	1224	929
radiation	graphite-monochromated Mo Kα	
scan mode	θ–2θ	
scan rate	variable (2.0–29.3° min^{-1})	
2θ, deg	$3.2 \leqslant 2\theta \leqslant 45°$	
μ(Mo Kα), cm^{-1}	58.9	39.52
no. of measd reflctns	3433	5423
no. of unique obsd reflctns	2430	4071
criterion for observn	$I \geqslant 3[\sigma(I)]$	

Despite the complete structural characterization of two such clusters, $[Pt_2(PPh_2)_2(PPh_3)_2]$ and $[Pt_3(PPh_2)_3(PPh_3)_2(Ph)]$,[24] rational synthetic routes to these and other compounds of more doubtful composition have not yet been described in the literature.

Experimental Section

$[PtCl(PPh_2)(PPh_2H)]_2$. The following convenient procedure, a modification of that described by Levason et al.,[25] gave improved yields. Potassium tetrachloroplatinite (K_2PtCl_4, 3.70 g) was refluxed overnight with diphenylphosphine (3.70 g) in degassed absolute ethanol (300 mL). Solvent was removed on a rotary evaporator and the white residue extracted with CH_2Cl_2. Addition of diethyl ether and overnight cooling afforded the pure dimer (4.40 g, 48.2%; mp 298 °C; lit.[25] mp > 250 °C).

$[Pt(PPh_2)(Ph_2PCH_2CH_2PPh_2)]_2Cl_2$. To a deoxygenated solution of $[PtCl(PPh_2)(PPh_2H)]_2$ (2.000 g) in hot dichloromethane (100 mL) was added $Ph_2PCH_2CH_2PPh_2$ (1.274 g) in CH_2Cl_2 (50 mL) dropwise. Refluxing overnight yielded a clear yellow solution, which afforded pale yellow needles of the required product on concentration and addition of diethyl ether (2.64 g, 72.2%; mp 345 °C).

Collection and Reduction of X-ray Data. Crystals of $[PtCl(PPh_2)(PPh_2H)]_2$ from dichloromethane showed a strong tendency to desolvate with consequent loss of crystallinity. A suitable crystal of dimensions 0.2 × 0.2 × 0.2 mm, grown from acetone, was quickly coated with epoxy to prevent loss of solvent of crystallization.

Preliminary photography revealed monoclinic symmetry ($2/m$). From the observed absences $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$, the space group was defined as $P2_1/n$, an alternative setting of $P2_1/c$.

Crystals of $[Pt(PPh_2)(PPh_2CH_2CH_2PPh_2)]_2Cl_2$ suitable for diffraction measurements were grown from dichloroethane/diethyl ether. The data crystal, an equidimensional prism (0.2 × 0.2 × 0.2 mm), was sealed in epoxy glue to minimize loss of solvent of crystallization. Preliminary photography indicated only Laue symmetry of $\bar{1}$ consistent with the triclinic system. The choice of $P\bar{1}$ as the space group was later justified by the successful refinement of the structure.

Table II. Atomic Positions (Fractional × 10^4) for $[PtCl(PPh_2)(PPh_2H)]_2 \cdot C_3H_6O$

atom	x	y	z
Pt	−566.8 (4)	958.0 (3)	419.1 (3)
Cl	−2161 (3)	1230 (2)	1195 (3)
P(1)	891 (2)	504 (2)	−296 (2)
P(2)	−46 (3)	2378 (2)	416 (2)
C(11)	2335 (9)	777 (6)	364 (8)
C(12)	2450 (10)	1089 (7)	1275 (8)
C(13)	3557 (11)	1293 (9)	1781 (9)
C(14)	4516 (11)	1195 (8)	1353 (9)
C(15)	4429 (11)	874 (8)	448 (11)
C(16)	3311 (10)	667 (7)	−56 (9)
C(21)	835 (9)	998 (7)	−1447 (7)
C(22)	42 (12)	679 (8)	−2190 (9)
C(23)	−89 (15)	1065 (10)	−3095 (10)
C(24)	608 (14)	1753 (9)	−3244 (11)
C(25)	1398 (12)	2069 (9)	−2485 (10)
C(26)	1503 (10)	1718 (7)	−1585 (9)
C(31)	398 (10)	2930 (7)	1538 (8)
C(32)	1541 (12)	3192 (8)	1798 (9)
C(33)	1865 (14)	3636 (9)	2652 (10)
C(34)	1047 (15)	3806 (9)	3219 (12)
C(35)	−101 (15)	3517 (12)	2964 (12)
C(36)	−422 (12)	3070 (9)	2093 (10)
C(41)	−1104 (12)	3100 (7)	−242 (8)
C(42)	−2224 (14)	2843 (11)	−521 (12)
C(43)	−3024 (19)	3443 (15)	−1047 (15)
C(44)	−2666 (21)	4241 (12)	−1231 (14)
C(45)	−1554 (22)	4495 (11)	−932 (14)
C(46)	−737 (17)	3914 (9)	−452 (11)
C(S1)[a]	2733 (19)	4121 (11)	−972 (12)
C(S2)[a]	2083 (22)	4836 (15)	−1529 (16)
C(S3)[a]	3904 (16)	3919 (20)	−1047 (17)
O(S)[a]	2261 (16)	3725 (9)	−438 (14)

[a] Atoms belonging to the solvent molecule.

