

STRUCTURAL CORRELATIONS AND NMR PROPERTIES OF MONONUCLEAR CYCLIC TRIPHOSPHORUS COMPLEXES

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Summary

The $[(\text{triphos})\text{Ni}(\eta^3\text{-P}_3)]\text{BF}_4 \cdot \text{C}_2\text{H}_5\text{OH}$ compound has been synthesized by treating $\text{Ni}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ with P_4S_3 , in the presence of the triphos ligand (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane). The crystal structure of the complex and that of the previously obtained platinum isomorph have been investigated by X-ray diffraction.

Correlations are drawn within the series of the monocationic $[(\text{triphos})\text{M}(\eta^3\text{-P}_3)]^+$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$) complexes and that of the neutral $[(\text{triphos})\text{M}(\eta^3\text{-P}_3)]$ ($\text{M} = \text{Co}, \text{Rh}, \text{Ir}$) compounds, as well as between the two series. Phosphorus NMR data are reported for the compounds of the two sets and trends are analyzed in terms of simple models of the bonding.

Introduction

In previous work it was shown the reaction of white phosphorus with the tritertiary phosphine 1,1,1-tris(diphenylphosphinomethyl)ethane ($\text{CH}_3\text{C}(\text{CH}_2\text{-PPh}_2)_3$, triphos) and compounds of the cobalt group give the uncharged complexes with formula $[(\text{triphos})\text{M}(\eta^3\text{-P}_3)]$ ($\text{M} = \text{Co}, \text{Rh}, \text{Ir}$) [1,2]. Such diamagnetic compounds, containing the cyclotriphosphorus unit as a ligand, are assigned the 18-electron configuration. The same stable configuration is attained in the $[(\text{triphos})\text{M}(\eta^3\text{-P}_3)]^+$ monocations of palladium and platinum [3]. The corresponding nickel compound, which was required in order to complete the above series of isoelectronic complexes has now been obtained by reaction of $\text{Ni}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ with tetraphosphorus trisulphide, P_4S_3 , in presence of the ligand triphos.

The structure of this nickel compound, $[(\text{triphos})\text{Ni}(\eta^3\text{-P}_3)]\text{BF}_4 \cdot \text{C}_2\text{H}_5\text{OH}$ and that of the isomorphous platinum derivative, $[(\text{triphos})\text{Pt}(\eta^3\text{-P}_3)]\text{BF}_4 \cdot \text{C}_2\text{H}_5\text{OH}$, have been investigated by X-ray diffraction methods in order to improve the correlations [4] within and between the two sets: that of the uncharged (cobalt group) and that of the monocationic (nickel group) isoelectronic complexes. ^{31}P NMR data are reported for the Co, Rh, Ir, and Ni complexes and trends, including

previous data for the Pd and Pt derivatives [3], are analyzed in the light of the known structures and of simple considerations on the bonding in such compounds. The first systematic account of NMR data for cyclotriphosphorus complexes is presented.

Experimental

Materials

All the solvents were reagent grade and were used without further purification. All reactions were performed under dry nitrogen. The triphos ligand was prepared by the literature method [5]. Tetrachlorophosphorus trisulphide was purchased from Fluka AG and used after recrystallization from benzene.

Physical measurements

Visible spectra and conductivities were obtained as previously described [6]. ^{31}P NMR spectra were measured on a Varian CFT20 spectrometer equipped with a ^{31}P probe (at 32.19 MHz) locally modified for investigation of the high field region. Positive chemical shifts are downfield relative to H_3PO_4 at 0.0 ppm.

