the absence of Cr⋯Cr bonding is due to subtle differences between Cr(III) and Tc(IV) coordination geometries, to the presence of hydroxy rather than oxo bridges in the Cr complex, or to an intrinsic difference in the propensity of Cr and Tc to form multiple bonds.

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Supplementary Material Available: A listing of structure factor amplitudes and anisotropic thermal parameters (13 pages). Ordering information is given on any current masthead page.

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Palladium and Platinum Complexes with *cyclo*-Triphosphorus and *tetrahedro*-Tetraphosphorus as Ligands

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Simple and triple-decker sandwich complexes of palladium and platinum containing the *cyclo*-triphosphorus unit as a η^3 ligand with general formulas $[(\text{triphos})M(\eta^3\text{-}P_3)]BF_4$ (triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane; M = Pd, Pt) and $[LPd(\mu\text{-}(\eta^3\text{-}P_3))PdL]Y$ (L = triphos, Y = BPh_4; L = np_3, Y = BF_4; np_3 = tris(2-(diphenylphosphino)ethyl)amine) have been synthesized and characterized. The structures of the complexes $[(\text{triphos})Pd(\eta^3\text{-}P_3)]BF_4\cdot C_2H_5OH$ (I) and $[(\text{triphos})Pd(\mu\text{-}(\eta^3\text{-}P_3))Pd(\text{triphos})]BPh_4$ (II) have been elucidated through complete X-ray analyses. The crystals of compound I are monoclinic with $a = 13.084$ (5) Å, $b = 20.467$ (7) Å, $c = 17.183$ (6) Å, $\beta = 105.35$ (4)°, space group $P2_1/n$, $Z = 4$, $R = 0.065$, and 1876 observed reflections. The crystals of the compound II are orthorhombic with $a = 20.973$ (7) Å, $b = 18.464$ (6) Å, $c = 25.299$ (8) Å, space group *Pccn*, $Z = 4$, $R = 0.072$, and 1872 observed reflections. Both in the simple and in the triple-decker sandwich complexes, the metal atom is six-coordinate. The palladium(0) compound $[(np_3)Pd(\eta\text{-}P_4)]$ contains the intact tetrahedral P_4 molecule σ bonded to the metal.

Introduction

In previous papers several complexes of 3d metals with the *cyclo*-triphosphorus (η^3-P_3) group have been described and characterized.[2] They present a simple or a triple-decker sandwich structure, the metal atom being coordinated by six phosphorus atoms. The ground state of the triple-decker complexes is a spin singlet, doublet, or triplet depending on the number of valence electrons of the complex cations.[3]

In order to extend this research, we tried to synthesize the analogous palladium and platinum derivatives.

By reacting the complexes $[MCl_2P(Bu)_3]_2$ (M = Pd, Pt) with white phosphorus and the tripodlike ligands 1,1,1-tris((diphenylphosphino)methyl)ethane (triphos) and tris(2-(diphenylphosphino)ethyl)amine (np_3) in appropriate conditions, the following complexes were synthesized: $[(\text{triphos})M(\eta^3\text{-}P_3)]BF_4$ (M = Pd, Pt) and $[LPd(\mu\text{-}(\eta^3\text{-}P_3))PdL]Y$ (L = triphos, Y = BPh_4; L = np_3, Y = BF_4). Finally, by reaction of white phosphorus with the palladium(0) complex $[Pd(np_3)]$, the compound $[(np_3)Pd(\eta\text{-}P_4)]$, containing the tetrahedral P_4 molecule bound to the metal through a phosphorus atom, was obtained.

Complete X-ray structural analyses have been carried out on the compounds $[(\text{triphos})Pd(\eta^3\text{-}P_3)]BF_4$ and $[(\text{triphos})Pd(\mu\text{-}(\eta^3\text{-}P_3))Pd(\text{triphos})]BPh_4$. $^{31}P\{^1H\}$ NMR spectra of the complexes have been recorded, and some interesting features are presented.

Experimental Section

All the solvents were reagent grade and were used without further purification. All reactions were routinely performed in an atmosphere of dry nitrogen.

The ligands triphos[4] and np_3[5] and the complexes $[MCl_2P(Bu)_3]_2$ (M = Pd, Pt)[6] were prepared according to published procedures.

Physical Measurements. Infrared and electronic spectra, conductivity measurements, and magnetic susceptibilities were measured with the use of methods already described.[7] ^{31}P NMR spectra were collected on a Varian CFT20 spectrometer operating at 31.19 MHz with proton-noise decoupling and deuterium lock. Positive chemical shifts are downfield, and they are reported relative to H_3PO_4 (0.0 ppm). The chemical shifts are reproducible to ±0.05 ppm, and the coupling constants are accurate to ±1.0 Hz. Coordination chemical shifts are reported in ppm relative to the corresponding phosphorus in the free ligand.

Analytical and conductometric data of the complexes are reported in Table I; Table II lists the $^{31}P\{^1H\}$ NMR spectra for the complexes.

Synthesis of the Complexes. $\mathbf{[(np_3)Pd(\eta\text{-}P_4)]}$. A solution of white phosphorus (1 mmol) in tetrahydrofuran (30 mL) was slowly added to a solution of $[Pd(np_3)]$ (1 mmol)[8] in benzene (30 mL), keeping the solution at 5 °C. Brown crystals which precipitated in a short time were collected and washed with benzene and light petroleum.

$\mathbf{[(triphos)M(\eta^3\text{-}P_3)]BF_4}$ **(M = Pd, Pt).** A large excess of white phosphorus (4 mmol) in tetrahydrofuran (30 mL) was added to a solution of $[PdCl_2P(Bu)_3]_2$ (1 mmol) and triphos (2 mmol) in methylene chloride (30 mL). The resulting solution was warmed for 30 min and $[N(Bu)_4]BF_4$ (2 mmol) dissolved in ethanol (10 mL) was added. Crystals of the compounds were obtained by adding ligroin (20 mL) and concentrating the solution. The crystals were collected, washed with ethanol and light petroleum, and then recrystallized from methylene chloride and ethanol; yield 45%.