The crystals were mounted on goniometer heads with glass fibers and epoxy cement. After centering, the Syntex P2$_1$ diffractometer was used to locate a set of 15 reflections from which accurately determined setting angles allowed autoindexing and the least-squares refinement of unit cell parameters. Crystal data and information pertinent to the collection of intensities are listed in Table I. Intensity data were collected on a Syntex P2$_1$ diffractometer at 291 ± 1 K in each case. Stationary background counts were measured at the beginning and end of each scan with a total background to scan time ratio of approximately 1. For $[PtCl(PPh_2)(PPh_2H)]_2$ the intensities of 2 standard reflections, monitored after every 100 measurements, dropped by ~24% during the course of data collection. Appropriate corrections for this decay were applied to the data set. No significant fluctuation in the intensities of the standard reflections occurred for the diphosphine derivative. Intensities were calculated from the total count minus the sum of the two background measurements for each reflection, and standard deviations $\sigma(I)$ were estimated from the formula $\sigma(I) = [T + b_1 + b_2]^{1/2}$, where T = total count and b_1 and b_2 = background counts. Intensities were corrected for Lorentz, polarization, and absorption effects and reduced to structure factors in the normal way.

Solution and Refinement of the Structure. Both structures were solved from three-dimensional Patterson functions, which yielded positions for the metal atoms. Light atoms were subsequently obtained from Fourier or difference Fourier maps.

For $[PtCl(PPh_2)(PPh_2H)]_2$ with two molecules per unit cell in space group $P2_1/n$, the dimer possesses a center of symmetry. A Fourier synthesis calculated from the position of the unique platinum atom gave an R value ($R = \sum||F_o| - |F_c||/\sum|F_o|$) of 0.231. This Fourier map revealed the positions of the two independent phosphorus atoms, a chlorine atom, and most of the carbon atoms of the phenyl rings. Subsequent Fourier syntheses revealed all remaining nonhydrogen atoms of the molecule, as well as the presence of 2 mol of acetone solvent of crystallization per unit cell. Inclusion of all nonhydrogen atoms with isotropic thermal parameters and least-squares refinement gave an R value of 0.071. The position of the hydrogen atom of the diphenylphosphine ligand was located from a difference Fourier map. Subsequent full-matrix least-squares refinement with anisotropic thermal parameters for Pt, P, Cl, and C atoms converged at $R = 0.036$.

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Table III. Atomic Positions (Fractional × 10^4) for $[Pt(Ph_2PCH_2CH_2PPh_2)(PPh_2)]_2Cl_2 \cdot 2.5\ C_2H_4Cl_2$

atom	*x*	*y*	*z*
Pt	413.1 (4)	−586.8 (3)	1188.4 (3)
Cl(1)	2988 (3)	773 (3)	6234 (3)
Cl(2)	5202 (10)	1404 (11)	4587 (10)
P(1)	127 (2)	−1053 (2)	−269 (2)
P(2)	1078 (3)	−2283 (2)	1940 (2)
P(3)	581 (3)	−62 (2)	2650 (2)
C(1)	195 (12)	−1147 (9)	3685 (8)
C(2)	999 (11)	−2223 (9)	3290 (9)
C(11)	1368 (9)	−1972 (9)	−1017 (8)
C(12)	1468 (11)	−3086 (9)	−798 (11)
C(13)	2515 (15)	−3724 (11)	−1343 (14)
C(14)	3414 (15)	−3321 (16)	−2050 (13)
C(15)	3285 (13)	−2194 (15)	−2236 (11)
C(16)	2254 (11)	−1547 (11)	−1691 (9)
C(21)	−1124 (9)	−1662 (8)	156 (8)
C(22)	−1256 (11)	−2330 (10)	−458 (9)
C(23)	−2305 (11)	−2672 (11)	−133 (11)
C(24)	−3154 (12)	−2392 (12)	760 (12)
C(25)	−2992 (14)	−1739 (14)	1361 (13)
C(26)	−1973 (11)	−1367 (11)	1063 (10)
C(31)	299 (11)	−3281 (8)	2061 (9)
C(32)	785 (14)	−4229 (10)	1604 (13)
C(33)	74 (19)	−4946 (13)	1698 (15)
C(34)	−1080 (17)	−4719 (12)	2295 (13)
C(35)	−1565 (17)	−3786 (14)	2744 (14)
C(36)	−879 (13)	−3066 (11)	2633 (12)
C(41)	2585 (10)	−2834 (9)	1322 (10)
C(42)	3203 (11)	−2302 (10)	448 (10)
C(43)	4375 (12)	−2749 (12)	−26 (12)
C(44)	4899 (14)	−3723 (13)	381 (15)
C(45)	4280 (14)	−4226 (12)	1266 (15)
C(46)	3114 (13)	−3832 (11)	1764 (12)
C(51)	−271 (9)	1135 (9)	3234 (8)
C(52)	230 (11)	1971 (9)	3239 (9)
C(53)	−455 (13)	2866 (10)	3738 (11)
C(54)	−1625 (13)	2914 (10)	4239 (10)
C(55)	−2118 (12)	2101 (10)	4249 (10)
C(56)	−1430 (12)	1205 (10)	3729 (10)
C(61)	2037 (10)	−45 (8)	2555 (9)
C(62)	2852 (11)	83 (11)	1569 (10)
C(63)	3964 (13)	159 (13)	1530 (13)
C(64)	4260 (14)	73 (13)	2447 (14)
C(65)	3446 (14)	−54 (13)	3384 (14)
C(66)	2328 (13)	−96 (11)	3465 (11)
Cl(S1)[a]	2989 (6)	3196 (5)	2448 (4)
Cl(S2)[a]	1564 (9)	4498 (6)	4492 (6)
Cl(S3)[a]	4806 (17)	5953 (19)	3685 (16)
C(S1)[a]	2966 (25)	2745 (18)	3736 (18)
C(S2)[a]	2673 (33)	3379 (21)	4435 (22)
C(S3)[a]	5085 (42)	5473 (37)	4722 (36)

[a] Atoms belonging to the solvent molecules. In the model refined the asymmetric unit contains one $C_2H_4Cl_2$ molecule on a general site (Cl(S1), Cl(S2), C(S1), C(S2)). A second molecule lies across a center of symmetry. This site [Cl(S3), C(S3)] is only half occupied. The anion is disordered over two sites (Cl(1), Cl(2)).