Synthesis of $[(\text{triphos})\text{Ni}(\eta^3\text{-P}_3)]\text{BF}_4 \cdot \text{C}_2\text{H}_5\text{OH}$

A solution of tetrachlorophosphorus trisulphide (1 mmol) in benzene (20 ml) was added to a solution obtained by mixing $\text{Ni}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ (1 mmol) in ethanol (15 ml) and triphos (1 mmol) in tetrahydrofuran (20 ml). The resulting mixture was refluxed for 2 h. Yellow crystals of the complex were obtained by concentrating the solution under nitrogen, and were filtered off, dried in vacuo and recrystallized from acetone and ethanol. Yield 45%. Found: C, 56.9; H, 5.2; Ni, 6.3; P, 20.2. $\text{C}_{43}\text{H}_{45}\text{BF}_4\text{NiOP}_6$ calcd.: C, 56.8; H, 5.0; Ni, 6.5; P, 20.4%. The molar conductance of the compound in ca. 10^{-3} nitroethane molar solution at 20°C ($\Lambda_{\text{M}} = 87$) is typical of a 1/1 electrolyte [7].

The complexes $[(\text{triphos})\text{M}(\eta^3\text{-P}_3)]$ (M = Co [1], Rh or Ir [2]) and $[(\text{triphos})\text{M}(\eta^3\text{-P}_3)]\text{BF}_4 \cdot \text{C}_2\text{H}_5\text{OH}$ (M = Pd, Pt [3]) were prepared as previously described.

Collection and reduction of X-ray data

Crystals of $[(\text{triphos})\text{Ni}(\eta^3\text{-P}_3)]\text{BF}_4 \cdot \text{C}_2\text{H}_5\text{OH}$ (I) were in form of yellow parallelepipeds and those of $[(\text{triphos})\text{Pt}(\eta^3\text{-P}_3)]\text{BF}_4 \cdot \text{C}_2\text{H}_5\text{OH}$ (II) were obtained as pale-yellow prisms by the procedures described above. The crystals used for lattice constant determinations and for intensity data collections had approximate dimensions $0.30 \times 0.25 \times 0.15$ mm (I) and $0.25 \times 0.20 \times 0.50$ mm (II). A four-circle Philips PW 1100 automated diffractometer and graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71069$ Å) were used for all operations. Cell parameters were determined at room temperature (23°C) for both compounds from the setting angles of 24 reflections with $13 < \theta < 18^\circ$. The two compounds are isomorphous to each other as well as to the previously investigated Pd analog, $[(\text{triphos})\text{Pd}(\eta^3\text{-P}_3)]\text{BF}_4 \cdot \text{C}_2\text{H}_5\text{OH}$ [3]. Details of crystal data and data collection are given in Tables 1 and 2, respectively. The intensities of 3 standard reflections monitored every 120 min during both data collections showed no systematic trends, deviations from the average values being $< 2\%$. Values of the "ignorance" factor p of 0.05 (I) and 0.04 (II) were used in the reduction of data [8]. The observed intensities were corrected

TABLE 1

CRYSTAL DATA FOR [(triphos)Ni(η^3 -P₃)]BF₄·C₂H₅OH (I) AND [(triphos)Pt(η^3 -P₃)]BF₄·C₂H₅OH (II)

	I	II
Space group	$P2_1/n$	$P2_1/n$
a (Å)	13.124(7)	13.094(5)
b (Å)	20.369(9)	20.537(9)
c (Å)	17.188(8)	17.299(7)
β (°)	104.42(6)	105.27(6)
V (Å ³)	4450.0	4487.7
Formula wt	909.20	1045.57
Z	4	4
ρ_{calcd} (g cm ⁻³)	1.357	1.547
ρ_{obsd} (g cm ⁻³)	1.38	1.56

for Lorentz and polarization effects as well as for absorption by a numerical procedure. All calculations were performed on a SEL 32/70 computer with the programs described in ref. [9]. The scattering factors for the neutral atoms were taken from ref. [10], those of the metal atoms being corrected for anomalous dispersion effects [11].