$\mathbf{[LPd(\mu\text{-}(\eta^3\text{-}P_3))PdL]Y}$ **(L = np_3, Y = BF_4; L = triphos, Y = BPh_4).** These complexes were prepared by the same procedure as the above derivatives by reacting white phosphorus and the palladium dimer complex $[PdCl_2P(Bu)_3]_2$ in 1:1 ratio. The complexes crystallize by

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(8) Unpublished results of this laboratory. The $[Pd(np_3)]$ complex has been synthesized by reduction under nitrogen of a solution of K_2PdCl_4 (1 mmol) and np_3 (1 mmol) in acetone (20 mL) and ethanol (15 mL) with sodium tetrahydroborate dissolved in ethanol.

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Table I. Analytical and Conductivity Data for the Complexes

compd	Λ_M,[a] cm²/Ω mol	% calcd C	H	N	P	M	% found C	H	N	P	M
$[(np_3)Pd(P_4)]$		57.06	4.79	1.58	24.53	12.04	57.07	4.80	1.51	24.02	11.97
$[Pd(P_3)(triphos)]BF_4 \cdot C_2H_5OH$	80	53.97	4.74		19.42	11.12	53.85	4.82		19.32	
$[Pt(P_3)(triphos)]BF_4$	77	49.27	3.93		18.59	19.52	49.18	4.08		18.42	
$[Pd_2(P_3)(triphos)_2]BPh_4$	72	67.93	5.27		14.87	11.35	67.94	5.39		15.01	
$[Pd_2(P_3)(np_3)_2]BF_4$	68	59.35	4.98	1.65	16.40	12.52	59.24	5.20	1.59	16.30	

[a] Molar conductance of ca. 10^{-3} solution in nitroethane at 20 °C.

Table II. $^{31}P\{^1H\}$ NMR Spectral Data for the Complexes

compd	chem shifts,[a] ppm P(phosphine)	$P(\eta^3-P_3)$	coord chem shift, Δ[b] ΔP	J, Hz P-P	Pt-P-(phosphine)	Pt-P-(η^3-P_3)
$[(triphos)Pd(\eta^3-P_3)]BF_4 \cdot C_2H_5OH$	4.9 q	−132.9 q	30.45	11.0		
$[(triphos)Pt(\eta^3-P_3)]BF_4$	−18.58 q	−217.43 q	6.97	8.3	2476	171
$[(triphos)Pd(\mu-(\eta^3-P_3))Pd(triphos)]BPh_4$	−13.30 q	−334.0 s	12.25	20.0		
$[(np_3)Pd(\mu-(\eta^3-P_3))Pd(np_3)]BF_4$	−4.60 q	−282.50 s	14.96	32.0		

[a] Chemical shifts are relative to 85% H_3PO_4. Positive chemical shifts are downfield: q = quartet, s = septet. [b] $\Delta P = \delta P_{\text{coord}} - \delta P_{\text{free ligand}}$. Samples were dissolved in CH_2Cl_2.

addition of $[N(Bu)_4]BF_4$ or $NaBPh_4$ dissolved in ethanol and may be recrystallized from methylene chloride and methanol.

Collection and Reduction of X-ray Intensity Data. [(triphos)Pd(η^3-P_3)]$BF_4 \cdot C_2H_5OH$ (I). The yellow crystals of this complex are parallelepiped shaped. The crystal used for the structure analysis had the dimensions 0.15 × 0.12 × 0.08 mm. Cell parameters were determined at room temperature (ca. 22 °C) by carefully measuring the setting angles of 25 reflections on a Phillips PW 1100 diffractometer. Details of crystal data and data collection are given in Table III. The standard deviations on the intensities were calculated as described elsewhere,[9] with the use of a value of the instability factor k of 0.03. The observed reflections were corrected for Lorentz and polarization effects and for absorption with the use of a numerical method. Atomic scattering factors were taken from ref 10. Corrections for anomalous dispersion effects were also applied.[10]

[(triphos)Pd(μ-(η^3-P_3))Pd(triphos)]BPh_4 (II). The red crystals of this complex are octahedrically shaped. In the crystal used for the structure analysis, the eight faces were distant from the center by about 0.1 mm. Cell parameters were determined as for compound I. Details of crystal data and data collection are given in Table III. The instability factor k, used in the calculation of the standard deviations of the intensities, was 0.03. The observed reflections were corrected for Lorentz and polarization effects and for absorption with the use of a numerical method. The atomic scattering factors and anomalous scattering corrections were the same as those used for compound I.

Solution and Refinement of the Structures. Three-dimensional Patterson syntheses yielded the positional parameters of the palladium and phosphorus atoms for both structures. Successive F_0 Fourier syntheses showed the positions of all nonhydrogen atoms including the three atoms of the ethanol molecule in compound I. The structures were refined by use of the full-matrix least squares of the SHELX program.[11] The minimized function is $\sum w(|F_o| - |F_c|)^2$, where w is the weight assigned to the F_o values according to the expression $w = 1/\sigma(F_o)^2$. For both structures the hydrogen atoms were introduced in calculated positions, with an overall temperature factor U of 0.05 Å² and were not refined. Their positions were varied in every cycle on the basis of the shift of the carbon atoms (the C–H distance was fixed at 1.07 Å). Isotropic temperature factors were used for the oxygen, carbon, and boron atoms, whereas anisotropic temperature factors were used for the other atoms. Phenyl groups were refined as rigid bodies, with the assumption of D_{6h} symmetry for the rings. The final conventional R factors were 0.065 and 0.072 for the compound I and II, respectively. The R_w factors, defined as $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, were 0.062 and 0.068 for compound I and II, respectively. A ΔF Fourier synthesis, calculated at the end of the refinement on compound I, showed some peaks of electron density in proximity of the tetrafluoroborate group. These peaks had heights of about 0.5 e/Å³. Attempts to fit the BF_4 group by alternative models were not successful. However, these residuals of electron density account for the high thermal parameters found for the atoms of this group. Some peaks of about 0.3–0.4 e/Å³ were found also in proximity of the ethanol solvent molecule, and also for this molecule some degree of disorder is hypothized. A final ΔF Fourier synthesis calculated on compound II did not show remarkable features. The final values of the parameters are reported in Tables IV–VII. Observed and calculated structure factors are available as supplementary material.