Table IV. Selected Bond Lengths (Å) and Bond Angles (Deg) for $[PtCl(PPh_2)(PPh_2H)]_2 \cdot C_3H_6O$

Pt–Cl	2.379 (4)	P(1)–C(21)	1.829 (11)
Pt–P(1)	2.260 (3)	P(2)–C(31)	1.830 (11)
Pt–P(1)′	2.329 (3)	P(2)–C(41)	1.815 (13)
Pt–P(2)	2.313 (3)	Pt···Pt′	3.585 (1)
P(1)–C(11)	1.832 (11)		

P(1)–Pt–Cl	172.0 (1)	C(31)–P(2)–Pt	119.2 (3)
P(1)′–Pt–Cl	94.8 (1)	C(41)–P(2)–Pt	116.7 (3)
P(2)–Pt–Cl	93.2 (1)	C(41)–P(2)–C(31)	103.1 (5)
P(1)′–Pt–P(1)	77.2 (0)	C(12)–C(11)–P(1)	119.9 (4)
P(2)–Pt–P(1)	94.8 (1)	C(16)–C(11)–P(1)	119.5 (5)
P(2)–Pt–P(1)′	172.0 (1)	C(22)–C(21)–P(1)	117.6 (5)
Pt′–P(1)–Pt	102.8 (0)	C(26)–C(21)–P(1)	122.7 (5)
C(11)–P(1)–Pt	112.7 (3)	C(32)–C(31)–P(2)	119.2 (5)
C(11)–P(1)–Pt′	113.1 (3)	C(36)–C(31)–P(2)	118.6 (6)
C(21)–P(1)–Pt	112.1 (3)	C(42)–C(41)–P(2)	119.8 (7)
C(21)–P(1)–Pt′	111.7 (3)	C(46)–C(41)–P(2)	118.6 (6)
C(21)–P(1)–C(11)	104.7 (4)		

Table V. Selected Bond Lengths (Å) and Bond Angles (Deg) for $[Pt(Ph_2PCH_2CH_2PPh_2)(PPh_2)]_2Cl_2 \cdot 2.5C_2H_4Cl_2$

Pt–P(1)	2.362 (3)	P(2)–C(31)	1.791 (13)
Pt–P(1)′	2.335 (3)	P(2)–C(41)	1.816 (13)
Pt–P(2)	2.331 (3)	P(3)–C(1)	1.850 (12)
Pt–P(3)	2.331 (3)	P(3)–C(51)	1.805 (11)
P(1)–C(11)	1.829 (11)	P(3)–C(61)	1.812 (14)
P(1)–C(21)	1.837 (12)	C(1)–C(2)	1.571 (17)
P(2)–C(2)	1.841 (12)	Pt···Pt′	3.699 (1)

P(1)–Pt–P(1)′	76.1 (0)	Pt–P(3)–C(51)	124.3 (3)
P(1)–Pt–P(2)	99.6 (1)	Pt–P(3)–C(61)	113.9 (3)
P(1)–Pt–P(3)	176.5 (1)	C(1)–P(3)–C(51)	103.8 (5)
P(1)′–Pt–P(2)	174.0 (1)	C(1)–P(3)–C(61)	105.3 (5)
P(1)′–Pt–P(3)	101.9 (1)	C(51)–P(3)–C(61)	103.9 (5)
P(2)–Pt–P(3)	82.7 (1)	P(3)–C(1)–C(2)	107.5 (4)
Pt–P(1)–Pt′	103.9 (0)	P(2)–C(2)–C(1)	110.3 (4)
Pt–P(1)–C(11)	113.4 (3)	P(1)–C(11)–C(12)	120.8 (5)
Pt–P(1)–C(21)	109.6 (3)	P(1)–C(11)–C(16)	117.3 (5)
Pt′–P(1)–C(11)	115.0 (3)	P(1)–C(21)–C(22)	121.0 (5)
Pt′–P(1)–C(21)	105.8 (3)	P(1)–C(21)–C(26)	117.5 (5)
C(11)–P(1)–C(21)	108.8 (4)	P(2)–C(31)–C(32)	123.6 (6)
Pt–P(2)–C(2)	110.0 (3)	P(2)–C(31)–C(36)	117.2 (6)
Pt–P(2)–C(31)	117.3 (3)	P(2)–C(41)–C(42)	120.7 (5)
Pt–P(2)–C(41)	113.4 (3)	P(2)–C(41)–C(46)	118.6 (6)
C(2)–P(2)–C(31)	103.2 (5)	P(3)–C(51)–C(52)	121.4 (5)
C(2)–P(2)–C(41)	104.0 (5)	P(3)–C(51)–C(56)	119.0 (5)
C(31)–P(2)–C(41)	107.7 (5)	P(3)–C(61)–C(62)	120.1 (5)
Pt–P(3)–C(1)	103.7 (4)	P(3)–C(61)–C(66)	119.4 (6)

The unique hydrogen atom on phosphorus was included in this calculation but not refined. No attempt was made to locate phenyl ring hydrogen atoms. With a weighting scheme of the type $w^{-1} = 2.43000 + 0.0250|F| + 0.00013|F|^2$ the final weighted R value ($R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$) was 0.042. A final difference map showed no prominent features, the maximum peak height being 0.4 e Å^{-3}. The final positional parameters are listed in Table II with anisotropic thermal parameters in Table S1 (supplementary data).