Solution and refinement of the structures

The initial positions for the nonhydrogen atoms in the cation and the anion of both compounds were obtained from the structure of the Pd isomorph [3]. In the full-matrix least-squares refinements the function $\sum w(|F_o| - |F_c|)^2$ was minimized with weights $w = 1/\sigma^2(F_o)$. The metal, phosphorus, and fluorine atoms were assigned anisotropic temperature factors whereas the lighter atoms were refined isotropically. The hydrogen atoms of the ligand molecule were introduced in calculated positions (C-H = 1.00 Å), each one being assigned a temperature factor ca. 20% higher than that of the relevant carbon atom. A ΔF Fourier map calculated at $R = 0.075$ for compound I showed a group of peaks with heights ca. $1 \text{ e } \text{Å}^{-3}$

TABLE 2

DETAILS OF DATA COLLECTION FOR [(triphos)Ni(η^3 -P₃)]BF₄·C₂H₅OH (I) AND [(triphos)Pt(η^3 -P₃)]BF₄·C₂H₅OH (II)

	I	II
Scan type	θ - 2θ	θ - 2θ
Scan width (°)	$1.10 + 0.30 \tan \theta$	$1.00 + 0.30 \tan \theta$
Scan speed (° min ⁻¹)	5	3
2θ limits (°)	5-44	5-50
Number of data	5684	7890
$\mu(\text{Mo-K}\alpha)(\text{cm}^{-1})$	6.97	34.16
Transmission factors	0.78-0.84	0.50-0.60
Number of data with $I > 3\sigma(I)$	3677	4727

(Continued on p. 190)

TABLE 3
 ATOMIC PARAMETERS FOR [(triphos)Ni(η^3 -P₃)]BF₄·C₂H₅OH^a

Fractional coordinates and isotropic thermal parameters ^b									
Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (Å ²)	Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (Å ²)
Ni	-0.19272(6)	0.54646(4)	0.13438(6)		C(20)	-0.4153(6)	0.7570(4)	0.1621(5)	0.058(1)
P(1)	-0.2762(1)	0.4600(1)	0.1703(1)		C(21)	-0.4796(6)	0.7534(4)	0.2134(5)	0.059(1)
P(2)	-0.2031(1)	0.6089(1)	0.2395(1)		C(22)	-0.4642(6)	0.7071(4)	0.2732(5)	0.057(1)
P(3)	-0.0305(1)	0.5136(1)	0.1995(1)		C(23)	-0.3814(5)	0.6615(4)	0.2821(4)	0.049(1)
P(4)	-0.1794(1)	0.6258(1)	0.0421(1)		C(24)	-0.0941(5)	0.6657(3)	0.2824(4)	0.046(1)
P(5)	-0.1910(2)	0.5271(1)	0.0022(1)		C(25)	-0.0491(6)	0.7011(4)	0.2316(5)	0.055(1)
P(6)	-0.3250(2)	0.5751(1)	0.0238(1)		C(26)	0.0310(6)	0.7470(4)	0.2632(5)	0.068(1)
F(1)	0.2144(6)	0.4551(3)	0.4190(4)		C(27)	0.0627(6)	0.7568(4)	0.3433(5)	0.075(2)
F(2)	0.2626(6)	0.3835(3)	0.5208(4)		C(28)	0.0202(7)	0.7224(4)	0.3948(6)	0.080(2)
F(3)	0.1092(6)	0.3746(3)	0.4305(6)		C(29)	-0.0597(6)	0.6763(4)	0.3646(5)	0.063(1)
F(4)	0.2522(6)	0.3510(4)	0.3984(4)		C(30)	0.0786(5)	0.5709(3)	0.1991(4)	0.039(1)
C(1)	-0.1164(6)	0.4623(4)	0.4110(5)	0.058(1)	C(31)	0.0866(6)	0.5942(4)	0.1271(5)	0.053(1)
C(2)	-0.1387(5)	0.4882(3)	0.3245(4)	0.042(1)	C(32)	0.1664(6)	0.6391(4)	0.1222(5)	0.062(1)
C(3)	-0.1953(5)	0.4323(3)	0.2689(4)	0.047(1)	C(33)	0.2356(6)	0.6585(4)	0.1912(5)	0.062(1)
C(4)	-0.2088(5)	0.5506(3)	0.3195(4)	0.045(1)	C(34)	0.2314(6)	0.6337(4)	0.2623(5)	0.065(2)
C(5)	-0.0298(5)	0.5039(3)	0.3075(4)	0.043(1)	C(35)	0.1516(6)	0.5889(4)	0.2686(5)	0.055(1)
C(6)	-0.4079(5)	0.4713(3)	0.1883(4)	0.042(1)	C(36)	0.0244(5)	0.4358(3)	0.1738(4)	0.035(1)
C(7)	-0.4655(5)	0.5278(3)	0.1668(4)	0.048(1)	C(37)	0.1216(5)	0.4142(3)	0.2216(4)	0.046(1)
C(8)	-0.5642(6)	0.5346(4)	0.1805(5)	0.057(1)	C(38)	0.1658(6)	0.3566(4)	0.2033(5)	0.051(1)
C(9)	-0.6058(7)	0.4856(4)	0.2156(5)	0.074(2)	C(39)	0.1147(5)	0.3206(4)	0.1381(4)	0.050(1)
C(10)	-0.5496(7)	0.4283(5)	0.2391(6)	0.087(2)	C(40)	0.0213(5)	0.3402(4)	0.0915(5)	0.053(1)
C(11)	-0.4511(6)	0.4203(4)	0.2223(5)	0.068(2)	C(41)	-0.0250(5)	0.3987(3)	0.1085(4)	0.043(1)
C(12)	-0.2990(5)	0.3879(3)	0.1045(4)	0.035(1)	C(42)	0.504(1)	0.343(1)	0.492(1)	0.166(2)