Table III. Crystal Data and Data Collection Details

	I	II
mol formula	$C_{43}H_{45}OBF_4P_6Pd$	$C_{106}H_{98}BP_9Pd_2$
mol wt	956.88	1874.34
a, Å	13.084 (5)	20.973 (7)
b, Å	20.467 (7)	18.464 (6)
c, Å	17.183 (6)	25.299 (8)
β, deg	105.35 (4)	90
d_{obsd},[a] g cm⁻³	1.43	1.27
d_{calcd}, g cm⁻³	1.432	1.269
V, Å³	4437.3	9796.9
Z	4	4
space group	$P2_1/n$	$Pccn$
λ, Å	0.7093	0.7093
abs coeff (Mo Kα), cm⁻¹	6.73	5.50
monochromator	flat graphite crystal	flat graphite crystal
takeoff angle, deg	3.0	3.0
method	ω–2θ	ω–2θ
scan speed, deg s⁻¹	0.05 (for ω)	0.06 (for ω)
scan range, deg	0.64 + 0.69 tan ω	0.64 + 0.69 tan ω
bkgd time	half of the peak time	half of the peak time
stds	3 every 120 min	3 every 120 min
2θ limit	$5 \leq 2\theta \leq 40°$	$5 \leq 2\theta \leq 40°$
no. of data	2479	2563
no. of obsd data	1876	1872

[a] Determined by flotation.

Results and Discussion

The compound $[(np_3)Pd(\eta-P_4)]$, obtained by reaction of white phosphorus with the complex $[Pd(np_3)]$, is quite air stable and fully insoluble in common organic solvents. The X-ray powder diagram clearly showed that this complex and the analogous nickel complex are isomorphous to each other;[12]

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Table IV. Positional Parameters ($\times 10^4$) and Anisotropic Temperature Factors[a] ($\times 10^3$) for Compound I

atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd	−1943 (2)	5450 (1)	1303 (1)	26 (1)	41 (1)	34 (1)	0 (2)	7 (1)	−2 (2)
P(1)	−2785 (5)	4531 (4)	1683 (4)	34 (5)	34 (5)	39 (5)	1 (5)	5 (4)	7 (5)
P(2)	−2013 (6)	6038 (4)	2471 (5)	30 (5)	44 (6)	43 (6)	−2 (5)	12 (5)	−7 (5)
P(3)	−227 (6)	5084 (4)	2033 (5)	25 (5)	41 (6)	45 (6)	−4 (4)	8 (5)	−4 (5)
P(4)	−1798 (7)	6270 (4)	328 (5)	65 (7)	62 (7)	53 (7)	−5 (6)	19 (6)	14 (6)
P(5)	−2038 (7)	5302 (5)	−102 (5)	67 (7)	65 (8)	45 (6)	5 (6)	19 (5)	−6 (6)
P(6)	−3308 (7)	5827 (4)	147 (5)	48 (6)	69 (7)	46 (6)	2 (5)	6 (5)	15 (6)
F(1)	2182 (22)	4561 (16)	4222 (17)	104 (23)	62 (24)	85 (23)	−63 (23)	−76 (19)	54 (23)
F(2)	2723 (23)	3835 (14)	5159 (19)	137 (25)	64 (24)	47 (26)	7 (20)	−17 (22)	24 (21)
F(3)	1285 (28)	3725 (17)	4256 (20)	87 (32)	20 (31)	234 (32)	12 (26)	12 (28)	133 (25)
F(4)	2710 (28)	3650 (18)	4048 (23)	136 (34)	231 (33)	51 (37)	38 (28)	21 (29)	−43 (29)

[a] The temperature factor is defined as $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + \ldots)]$.

Table V. Positional Parameters ($\times 10^4$) and Isotropic Temperature Factors ($\times 10^3$) for "Nongroup" and "Group" Atoms of Compound I