With one molecule in a triclinic $P\bar{1}$ cell, molecules of $[Pt(PPh_2)(Ph_2PCH_2CH_2PPh_2)]_2Cl_2$ possess a center of symmetry. A Patterson map readily revealed the position of the unique platinum atom, and a Fourier synthesis phased with the heavy metal atom ($R = 0.269$) afforded reasonable positions for the remaining atoms of the cation. Refinement of positions and isotropic temperature factors for these atoms gave $R = 0.089$. At this stage it became clear that the anion (Cl^-) was disordered over two sites. In subsequent calculations, this disorder was refined with occupancy factors of 0.75 and 0.25 for the two sites. Electron density maps also suggested the presence of solvent dichloroethane in the lattice, and difference maps were consistent with the presence of 1.25 mol of $C_2H_4Cl_2$ per asymmetric unit. In final least-squares cycles, all nonhydrogen atoms, including atoms of the solvent, were refined with anisotropic thermal parameters. The final R value was 0.043; a weighting scheme of the type $w^{-1} = 2.45000 + 0.03100|F|^2 + 0.00036|F|^2$ yielded an R_w of 0.054. A difference map contained no peaks higher than 0.5 e Å^3 and was basically featureless. Atomic positions are listed in Table III and thermal parameters in Table S2 (supplementary data).

Scattering factors used in structure factor calculations, which included corrections for anomalous scattering for Pt, Cl, and P, were taken from the compilations of ref 26. Listings of structure factors for both structures are available as supplementary data.

All calculations were carried out on IBM systems in the University of Waterloo Computing Center. Programs used have been previously described in detail.[3]

Results and Discussion

Selected bond lengths and bond angles for $[PtCl(PPh_2)(PPh_2H)]_2$ are grouped in Table IV, with corresponding data for $[Pt(PPh_2)(Ph_2PCH_2CH_2PPh_2)]_2Cl_2$ in Table V. Distances and angles within the phenyl rings of these two structures and

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(26) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table VI. Correlation of M· · ·M Distances and M–P–M Angles in Some Phosphido-Bridged Complexes

compd	M· · ·M dist, Å	M–P–M angle, deg	ref
$Ir_2(CO)_2(PPh_3)_2(PPh_2)_2$	2.551 (1)	67.4 (1)	29
$Ru_2(NO)_2(PPh_3)_2(PPh_2)_2$	2.629 (1)	69.7 (1)	30
$Fe_2(CO)_6(Cl)(PPh_2)$	2.5607 (5)	69.8 (0)	31
$Pt_2(PPh_3)_2(PPh_2)$	2.604 (1)	68.7 (1)	24
$Ni_2(CO)_2(PPh_2)_2$	2.510 (av)	70.1 (1)	32
$Fe_2(CO)_6(PPh_2)_2$	2.623 (2)	72.0 (1)	33
$Ru_5(CO)_{13}(C_2Ph)(PPh_2)$	2.696 (1)	72.3 (0)	34
$Co_2(\eta^5\text{-}C_5H_5)_2(PPh_2)_2$	2.56 (1)	72.5 (5)	35
$Fe_3(CO)_7(Ph_2PC_4(CF_3)_2)(PPh_2)^a$	2.665 (8)	73.3 (2)	36
$Ru_3(CO)_8(C_2t\text{-}Bu)(PPh_2)^b$	2.7084 (4)	74.4 (0)	9
$Fe_2(NO)_2(PPh_2)_2$	2.710 (2)	74.83 (5)	37
$Fe_2(CO)_6(CH_2C(Ph)NMe)(PPh_2)$	2.707 (1)	75.6 (0)	38
$[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(PMe_2)]^-$	3.157 (2)	83.6 (1)	39
$Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(H)(PMe_2)$	3.262 (2)	84.8 (1)	40
$Ru_3(CO)_9(C_2\text{-}i\text{-}Pr)(PPh_2)^b$	3.466 (1)	92.8 (1)	9
$Fe_3(CO)_8(Ph_2PC_4(CF_3)_2)(PPh_2)^a$	3.591 (2)	98.0 (1)	41
$Ir(\eta^5\text{-}C_5H_5)(C(Ph)O)(C(Me)O)(PPh_2)Mn(CO)_3$	3.543 (2)	99.1 (1)	42
$Pt_3(PPh_3)_3(Ph)(PPh_2)_3$	2.785 (1)	76.4 (1)	24
	3.630 (1)	104.3 (1)	
$Ni_2(\eta^5\text{-}C_5H_5)_2(PPh_2)_2$	3.36 (1)	102.4 (2)	35
$Fe_2(CO)_6I_2(PMe_2)_2$	3.590 (4)	102.4 (2)	43
$Pt_2Cl_2(PPh_2H)_2(PPh_2)_2$	3.585 (1)	102.8 (0)	this work
$[Pt_2(Ph_2PCH_2CH_2PPh_2)_2(PPh_2)_2]Cl_2$	3.699 (1)	103.9 (0)	this work
$[Fe_2(CO)_6(PPh_2)_2]^{2-}$	3.630 (3)	105.5 (1)	4

[a] These compounds are related by loss of one CO and formation of an M–M bond. [b] These compounds are also related by loss of one CO and formation of an M–M bond.