C(13)	-0.3748(5)	0.3936(4)	0.0331(4)	0.048(1)	C(43)	0.573(1)	0.308(1)	0.456(1)	0.166(2)
C(14)	-0.3950(5)	0.3421(4)	-0.0212(5)	0.053(1)	C(44)	0.668(1)	0.342(1)	0.467(1)	0.166(2)
C(15)	-0.3387(5)	0.2838(4)	-0.0042(5)	0.050(1)	C(45)	0.538(1)	0.344(1)	0.548(1)	0.166(2)
C(16)	-0.2643(5)	0.2778(4)	0.0660(5)	0.053(1)	C(46)	0.563(1)	0.408(1)	0.530(1)	0.166(2)
C(17)	-0.2433(5)	0.3294(3)	0.1222(5)	0.049(1)	C(47)	0.662(1)	0.409(1)	0.512(1)	0.166(2)
C(18)	-0.3157(5)	0.6643(3)	0.2309(4)	0.040(1)	C(48)	0.511(1)	0.323(1)	0.476(1)	0.166(2)
C(19)	-0.3317(5)	0.7114(4)	0.1711(5)	0.051(1)	C(49)	0.609(1)	0.325(1)	0.532(1)	0.166(2)
					C(50)	0.689(1)	0.336(1)	0.492(1)	0.166(2)
					B	0.2096(9)	0.3921(7)	0.4419(8)	0.095(2)

Anisotropic thermal parameters ^c

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni	0.0342(5)	0.0329(5)	0.0402(5)	0.0005(4)	0.0115(4)	-0.0032(5)
P(1)	0.0338(8)	0.0323(9)	0.0446(10)	0.0010(8)	0.0085(8)	0.0010(8)
P(2)	0.0352(9)	0.0381(9)	0.0458(10)	0.0025(8)	0.0121(8)	-0.0084(8)
P(3)	0.0323(9)	0.0382(9)	0.0449(10)	-0.0002(8)	0.0125(8)	-0.0055(8)
P(4)	0.0749(11)	0.0477(10)	0.0573(11)	-0.0079(9)	0.0245(10)	0.0055(10)
P(5)	0.0812(11)	0.0537(11)	0.0479(11)	0.0106(10)	0.0214(10)	-0.0057(9)
P(6)	0.0471(10)	0.0758(12)	0.0563(11)	0.0049(9)	0.0073(9)	0.0153(10)
F(1)	0.1865(16)	0.0920(15)	0.1340(16)	-0.0469(16)	-0.0297(16)	0.0396(15)
F(2)	0.1946(16)	0.1311(16)	0.0713(15)	0.0544(16)	0.0265(15)	0.0126(15)
F(3)	0.1223(16)	0.1066(16)	0.3482(16)	0.0080(16)	0.0339(16)	0.0688(16)
F(4)	0.2075(16)	0.2072(16)	0.0947(16)	0.0634(16)	0.0458(16)	-0.0152(16)