atom	x/a	y/b	z/c	U, Å^2
C(1)	−1099 (20)	4527 (15)	4115 (16)	55 (9)
C(2)	−1351 (20)	4801 (12)	3242 (16)	34 (8)
C(3)	−1933 (20)	4244 (12)	2671 (15)	34 (8)
C(4)	−2009 (20)	5426 (15)	3250 (16)	49 (8)
C(5)	−256 (20)	4972 (12)	3091 (15)	35 (8)
C(6)	−4102 (14)	4641 (8)	1842 (10)	33 (7)
C(7)	−4657 (14)	5228 (8)	1662 (10)	49 (9)
C(8)	−5640 (14)	5300 (8)	1826 (10)	50 (9)
C(9)	−6067 (14)	4785 (8)	2169 (10)	60 (10)
C(10)	−5513 (14)	4199 (8)	2349 (10)	79 (11)
C(11)	−4530 (14)	4126 (8)	2185 (10)	50 (9)
C(12)	−2989 (13)	3845 (7)	1034 (12)	35 (8)
C(13)	−3705 (13)	3944 (7)	282 (12)	43 (9)
C(14)	−3900 (13)	3445 (7)	−291 (12)	53 (9)
C(15)	−3378 (13)	2847 (7)	−113 (12)	49 (10)
C(16)	−2662 (13)	2749 (7)	639 (12)	59 (10)
C(17)	−2467 (13)	3248 (7)	1212 (12)	40 (9)
C(18)	−3122 (13)	6573 (9)	2401 (10)	30 (8)
C(19)	−3291 (13)	7056 (9)	1808 (10)	44 (9)
C(20)	−4114 (13)	7505 (9)	1737 (10)	47 (9)
C(21)	−4768 (13)	7470 (9)	2258 (10)	41 (8)
C(22)	−4599 (13)	6987 (9)	2851 (10)	53 (10)
C(23)	−3776 (13)	6538 (9)	2923 (10)	51 (9)
C(24)	−939 (15)	6579 (9)	2887 (9)	37 (8)
C(25)	−463 (15)	6928 (9)	2380 (9)	52 (9)
C(26)	337 (15)	7378 (9)	2705 (9)	58 (10)
C(27)	661 (15)	7479 (9)	3537 (9)	83 (11)
C(28)	184 (15)	7130 (9)	4044 (9)	71 (11)
C(29)	−616 (15)	6680 (9)	3719 (9)	69 (11)
C(30)	879 (13)	5628 (9)	2084 (10)	41 (9)
C(31)	932 (13)	5909 (9)	1356 (10)	53 (9)
C(32)	1736 (13)	6354 (9)	1344 (10)	63 (10)
C(33)	2486 (13)	6517 (9)	2059 (10)	58 (10)
C(34)	2432 (13)	6235 (9)	2787 (10)	57 (10)
C(35)	1629 (13)	5790 (9)	2799 (10)	52 (9)
C(36)	272 (14)	4324 (9)	1738 (9)	36 (8)
C(37)	1241 (14)	4094 (9)	2212 (9)	50 (9)
C(38)	1653 (14)	3506 (9)	2017 (9)	45 (9)
C(39)	1095 (14)	3147 (9)	1349 (9)	49 (9)
C(40)	125 (14)	3377 (9)	875 (9)	48 (9)
C(41)	−286 (14)	3965 (9)	1069 (9)	43 (9)
B	2136 (67)	4026 (40)	4478 (54)	113 (28)
O	366 (41)	1772 (26)	161 (37)	220 (22)
C(42)	365 (41)	1931 (26)	−636 (34)	199 (22)
C(43)	1691 (41)	1763 (24)	−446 (31)	170 (21)

thus the coordination polyhedron can be described as a distorted tetrahedron with the palladium atom bound to the three phosphorus atoms of the ligand np$_3$ and to one atom of the intact P$_4$ molecule, the nitrogen of the tripod ligand not being coordinated to the metal. Also in this case the metal atom reaches the closed shell configuration.

The mononuclear [(triphos)M(η^3-P$_3$)]BF$_4$ (M = Pd, Pt) and the triple-decker [LPd(μ-(η^3-P$_3$))PdL]Y (L = np$_3$, Y = BF$_4$; L = triphos, Y = BPh$_4$) complexes are diamagnetic and air stable both in the solid state and in solution; they are soluble in methylene chloride, acetone, and nitroethane. In this latter solvent, the compounds behave as 1:1 electrolytes (Table I).

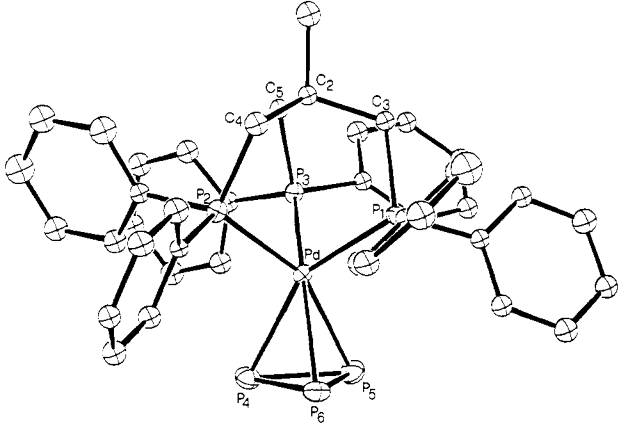

Figure 1. Perspective view of the [(triphos)Pd(η^3-P$_3$)]$^+$ cation.

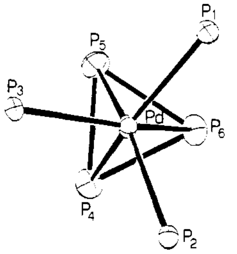

Figure 2. View of the coordination polyhedron of [(triphos)Pd(η^3-P$_3$)]$^+$ along the pseudoternary axis.

The structure of the compound [(triphos)Pd(η^3-P$_3$)]BF$_4$·C$_2$H$_5$OH consists of [(triphos)Pd(η^3-P$_3$)]$^+$ cations, tetrafluoborate anions, and interposed ethanol molecules. This is the first cationic sandwich complex of *cyclo*-triphosphorus. A perspective view of the cation is shown in Figure 1. The palladium atom is coordinated by the three phosphorus atoms of the triphos ligand and by the three phosphorus atoms of the *c*-P$_3$ unit. As in the previously described sandwich complexes,[13-15] the geometry around the metal atom can be described as distorted octahedral (Figure 2). Selected distances and angles are reported in Table VIII. The Pd–P(triphos) distances (average 2.368 Å) are significantly longer than the previously reported M–P distances of 2.186, 2.294, and 2.227 Å for the cobalt, rhodium, and iridium derivatives, respectively. The Pd–P(*cyclo*-triphosphorus) distances (average 2.412 Å), on the contrary, are comparable to those found for the rhodium