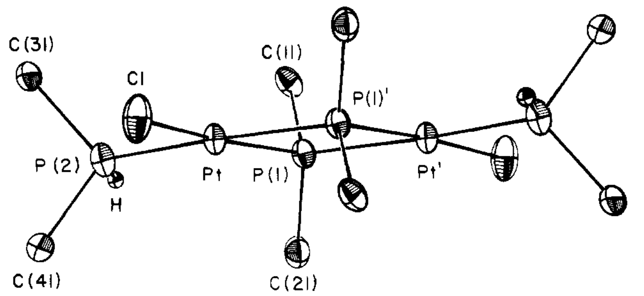

Figure 1. View of the molecular structure of the dimer $[PtCl(PPh_2)(PPh_2H)]_2$ drawn to illustrate the skeletal geometry. Only one carbon atom of each phenyl ring is shown for clarity.

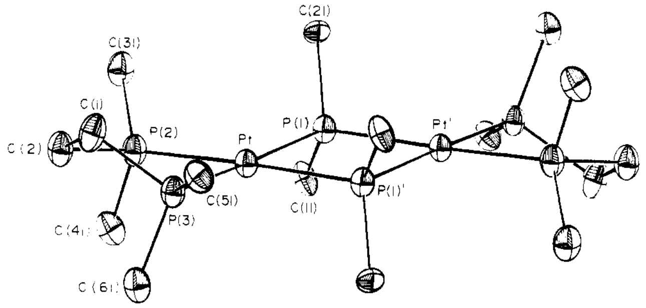

Figure 2. Skeletal structure of $[Pt(Ph_2PCH_2CH_2PPh_2)(PPh_2)]_2Cl_2$. Only one carbon atom of each phenyl ring is shown. Chloride anions and solvent are not included.

within solvent molecules are listed as Tables S3–6 (supplementary data). ORTEP plots, drawn to illustrate the major skeletal features of the two dimers, are shown in Figures 1 and 2. The structure of $[PtCl(PPh_2)(PPh_2H)]_2$ consists of discrete dimers with no unusual intermolecular contacts. The acetone molecule of solvation does not interact with the metal atoms, the nearest contact with the dimer being between the solvent oxygen atom and the hydrogen atom of the diphenylphosphine ligand at a distance of 2.344 Å.

In the diphosphine complex, the dimeric cations $[Pt(PPh_2)(Ph_2PCH_2CH_2PPh_2)]_2^{2+}$ are packed together with isolated but disordered chloride ions and dichloroethane molecules of crystallization. The shortest Cl^-···Pt distance is 5.829 Å, and the closest contact of the solvent with the dimer unit is between the C(S1) and C(65) atoms at 3.649 Å.

Of major interest in the context of this structural study are the Pt_2P_2 rings, the metal–metal distances, and the angles at the phosphorus atoms of the phosphido bridges. Due to crystallographically imposed symmetry the Pt_2P_2 rings are rigidly planar. However, because the symmetry-unrelated internal angles differ markedly, the rings are best described as parallelograms with slightly unequal edges.

A wealth of data has recently been amassed for platinum–platinum bonding and nonbonding distances in platinum dimers and clusters[27,28] from which it would appear that a "normal" single bond between two Pt(0) or Pt(I) centers would fall within the range 2.58–2.80 Å with most Pt(I)–Pt(I) bond lengths lying at the lower end of this scale. A value of 2.76 Å has been suggested as a standard Pt(0)–Pt(0) single-bond distance, this corresponding well with the Pt–Pt separation in platinum metal.[27] These observations suggest that it would not be unreasonable to predict a Pt(II)–Pt(II) single-bond length of ~2.50–2.60 Å. On this basis the Pt···Pt distances in $[PtCl(PPh_2)(PPh_2H)]_2$ (3.585 (1) Å) and $[Pt(PPh_2)(Ph_2PCH_2CH_2PPh_2)]_2Cl_2$ (3.699 (1) Å) are clearly nonbonding. A stereochemical consequence of the long Pt···Pt distances in the two planar Pt_2P_2 rings is the presence of large angles subtended by the metals at the bridging phosphorus atoms. Indeed, the Pt–P–Pt′ angles (102.8 (0)° in $[PtCl(PPh_2)(PPh_2H)]_2$ and 103.9 (0)° in $[Pt(PPh_2)(Ph_2PCH_2CH_2PPh_2)]_2Cl_2$) lie close to the top of the range observed for M–P–M angles in bis(phosphido)-bridged complexes. Table VI illustrates the variation of M–P–M angles with M–M distances for a selected wide range of phosphido-bridged bi- and polynuclear compounds. At the lower extreme, very acute M–P–M angles accompany strong and in some cases [e.g., $Ir_2(CO)_2(PPh_3)_2(\mu\text{-}PPh_2)_2$[29] and $Ru_2(NO)_2(PPh_3)_2(\mu\text{-}PPh_2)_2$[30]]