^a Estimated standard deviations on the last significant digits are given in parentheses. Atoms C(42)–C(50) belong to the three fragments of the solvate ethanol molecule, each with occupancy factor equal to 0.33. ^b Isotropic temperature factors are of the form $\exp[-8\pi^2 U(\sin^2\theta)/\lambda^2]$. ^c Anisotropic temperature factors are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^* + \dots)]$.

TABLE 4
 ATOMIC PARAMETERS FOR [(triphos)Pt(η^3 -P₃)]BF₄·C₂H₅OH ^a

Fractional coordinates and isotropic thermal parameters ^b									
Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (Å ²)	Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> (Å ²)
Pt	-0.19402(3)	0.54426(2)	0.13427(2)		C(18)	-0.3150(7)	0.6562(4)	0.2407(6)	0.039(2)
P(1)	-0.2769(2)	0.4534(1)	0.1715(1)		C(19)	-0.3333(8)	0.7033(5)	0.1799(6)	0.049(3)
P(2)	-0.2031(2)	0.6019(1)	0.2487(2)		C(20)	-0.4152(8)	0.7480(5)	0.1710(6)	0.052(3)
P(3)	-0.0253(2)	0.5086(1)	0.2060(2)		C(21)	-0.4776(8)	0.7457(5)	0.2224(6)	0.057(3)
P(4)	-0.1752(2)	0.6260(1)	0.0374(2)		C(22)	-0.4623(8)	0.6996(5)	0.2817(6)	0.054(3)
P(5)	-0.2030(2)	0.5279(1)	-0.0069(2)		C(23)	-0.3817(7)	0.6546(5)	0.2908(6)	0.049(3)
P(6)	-0.3299(2)	0.5839(1)	0.0193(2)		C(24)	-0.0940(7)	0.6575(4)	0.2921(6)	0.045(2)
F(1)	0.2220(9)	0.4546(5)	0.4219(7)		C(25)	-0.0452(8)	0.6918(5)	0.2427(6)	0.049(3)
F(2)	0.2726(10)	0.3816(5)	0.5204(5)		C(26)	0.0324(9)	0.7374(6)	0.2744(7)	0.065(3)
F(3)	0.1268(8)	0.3687(5)	0.4236(8)		C(27)	0.0636(9)	0.7483(6)	0.3551(8)	0.071(4)
F(4)	0.2717(11)	0.3599(7)	0.4010(7)		C(28)	0.0193(10)	0.7161(6)	0.4034(8)	0.082(4)
C(1)	-0.1142(8)	0.4506(5)	0.4114(6)	0.053(3)	C(29)	-0.0611(9)	0.6682(6)	0.3746(7)	0.066(3)
C(2)	-0.1385(7)	0.4796(4)	0.3274(6)	0.038(2)	C(30)	0.0837(7)	0.5638(4)	0.2095(6)	0.042(2)
C(3)	-0.1952(7)	0.4254(4)	0.2686(6)	0.041(2)	C(31)	0.0927(8)	0.5903(5)	0.1375(7)	0.055(3)
C(4)	-0.2086(7)	0.5419(4)	0.3244(6)	0.038(2)	C(32)	0.1725(8)	0.6351(5)	0.1357(7)	0.063(3)
C(5)	-0.0293(7)	0.4953(4)	0.3111(5)	0.040(2)	C(33)	0.2443(9)	0.6521(5)	0.2051(7)	0.065(3)
C(6)	-0.4093(7)	0.4645(4)	0.1868(5)	0.036(2)	C(34)	0.2404(9)	0.6243(5)	0.2754(7)	0.064(3)
C(7)	-0.4653(7)	0.5207(5)	0.1680(6)	0.042(2)	C(35)	0.1624(8)	0.5799(5)	0.2804(7)	0.055(3)
C(8)	-0.5631(8)	0.5286(5)	0.1815(6)	0.052(3)	C(36)	0.0259(7)	0.4335(4)	0.1762(6)	0.038(2)
C(9)	-0.6048(9)	0.4782(5)	0.2163(7)	0.063(3)	C(37)	0.1217(7)	0.4081(5)	0.2222(6)	0.048(3)