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Table VI. Positional Parameters ($\times 10^4$) and Anisotropic Temperature Factors ($\times 10^3$) for Compound II

atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd	1485 (1)	7715 (1)	739 (1)	46 (1)	40 (1)	25 (1)	2 (1)	1 (1)	5 (1)
P(1)	2500	7500	249 (3)	42 (7)	60 (8)	31 (5)	7 (6)	0	0
P(2)	2413 (4)	6934 (4)	985 (2)	54 (5)	43 (5)	38 (4)	5 (4)	−5 (4)	−3 (4)
P(3)	1031 (3)	8770 (4)	350 (3)	66 (5)	37 (4)	34 (4)	6 (4)	1 (4)	12 (4)
P(4)	740 (3)	6909 (4)	347 (3)	57 (5)	50 (5)	37 (5)	0 (4)	−5 (4)	6 (4)
P(5)	828 (3)	7895 (3)	1494 (2)	57 (5)	51 (5)	29 (4)	12 (4)	7 (4)	6 (4)

Table VII. Positional Parameters ($\times 10^4$) and Isotropic Temperature Factors ($\times 10^3$) for "Nongroup" and "Group" Atoms of Compound II

atom	x/a	y/b	z/c	U, Å^2
C(1)	−871 (12)	8166 (13)	627 (10)	64 (8)
C(2)	−142 (10)	8028 (12)	665 (9)	39 (7)
C(3)	174 (10)	8572 (11)	275 (8)	33 (6)
C(4)	−48 (10)	7210 (13)	557 (8)	49 (7)
C(5)	37 (12)	8226 (12)	1266 (9)	53 (8)
C(6)	1050 (6)	9618 (9)	734 (6)	50 (7)
C(7)	535 (6)	10094 (9)	775 (6)	57 (7)
C(8)	600 (6)	10736 (9)	1060 (6)	72 (9)
C(9)	1178 (6)	10904 (9)	1303 (6)	85 (10)
C(10)	1693 (6)	10428 (9)	1262 (6)	113 (12)
C(11)	1629 (6)	9785 (9)	977 (6)	68 (9)
C(12)	1299 (9)	9075 (10)	−312 (7)	49 (7)
C(13)	1432 (9)	9796 (10)	−432 (7)	125 (13)
C(14)	1626 (9)	9987 (10)	−941 (7)	160 (16)
C(15)	1688 (9)	9455 (10)	−1329 (7)	99 (12)
C(16)	1555 (9)	8733 (10)	−1209 (7)	138 (14)
C(17)	1360 (9)	8543 (10)	−700 (7)	122 (11)
C(18)	715 (7)	6845 (7)	−391 (7)	60 (8)
C(19)	207 (7)	7097 (7)	−695 (7)	68 (8)
C(20)	252 (7)	7100 (7)	−1245 (7)	70 (9)
C(21)	805 (7)	6850 (7)	−1491 (7)	98 (11)
C(22)	1313 (7)	6597 (7)	−1187 (7)	98 (11)
C(23)	1268 (7)	6594 (7)	−637 (7)	93 (11)
C(24)	781 (7)	5948 (9)	498 (6)	53 (8)
C(25)	1378 (7)	5616 (9)	520 (6)	78 (9)
C(26)	1427 (7)	4888 (9)	663 (6)	99 (10)
C(27)	879 (7)	4493 (9)	785 (6)	83 (9)
C(28)	283 (7)	4826 (9)	764 (6)	85 (9)
C(29)	233 (7)	5553 (9)	621 (6)	67 (8)
C(30)	622 (8)	7098 (8)	1889 (7)	54 (8)
C(31)	125 (8)	7130 (8)	2256 (7)	70 (9)
C(32)	6 (8)	6542 (8)	2587 (7)	75 (9)
C(33)	383 (8)	5921 (8)	2552 (7)	89 (11)
C(34)	879 (8)	5889 (8)	2186 (7)	106 (12)
C(35)	998 (8)	6477 (8)	1854 (7)	67 (9)
C(36)	1092 (7)	8551 (11)	1992 (7)	62 (8)
C(37)	741 (7)	9143 (11)	2172 (7)	92 (11)
C(38)	1019 (7)	9642 (11)	2516 (7)	101 (11)
C(39)	1649 (7)	9550 (11)	2680 (7)	90 (10)
C(40)	2000 (7)	8958 (11)	2500 (7)	84 (10)
C(41)	1722 (7)	8458 (11)	2156 (7)	72 (9)
C(42)	8031 (8)	7060 (7)	−2793 (7)	58 (8)
C(43)	8234 (8)	7352 (7)	−2313 (7)	94 (10)
C(44)	8700 (8)	6998 (7)	−2017 (7)	98 (11)
C(45)	8963 (8)	6351 (7)	−2201 (7)	80 (10)
C(46)	8760 (8)	6059 (7)	−2681 (7)	86 (10)
C(47)	8294 (8)	6413 (7)	−2977 (7)	84 (10)
C(48)	7912 (8)	8095 (10)	−3533 (8)	63 (8)
C(49)	7656 (8)	8340 (10)	−4010 (8)	128 (13)
C(50)	7963 (8)	8888 (10)	−4292 (8)	150 (14)
C(51)	8525 (8)	9192 (10)	−4097 (8)	111 (11)
C(52)	8780 (8)	8948 (10)	−3621 (8)	89 (10)
C(53)	8474 (8)	8399 (10)	−3338 (8)	71 (8)
B	7500	7500	−3183 (16)	56 (12)

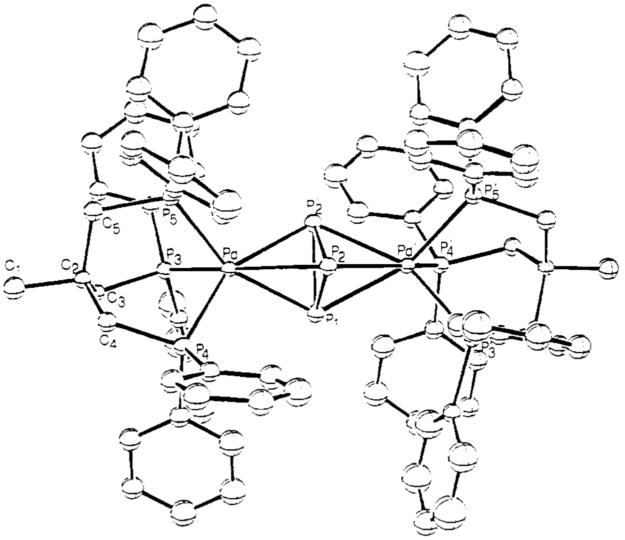

Figure 3. Perspective view of the [(triphos)Pd(μ-(η^3-P_3))Pd(triphos)]$^+$ cation.