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multiple M–M bonds while angles closer to the tetrahedral value are found for doubly bridged systems where M–M bonding is absent. Although the recently characterized anion $[Fe_2(CO)_6(\mu\text{-}PPh_2)_2]^{2-}$[4] exhibits an angle (105.5 (1)°) that may well be close to the upper limit for bis(diphenylphosphido)-bridged binuclear systems, it is clear from the work of Vahrenkamp[5,44] that much larger bond angles at the group 5 atom are possible in monobridged dialkylarsine complexes. Thus a Cr–As–Mn angle of 121.56 (6)° is present in the compound $(CO)_5Cr(\mu\text{-}AsMe_2)Mn(CO)_5$,[44] and an even larger value of 123.08 (5)° is found in the non-metal–metal-bonded dimer $(\eta^5\text{-}C_5H_5)(PMe_3)(CO)_2Mo(\mu\text{-}AsMe_2)Mo(CO)_2(PMe_3)(\eta^5\text{-}C_5H_5)$.[5] These results provide a dramatic illustration of the flexibility and versatility of R_2M (M = P, As) bridges. The large Pt–P–Pt′ angles observed for $[PtCl(PPh_2)(PPh_2H)]_2$ and $[Pt(PPh_2)(Ph_2PCH_2CH_2PPh_2)]_2Cl_2$ contrast sharply with the acute angle (68.7°) in the platinum(I) compound $Pt_2(PPh_3)_2(PPh_2)_2$ (Table VI) where a strong Pt–Pt bond is present.[24] On the other hand a comparable Pt–P–Pt angle (104.3°) was found for the phosphido bridge between nonbonded platinum atoms in the trimer $Pt_3(PPh_3)_2(PPh_2)_3(Ph)$.[24] The absence of Pt---Pt bonding and the presence of large angles in the dimers examined here are quite consistent with the very high field NMR shifts of the ^{31}P resonances for the PPh_2 bridges in these compounds,[16,17] thus providing confirmatory evidence that $\delta_{^{31}P}(PPh_2)$ is a useful spectroscopic probe of M···M bonding.

A further result of the long Pt···Pt distances and large Pt–P–Pt′ angles in the two platinum dimers are the small P–Pt–P′ angles (77.2 (0)° in $[PtCl(PPh_2)(PPh_2H)]_2$ and 76.1 (0)° in $[Pt(PPh_2)(Ph_2PCH_2CH_2PPh_2)]_2Cl_2$) within the four-membered rings. As a consequence, the remaining angles at the metal atom in the PPh_2H compound are all greater than the ideal 90° value for a square plane, while in the diphosphine complex where the angle P(2)–Pt–P(3) is constrained by the methylene chain, the P(1)–Pt–P(2) (99.6 (1)°) and P(1)–Pt–P(3) (101.9 (1)°) angles are ~10° above normal.

Within the coordination sphere of platinum the metal–ligand bond lengths appear to reflect the relative trans-directing influences of the various ligands. Thus for $[PtCl(PPh_2)(PPh_2H)]_2$ the Pt–P(1) (trans to Cl) bond length (2.260 (3) Å) is shorter than Pt–P(1)′ (trans to PPh_2H) (2.329 (3) Å). A key feature of interest here is the relative trans influence of a bridging phosphido group. Although NMR coupling constants have been interpreted in terms of a high trans influence for PPh_2,[16,17] structural confirmation of such an effect was precluded by the lack of X-ray data for any phosphido-bridged platinum(II) complexes. We were thus interested to know whether the X-ray data for $[PtCl(PPh_2)(PPh_2H)]_2$ and $[Pt(PPh_2)(Ph_2PCH_2CH_2PPh_2)]_2Cl_2$ provided any clear-cut evidence pertinent to the trans influence of PPh_2. In the diphosphine complex, which is to our knowledge the first square-planar Pt(II) complex to be structurally characterized in which all four bonds are to phosphorus, the Pt–P(2) and Pt–P(3) distances (average 2.331 Å) are slightly longer than the mean Pt–P distance of 2.302 Å obtained by averaging results from 22 platinum complexes with mutually trans phosphines.[45] The Pt–P(2) distance to the terminal phosphine in the chloro complex (2.313 (3) Å) is also longer than the average although marginally so. The Pt–Cl (trans to PPh_2) bond length (2.379 (4) Å) is virtually identical with that trans to PEt_3 in $Et_4N[PtCl_3(PEt_3)]$ (2.382 (4) Å)[46] and also similar to the Pt–Cl (trans to PPh_2) distance in $PtCl_2[Ph_2PCH_2CH_2P(CF_3)_2]$.[47] Thus overall these results suggest that a PPh_2 bridge has a bond-lengthening influence as high as a terminal tertiary phosphine ligand. Further refinement of the relative ranking of phosphines and phosphido bridges in the trans-influence series will have to await the acquisition of structural data for a wider range of phosphido-bridged derivatives of the type $[Pt(X)(PPh_2)(L)]_2$ (X = halide, hydride; L = tertiary phosphine). Thus while the Pt–P distances to the phosphido bridge (average 2.348 Å) are marginally longer than the Pt–P(diphosphine) bond lengths (average 2.331 Å) in $[Pt(PPh_2)(Ph_2PCH_2CH_2PPh_2)]_2Cl_2$, uncertainty surrounding the effects of bridging on the Pt–P bond lengths precludes a firm conclusion.