C(10)	-0.5523(9)	0.4203(6)	0.2362(7)	0.072(3)	C(38)	0.1630(8)	0.3507(5)	0.2015(6)	0.054(3)
C(11)	-0.4545(8)	0.4137(6)	0.2195(7)	0.061(3)	C(39)	0.1076(8)	0.3170(5)	0.1339(6)	0.051(3)
C(12)	-0.2990(7)	0.3845(4)	0.1039(5)	0.035(2)	C(40)	0.0126(8)	0.3404(5)	0.0876(6)	0.053(3)
C(13)	-0.3702(7)	0.3933(5)	0.0292(6)	0.044(3)	C(41)	-0.0294(7)	0.3982(5)	0.1077(6)	0.044(2)
C(14)	-0.3892(8)	0.3441(5)	-0.0271(7)	0.052(3)	B	0.2195(17)	0.3940(10)	0.4461(13)	0.091(6)
C(15)	-0.3374(8)	0.2850(5)	-0.0105(6)	0.052(3)	O	0.031(1)	0.179(1)	0.018(1)	0.26(1)
C(16)	-0.2652(8)	0.2752(5)	0.0634(6)	0.055(3)	C(42)	0.026(2)	0.197(2)	-0.061(2)	0.26(1)
C(17)	-0.2475(7)	0.3245(5)	0.1201(6)	0.046(3)	C(43)	0.151(2)	0.179(1)	-0.045(2)	0.26(1)

Anisotropic thermal parameters ^c

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	0.0299(2)	0.0361(2)	0.0304(2)	-0.0011(2)	0.0066(1)	-0.0024(2)
P(1)	0.0293(11)	0.0369(12)	0.0351(14)	0.0001(12)	0.0035(10)	0.0008(13)
P(2)	0.0334(13)	0.0411(14)	0.0357(16)	0.0005(11)	0.0067(11)	-0.0061(12)
P(3)	0.0307(13)	0.0409(14)	0.0389(16)	-0.0016(11)	0.0066(11)	-0.0055(12)
P(4)	0.0694(20)	0.0526(18)	0.0471(19)	-0.0095(15)	0.0224(16)	0.0046(15)
P(5)	0.0706(20)	0.0632(21)	0.0354(17)	0.0086(15)	0.0167(15)	-0.0049(14)
P(6)	0.0443(16)	0.0658(20)	0.0444(18)	0.0057(14)	0.0024(14)	0.0105(15)
F(1)	0.187(10)	0.118(8)	0.171(10)	-0.058(8)	-0.062(8)	0.068(8)
F(2)	0.257(13)	0.148(9)	0.061(6)	0.027(9)	-0.003(7)	0.032(6)
F(3)	0.121(8)	0.129(8)	0.310(17)	0.007(7)	0.025(10)	0.120(10)
F(4)	0.226(14)	0.288(17)	0.102(8)	0.087(12)	0.033(9)	-0.016(10)

^a Estimated standard deviations on the last significant digits are given in parentheses. Atoms O–C(43) belong to the solvate ethanol molecule. ^b Isotropic temperature factors are of the form $\exp[-8\pi^2 U(\sin^2\theta/\lambda^2)]$. ^c Anisotropic temperature factors are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^{*}h^{*} + \dots)]$.