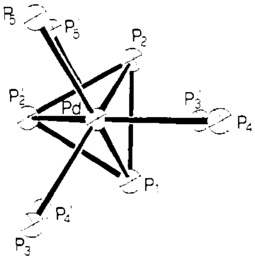

Figure 4. View of the coordination polyhedron of [(triphos)Pd(μ-(η^3-P_3))Pd(triphos)]$^+$ along the pseudoternary axis.

and iridium complexes (2.418 and 2.436 Å), but they are longer than the analogous Co–P distances (2.301 Å). On the other hand, the P–P(*cyclo*-triphosphorus) distances (average 2.115 Å) are shorter than those found in the previously reported complexes (2.141, 2.152, and 2.159 Å) in the cobalt, rhodium, and iridium derivatives, respectively. The shortening of the P–P distances in the cationic complex with respect to the neutral ones may be ascribed to a larger delocalization of electron density in the former compound, from the *cyclo*-triphosphorus group to the metal atom, with a consequent decrease in the Coulumbic-pair repulsions between phosphorus atoms of the c-P_3 group.[16] Such larger delocalization in the cationic complex should be caused in turn by the greater fractional charge on its metal atom, which has the effect of stabilizing the metal d orbitals, thus favoring their interaction with the ligand orbitals. The lengthening of the Pd–P(triphos) bonds is rationalized by the same considerations. In fact, according to a simple MO model for the bonding in these complexes,[17] the highest occupied molecular orbitals, which should gain metal d character with increasing cationic charge as expressed above, are essentially antibonding with respect to the Pd–P(triphos) interactions.

The structure of the [(triphos)Pd(μ-(η^3-P_3))Pd(triphos)]-BPh_4 complex consists of [(triphos)Pd(μ-(η^3-P_3))Pd(triphos)]$^+$ cations and tetraphenylborate anions. A perspecive view of the cation is shown in Figure 3. Each palladium atom is coordinated by the three phosphorus atoms of the triphos ligand and by the three phosphorus atoms of the cyclic P_3 unit

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Table VIII. Selected Bond Distances (Å) and Angles (Deg) with Their Estimated Standard Deviations for Compound I

Bond Distances

Pd-P(1)	2.357 (7)	P(2)-C(18)	1.80 (2)
Pd-P(2)	2.363 (7)	P(2)-C(24)	1.78 (2)
Pd-P(3)	2.384 (7)	P(3)-C(5)	1.84 (2)
Pd-P(4)	2.414 (8)	P(3)-C(30)	1.81 (2)
Pd-P(5)	2.403 (8)	P(3)-C(36)	1.81 (2)
Pd-P(6)	2.419 (8)	C(1)-C(2)	1.55 (3)
P(4)-P(5)	2.108 (11)	C(2)-C(3)	1.56 (3)
P(4)-P(6)	2.121 (11)	C(2)-C(4)	1.54 (3)
P(5)-P(6)	2.116 (10)	C(2)-C(5)	1.56 (3)
P(1)-C(3)	1.86 (2)	B-F(1)	1.19 (7)
P(1)-C(6)	1.83 (2)	B-F(2)	1.28 (7)
P(1)-C(12)	1.77 (2)	B-F(3)	1.24 (7)
P(2)-C(4)	1.83 (3)	B-F(4)	1.41 (6)

Bond Angles

P(1)-Pd-P(2)	92.6 (2)	P(4)-P(5)-P(6)	60.3 (4)
P(1)-Pd-P(3)	92.7 (2)	Pd-P(6)-P(4)	63.8 (3)
P(1)-Pd-P(4)	151.1 (3)	Pd-P(6)-P(5)	63.6 (3)
P(1)-Pd-P(5)	105.9 (3)	P(4)-P(6)-P(5)	59.7 (4)
P(1)-Pd-P(6)	100.6 (2)	Pd-P(1)-C(3)	107.1 (7)
P(2)-Pd-P(3)	87.5 (2)	Pd-P(1)-C(6)	118.1 (5)
P(2)-Pd-P(4)	105.3 (3)	Pd-P(1)-C(12)	117.5 (5)
P(2)-Pd-P(5)	156.1 (3)	Pd-P(2)-C(4)	106.2 (8)
P(2)-Pd-P(6)	110.4 (3)	Pd-P(2)-C(18)	117.8 (6)
P(3)-Pd-P(4)	110.3 (3)	Pd-P(2)-C(24)	117.0 (6)
P(3)-Pd-P(5)	106.3 (3)	Pd-P(3)-C(5)	107.2 (8)
P(3)-Pd-P(6)	156.9 (2)	Pd-P(3)-C(30)	117.5 (6)
P(4)-Pd-P(5)	51.9 (3)	Pd-P(3)-C(36)	118.8 (6)
P(4)-Pd-P(6)	52.1 (3)	F(1)-B-F(2)	122.9 (68)
P(5)-Pd-P(6)	52.0 (3)	F(1)-B-F(3)	118.2 (66)
Pd-P(4)-P(5)	63.8 (3)	F(1)-B-F(4)	102.9 (60)
Pd-P(4)-P(6)	64.1 (3)	F(2)-B-F(3)	113.7 (63)
P(5)-P(4)-P(6)	60.1 (4)	F(2)-B-F(4)	92.3 (52)
Pd-P(5)-P(4)	64.3 (3)	F(3)-B-F(4)	97.3 (54)
Pd-P(5)-P(6)	64.4 (3)		

that bridges the two parts of the dinuclear cation. The geometry of the whole coordination polyhedron, which possesses an approximate C_{3v} symmetry, is confacial bioctahedral (Figure 4). A binary axis passes through a phosphorus atom of the *c*-P_3 group so that only half of the cation is symmetry independent. Selected distances and angles are reported in Table IX. If the geometry of this complex is compared with that found for the analogous nickel, cobalt,[2] and rhodium[3] triple-decker derivatives which have an intermediate geometry between the octahedral and the trigonal prismatic, we observe that the palladium derivative attains a more regular geometry. The palladium complex may be assigned 34 valence electrons, and according to the MO diagram proposed for this kind of complexes,[2] the 6e orbitals are completely filled.