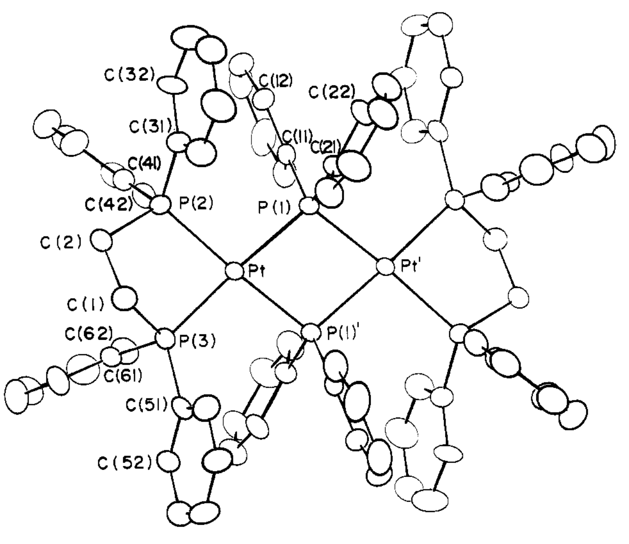

Figure 3. View of $[Pt(Ph_2PCH_2CH_2PPh_2)(PPh_2)]_2Cl_2$ drawn to illustrate phenyl ring interactions. Anions and solvent of crystallization are not shown.

Bond lengths and angles within the phosphine ligands appear normal. However, it is apparent that the phenyl rings of the bridging PPh_2 groups in the diphosphine structure interact strongly with phenyl rings of the diphosphine ligand (Figure 3). As a result, the carbon atoms (C(11) and C(21)) attached to bridging phosphorus atoms are twisted out of an imaginary vertical plane passing through P(1) and P(1)′ and perpendicular to the Pt_2P_2 rings. This distortion also evident in the anion $[Fe_2(CO)_6(PPh_2)_2]^{2-}$[4] is less noticeable in $[PtCl(PPh_2)(PPh_2H)]_2$ where the terminal ligands are less bulky. Within the diphosphine ligand one methylene carbon atom lies well out of and the other approximately in the plane defined by the central core of the molecule.

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Acknowledgment. We are grateful to the Natural Science and Engineering Research Council for financial support of this work.

Registry No. $[PtCl(PPh_2)(PPh_2H)]_2\cdot C_3H_6O$, 80374-73-8; $[Pt(Ph_2PCH_2CH_2PPh_2)(PPh_2)]_2Cl_2\cdot 2.5C_2H_4Cl_2$, 80340-26-7.

Supplementary Material Available: Tables of observed and calculated structure factors for $[PtCl(PPh_2)(PPh_2H)]_2\cdot C_3H_6O$ and $[Pt(Ph_2PCH_2CH_2PPh_2)(PPh_2)]_2Cl_2\cdot 2.5C_2H_4Cl_2$ as well as tables containing thermal parameters, phenyl ring bond lengths and angles, and solvent molecule bond lengths and angles (42 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, University of Alabama, University, Alabama 35486, and The University of Texas at Austin, Austin, Texas 78712

Pyrrolyl Compounds of Main-Group Elements. 1. Synthesis of $(\eta^1\text{-}C_4H_4N)_3As$ and Crystal and Molecular Structures of $(\eta^1\text{-}C_4H_4N)_3P$ and $(\eta^1\text{-}C_4H_4N)_3As$

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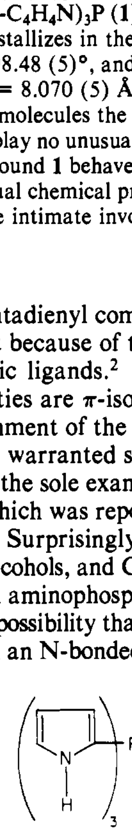
Received August 12, 1981

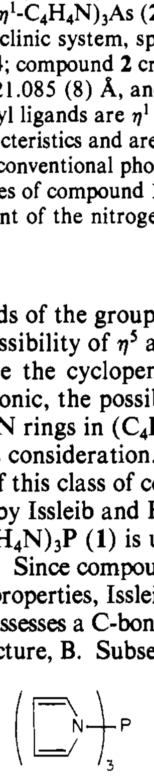
$(\eta^1\text{-}C_4H_4N)_3As$ has been prepared by the action of C_4H_4NLi on $AsCl_3$ in diethyl ether solution. The molecular structures of $(\eta^1\text{-}C_4H_4N)_3P$ (**1**) and $(\eta^1\text{-}C_4H_4N)_3As$ (**2**) have been determined by single-crystal X-ray diffraction methods. Compound **1** crystallizes in the monoclinic system, space group $P2_1/n$, with $a = 12.428$ (6) Å, $b = 5.858$ (3) Å, $c = 17.071$ (8) Å, $\beta = 98.48$ (5)°, and $Z = 4$; compound **2** crystallizes in the orthorhombic system, space group $P2_12_12_1$, with $a = 7.251$ (4) Å, $b = 8.070$ (5) Å, $c = 21.085$ (8) Å, and $Z = 4$. The molecular structures of compounds **1** and **2** are very similar; in both molecules the pyrrolyl ligands are η^1 and N bonded. The N–P–N bond angles and N–P bond lengths in compound **1** display no unusual characteristics and are quite normal for a PN_3 system with trigonal-planar nitrogen atoms. Moreover, compound **1** behaves as a conventional phosphine ligand and reacts with $Fe_2(CO)_9$ to afford $(C_4H_4N)_3PFe(CO)_4$ (**3**). The unusual chemical properties of compound **1** such as hydrolytic stability and unreactivity toward alcohols are due therefore to the intimate involvement of the nitrogen lone pair in the pyrrolyl π system.