which were attributed to a solvate ethanol molecule in a highly disordered position. Various models were tested for this solvent molecule; the one finally adopted consisted of three C-C-C fragments which were assigned fixed 0.33 population parameters and an overall temperature factor. Their positions were refined by applying a damping factor and imposing a unique value on all C-C bond lengths. In spite of its limitations, this model accounted reasonably well for the residual density in the ΔF map and led to a significant improvement in R (ca. 0.01). The solvate ethanol molecule in the structure of the compound II was essentially distributed about the same position as in the structure of the Pd isomorph [3]. The location of the oxygen atom, identified on the basis of the peak height and probable existence of a hydrogen bond with the anion, was consistent with that found for the Pd derivative. An overall temperature factor was applied but no geometrical constraints were imposed on the O-C-C chain. The refinements converged at $R = 0.060$ and $R_w = 0.063$ for I, $R = 0.044$ and $R_w = 0.044$ for II, where $R = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|$ and $R_w = [\Sigma w(|F_0| - |F_c|)^2 / \Sigma w(F_0)^2]^{1/2}$. Final ΔF maps showed few peaks with heights $\leq 0.6 \text{ e } \text{\AA}^{-3}$ in the region of the solvate molecule (I) or close to the metal atom position (II). Final atomic parameters are listed in Tables 3 and 4 for compounds I and II, respectively. Listings of the structure factor amplitudes are available from the authors on request.

Results and discussion

The compound $[(\text{triphos})\text{Ni}(\eta^3\text{-P}_3)]\text{BF}_4 \cdot \text{C}_2\text{H}_5\text{OH}$ is air stable in the solid state and soluble in polar organic solvents. It decomposes in solution in a few hours in the air. The reflectance spectrum shows a shoulder at ca. 26600 cm^{-1} ; the spectrum in nitroethane solution exhibits a band at ca. 27000 cm^{-1} ($\epsilon_M = 2700$). This transition occurs at higher energy than the transitions with substantial $d-d$ character observed in the spectra of the cobalt (24000 cm^{-1}) and the palladium ($22600\text{--}28500 \text{ cm}^{-1}$) derivatives [4].

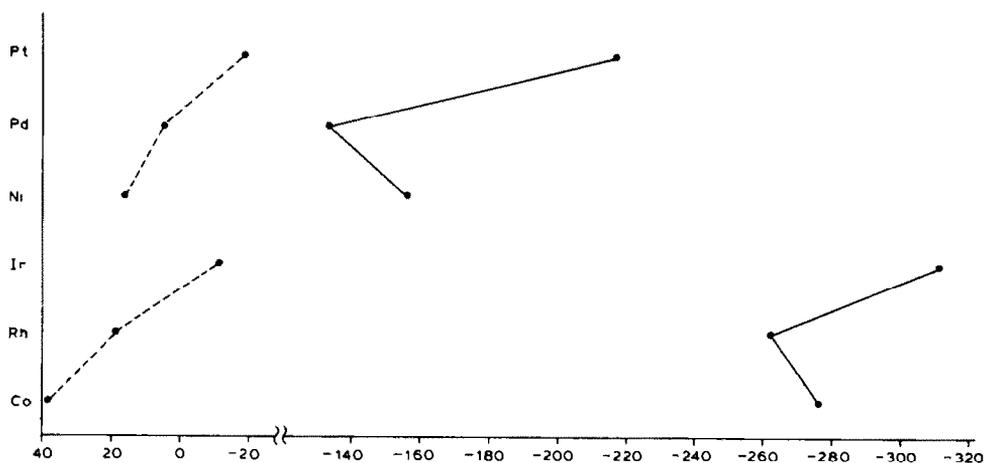


Fig. 1. $\delta(^{31}\text{P})$ values for P(triphos) (-----) and P($\eta^3\text{-P}_3$) (————) for the $[(\text{triphos})\text{M}(\eta^3\text{-P}_3)]^{n+}$ complexes ($n = 0$, M = Co, Rh, Ir; $n = 1$, M = Ni, Pd, Pt).