The Pd-P(triphos) distances are close to those found in the monomeric cation previously reported; the Pd-P(*cyclo*-triphosphorus) distances, on the contrary, are significantly longer (2.498 Å (average) vs. 2.412 Å (average)). These distances are also longer than in the analogous cobalt[2] and rhodium[3] complexes (by about 0.15 Å). As a consequence, the Pd···Pd′ distance (4.33 Å) is remarkably longer than the M···M′ distances (all below 4 Å) previously found for the analogous dinuclear triple-decker complexes. This lengthening is too large to be ascribed only to the presence of two 4d metals in the palladium derivative. In fact the M···M′ distances are practically unchanged on going from metal complexes having two 3d metals to derivatives having one 3d and one 4d metal (3.99 Å in the Ni···Ni and 3.93 Å in the Co···Ni derivative vs. 4.04 and 3.87 Å found in the two 3d–4d metal complexes whose structures have been determined).[2,3] The larger metal···metal separation in the palladium derivative should be ascribed (a) to the larger number of valence electrons (34) in this compound and (b) to the lower cationic charge (+1 vs. +2) which determines an increase in the size of the metal d orbitals.

Table IX. Selected Bond Distances (Å) and Angles (Deg) with Their Estimated Standard Deviations for Compound II

Bond Distances

Pd-P(1)	2.495 (4)	P(4)-C(4)	1.82 (2)
Pd-P(2)	2.500 (7)	P(4)-C(18)	1.87 (2)
Pd-P(3)	2.381 (7)	P(4)-C(24)	1.82 (2)
Pd-P(4)	2.374 (7)	P(5)-C(5)	1.86 (2)
Pd-P(5)	2.379 (6)	P(5)-C(30)	1.83 (2)
P(1)-P(2)	2.143 (9)	P(5)-C(36)	1.83 (2)
P(2)-P(2′)	2.120 (13)	C(1)-C(2)	1.55 (3)
P(3)-C(3)	1.84 (2)	C(2)-C(3)	1.56 (3)
P(3)-C(6)	1.84 (2)	C(2)-C(4)	1.55 (3)
P(3)-C(12)	1.85 (2)	C(2)-C(5)	1.61 (3)

Bond Angles

P(1)-Pd-P(2)	50.8 (2)	P(2)-P(1)-P(2′)	59.3 (4)
P(1)-Pd-P(2′)	51.0 (2)	P(1)-P(2)-P(2′)	60.3 (4)
P(1)-Pd-P(3)	105.4 (2)	Pd-P(1)-P(2)	64.7 (3)
P(1)-Pd-P(4)	104.8 (2)	Pd-P(1)-P(2′)	64.1 (3)
P(1)-Pd-P(5)	156.2 (2)	Pd-P(2)-P(1)	64.5 (2)
P(2)-Pd-P(2′)	50.4 (2)	Pd-P(2)-P(2′)	64.3 (2)
P(2)-Pd-P(3)	152.3 (2)	Pd-P(2′)-P(1)	64.9 (2)
P(2)-Pd-P(4)	104.8 (2)	Pd-P(2′)-P(2)	65.3 (2)
P(2)-Pd-P(5)	109.3 (2)	Pd-P(3)-C(3)	105.7 (7)
P(3)-Pd-P(2′)	105.2 (2)	Pd-P(3)-C(6)	118.0 (5)
P(3)-Pd-P(4)	94.4 (2)	Pd-P(3)-C(12)	120.0 (6)
P(3)-Pd-P(5)	89.2 (2)	Pd-P(4)-C(4)	106.5 (8)
P(4)-Pd-P(2′)	151.9 (2)	Pd-P(4)-C(18)	118.3 (5)
P(4)-Pd-P(5)	92.4 (2)	Pd-P(4)-C(24)	119.5 (6)
P(5)-Pd-P(2′)	107.5 (2)	Pd-P(5)-C(5)	108.2 (8)
Pd-P(1)-Pd′	120.4 (2)	Pd-P(5)-C(30)	117.6 (5)
Pd-P(2)-Pd′	120.8 (2)	Pd-P(5)-C(36)	118.0 (6)

Preliminary results of an X-ray diffraction analysis carried out on the $[(np_3)Pd(\mu\text{-}(\eta^3\text{-}P_3))Pd(np_3)]BF_4$ complex show that the compound has a triple-decker stereochemistry and the same inner coordination as the triphos derivative, the nitrogen atom of the ligand not being coordinated to the metal. $^{31}P\{^1H\}$ NMR spectra of the complexes are reported in Table II. The compounds $[(triphos)M(\eta^3\text{-}P_3)]BF_4$ (M = Pd, Pt) exhibit two distinct quartets of 1:1 intensity typical of an A_3X_3 pattern; these signals are accompanied for the platinum derivative by satellites due to coupling to ^{195}Pt (33.7% natural abundance). The lower field quartet is assigned to the three phosphorus atoms of the triphos ligand, and the quartet at higher field is assigned to the η^3-P_3 phosphorus atoms. The coordination chemical shift of the triphos ligand is higher for the palladium derivative; the η^3-P_3 signal has an increase in shielding in the palladium derivative with respect to the platinum complex. The coupling constants of the two sets of phosphorus donor atoms are $^1J(\text{Pt–P}_{\text{triphos}})$ = 2476 Hz (this is in the range of the observed platinum–phosphine coupling constants[18]) and $^1J(\text{Pt–P}_{c\text{-}P_3})$ = 171 Hz; the latter coupling constant is more than 1 order of magnitude smaller than the coupling constants found in phosphine complexes of platinum. A comparable reduction in the coupling constant has been found for ^1J(Pt–^{13}C) on going from complexes containing σ Pt–C bonds to those containing olefin π Pt–C bonds.[19] The triple-decker compounds exhibit a typical A_3X_6 pattern. The coordination chemical shifts of the triphos and np_3 ligand are comparable. An interesting feature of these compounds is the variability of the phosphorus$_L$–phosphorus$_{c\text{-}P_3}$ coupling constants which change with the chelate chain length. The coupling constant is lower than the ligand forms with the metal six-member chelate ring (triphos) than when the ring contains more than six members (np_3). Both phosphorus signals (that of triphos and that of the η^3-P_3 system) increase in shielding in the triple-decker complexes with respect to the mononuclear derivatives.