Introduction

Tricyclopentadienyl compounds of the group 5A elements are of interest because of the possibility of η^5 attachment of the carbocyclic ligands.[2] Since the cyclopentadienyl and pyrrolyl moieties are π-isoelectronic, the possibility of *multihapto* attachment of the C_4H_4N rings in $(C_4H_4N)_3E$ (E = P, As, Sb, Bi) warranted serious consideration. Prior to the present work, the sole example of this class of compound was $(C_4H_4N)_3P$ which was reported by Issleib and Brack[3] almost 25 years ago. Surprisingly, $(C_4H_4N)_3P$ (**1**) is unreactive toward water, alcohols, and CS_2.[3,4] Since compound **1** does not exhibit typical aminophosphine properties, Issleib and Brack[3] suggested the possibility that it possesses a C-bonded structure, A, rather than an N-bonded structure, B. Subsequent IR and NMR data,[4] however, indicate that B is the preferred structure. One of the objectives of the present work was to establish the molecular structure of **1** by means of single-crystal X-ray diffraction. Furthermore, realizing that the structures of $(C_4H_4N)_3E$ compounds might be dependent on, e.g., the covalent radius of the central atom, we decided to attempt the synthesis of heavier congeners of **1**. These efforts resulted in the synthesis of $(pyrl)_3As$ (**2**) (pyrl = pyrrolyl), which has also been investigated by X-ray crystallography.



A



B

Experimental Section

Materials and General Procedures. Pyrrole, *n*-BuLi, and ECl_3 (E = P, As, Sb, Bi) were procured commercially and used as supplied, and $Fe_2(CO)_9$ was prepared by UV irradiation of $Fe(CO)_5$ in hexane solution. All solvents were dried carefully prior to use.

Most of the materials described herein are moisture sensitive. Accordingly, it was prudent to perform all operations in vacuo or under an inert atmosphere.

Spectroscopic Measurements. The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded in the FT mode at spectrometer frequencies of 90, 20, and 32.84 MHz, respectively, on Varian EM 390 (^1H) and Varian FT-80 (^{13}C and ^{31}P) instruments. Dichloromethane (54.19 ppm relative to Me_4Si) was employed as the internal reference for the ^{13}C spectra, and 85% H_3PO_4 was used as the external reference for the ^{31}P spectra. All positive chemical shifts are downfield (deshielded) and vice versa.

The mass spectra were measured on a CEC 21-491 spectrometer operating at an ionizing voltage of 70 eV.

Preparation of $(C_4H_4N)_3P$ (1) and $(C_4H_4N)_3As$ (2). Both compounds were prepared by the same route; however, since $(C_4H_4N)_3P$ is a known compound,[3,4] only the preparation of the arsenical is described. In a typical reaction, 139 mL of a 1.55 M solution of *n*-BuLi in hexane was added slowly to a solution of 14.5 g (216.1 mmol) of pyrrole in 300 mL of diethyl ether at −78 °C. The formation of C_4H_4NLi was signalled by the immediate formation of a white solid. The stirred solution was brought slowly to room temperature in order to eliminate the butane which had formed. After the C_4H_4NLi solution was recooled to −30 °C, a solution of 13.06 g (72.0 mmol) of $AsCl_3$ in 40 mL of diethyl ether was added dropwise. After slow warming to room temperture, the reaction mixture was refluxed for 3 h. Removal of lithium chloride by filtration followed by vacuum evaporation of the solvent left a dark-colored oil which was purified by distillation (bp 125–132 °C at 1 torr). This afforded 7.0 g (35.5% yield) of colorless oily $(C_4H_4N)_3As$, which solidified solwly upon cooling to −15 °C. The compound decomposes slowly at room temperature, thus precluding commercial elemental analysis. Unequivocal characterization of $(C_4H_4N)_3As$ was accomplished by means of single-crystal X-ray diffraction (vide infra). NMR data for **2**: ^1H, α-H's δ 6.84 (m), β-H's δ 6.50 (m); $^{13}C\{^1H\}$ α-C's 122.9 ppm (s), β-C's 112.6 ppm (s). The mass spectrum of **2** exhibits a parent peak at *m/e* 273 (29.7%), and peaks at *m/e* 207 (75.7%) and 141 (70.3%),

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(1) (a) University of Alabama. (b) The University of Texas at Austin.

(2) The compounds $(C_5H_5)_3Sb$ and $(C_5H_5)_3Bi$ were first prepared by: Fischer, E. O.; Schreiner, S. *Chem. Ber.* **1960**, *93*, 1417–1422. The bismuth compound exists in orange and black modifications. It was suggested that $(C_5H_5)_3Sb$ and the orange form of $(C_5H_5)_3Bi$ involve σ-bonded C_5H_5 rings but that the black form involves π-bonded C_5H_5 rings. The *monohapto* structure, $(\eta^1\text{-}C_5H_5)_3Sb$, has been confirmed recently by single-crystal X-ray diffraction: Birkhahn, M.; Krommes, P.; Massa, W.; Lorbeth, J. *J. Organomet. Chem.* **1981**, *208*, 161–167.

(3) Issleib, K.; Brack, A. *Z. Anorg. Allg. Chem.* **1957**, *292*, 245–253.

(4) Fischer, S.; Hoyano, J.; Johnson, I.; Peterson, L. K. *Can. J. Chem.* **1976**, *54*, 2706–2709.

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