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Registry No. I, 78355-34-7; II, 78355-36-9; [$(np_3)Pd(P_4)$], 78355-37-0; [$Pt(P_3)$(triphos)]BF_4, 78355-39-2; [$Pd_2(P_3)(np_3)_2$]BF_4, 78355-41-6.

Supplementary Material Available: Listings of structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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Preparations and X-ray Crystal Structures of Iodo-*cyclo*-heptasulfur Hexafluoroantimonate(V) and Hexafluoroarsenate(V), S_7ISbF_6 and S_7IAsF_6

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S_7IAsF_6 and S_7ISbF_6 were prepared essentially quantitatively by a variety of routes. Attempts to prepare S_8I^+ salts were unsuccessful. S_7ISbF_6 crystallizes in the orthorhombic space group $P2_12_12_1$ with $a = 11.786$ (2) Å, $b = 9.187$ (1) Å, $c = 12.400$ (3) Å, and $d_{calcd} = 2.90$ Mg m^{-3} for $Z = 4$. The structure has been determined by multiple-solution direct methods and refined by least squares to final agreement indices $R_1 = 0.046$ and $R_2 = 0.061$ for 1628 independent reflections with $I \geq 2\sigma(I)$. S_7IAsF_6 crystallizes in the triclinic space group $P\bar{1}$ with $a = 15.516$ (11) Å, $b = 11.813$ (8) Å, $c = 11.650$ (8) Å, $\alpha = 107.30$ (4)°, $\beta = 74.71$ (5)°, $\gamma = 104.62$ (5)°, and $d_{calcd} = 2.78$ Mg m^{-3} for $Z = 6$. The structure was refined to a final agreement index $R = 0.14$. The S_7I^+ cations in both salts and in $(S_7I)_4S_4(AsF_6)_6$ are essentially identical. S_7I^+ contains a seven-membered sulfur ring with a slightly twisted chair conformation, similar to that of S_7, with an exocyclic iodine, and has a geometry similar to that of S_7O. The sulfur–iodine bond length is 2.342 (3) Å and corresponds to a bond order of 1. The sulfur–sulfur distances within the ring vary from 1.906 (5) to 2.389 (4) Å. There is one short intracationic iodine–sulfur contact of 3.394 (3) Å. The geometry and bond length variations in S_7I^+ are discussed and compared with those of related systems. Some experimental observations on $S_x(AsF_6)_2$, $19 \geq x \geq 16$, are presented and the nature of these species is discussed.

Introduction

Generally any pair of main-group elements, excepting those of group 8A, form binary compounds or alloys. At one time sulfur and iodine were thought[1] to be one of the pairs of elements that were an exception to this generalization. Since then, evidence has been presented for sulfur iodides prepared at low temperatures, although they are unstable under ambient conditions. Solid S_2I_2 has been characterized at −90 °C by its infrared and electronic spectra,[2,3] and infrared evidence has been presented[4] for SI_2 isolated in an argon matrix at 9 K. An attempted preparation of SI_3^+ (cf. SeI_3^+) led instead[5] to the relatively stable S_7IMF_6 (M = As and Sb) salts, containing a binary sulfur–iodine cation, and a full account of this work is reported below. Subsequently, $[(S_7I)_2I](SbF_6)_3{\cdot}2AsF_3$[6] and $S_2I_4(AsF_6)_2$,[7] which also contain stable sulfur–iodine cations, were prepared and characterized.

The ability of sulfur to catenate is well established; however, for many years the only known sulfur rings were S_8 and S_6.[8] More recently other allotropes have been prepared,[8] and the X-ray crystal structures of S_n (n = 7,[9] 10,[10] 12,[11] 18,[8] and 20[8]) and the derivatives S_nO (n = 7,[12] 8[13]), $S_{12}O_2{\cdot}2SbCl_5{\cdot}3CS_2$,[14] and $S_8O{\cdot}SbCl_5$[15] have been determined. The sulfur homopolyatomic cations S_4^{2+},[16] S_8^{2+},[17] and S_{19}^{2+}[18] contain 4, 8, or two S_7 membered rings joined by S_5 chain, respectively. The radical cation S_5^+ has also been characterized by ESR spectroscopy.[19] Clearly, there is emerging a rich chemistry of sulfur rings, and S_7IMF_6, containing an S_7^+ ring, is of interest in this context. A preliminary account of this work has been reported.[5]

Experimental Section

Techniques and reagents, except those listed below, have been described in ref 20. S_8 (McArthur, precipitated), KI (Anachemia), and CaH_2 (Alfa-Ventron) were used without further purification. SO_2 (Matheson, anhydrous) was vacuum distilled onto and stored over CaH_2. SO_2ClF (Aldrich, spectrograde) was vacuum distilled onto and stored over NaF. $I_2Sb_2F_{11}$ and I_3AsF_6 were prepared according

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