TABLE 5

 $^{31}\text{P}\{^1\text{H}\}$ NMR SPECTRAL DATA FOR THE COMPLEXES ^a

Compound	Chemical shifts (ppm)		<i>J</i> (Hz)		
	P($\eta^3\text{-P}_3$)	P(triphos)	P-P	M-P($\eta^3\text{-P}_3$)	M-P(triphos)
[(triphos)Co($\eta^3\text{-P}_3$)]	-276.21m	38.16m			
[(triphos)Rh($\eta^3\text{-P}_3$)]	-261.04q	18.65q	12	13	138
[(triphos)Ir($\eta^3\text{-P}_3$)]	-312.89q	-11.85q	13		
[(triphos)Ni($\eta^3\text{-P}_3$)]BF ₄ ·C ₂ H ₅ OH	-155.66q	16.33q	14		
[(triphos)Pd($\eta^3\text{-P}_3$)]BF ₄ ·C ₂ H ₅ OH	-132.90q	4.90q	11		
[(triphos)Pt($\eta^3\text{-P}_3$)]BF ₄ ·C ₂ H ₅ OH	-217.43q	-18.58q	9	171	2476

^a Measured in CD₂Cl₂. Chemical shifts are relative to 85% H₃PO₄. Positive chemical shifts are downfield: q = quartet, m = multiplet. The spectra do not vary with temperature on cooling the solution down to -80°C, except for the Co compound (see text).

$^{31}\text{P}\{^1\text{H}\}$ NMR data for the nickel complex and for the isoelectronic cobalt, rhodium, iridium, palladium and platinum derivatives are listed in Table 5. The [(triphos)M($\eta^3\text{-P}_3$)]BF₄·C₂H₅OH (M = Ni, Pd [3]) and [(triphos)Ir($\eta^3\text{-P}_3$)] complexes exhibit a typical A₃X₃ pattern. In the spectrum of the platinum derivative [3] each of the above signals is accompanied by satellites due to the coupling to ¹⁹⁵Pt (33.7% natural abundance). The rhodium compound gives a spectrum of the type A₃X₃Y (Y = ¹⁰³Rh). The cobalt derivative shows two resonances at room temperature which become narrower on cooling but are not resolved into a fine structure even at -80°C. The spectra of the other compounds do not vary with the temperature. The low field resonances in each spectrum are assigned to the three phosphorus atoms of the triphos ligand, whereas the higher field signals are assigned to the cyclo-P₃ phosphorus atoms.

Figure 1 shows the trends in chemical shifts (δ) of both the phosphine and the cyclo-P₃ phosphorus atoms among the two groups, of the neutral and of the cationic

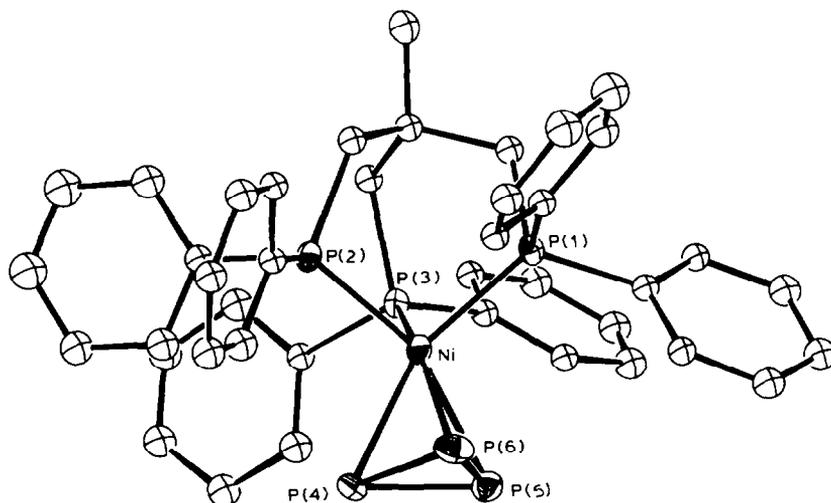


Fig. 2. View of the [(triphos)Ni($\eta^3\text{-P}_3$)]⁺ cation with 20% probability ellipsoids.

complexes. The P(triphos) chemical shifts (Fig. 1 and Table 5) decrease in a similar way on descending each group. Such trends are consistent with that reported for phosphine complexes formed by metal atoms of different transition rows, having the same coordination number, molecular geometry, phosphine ligand and oxidation state of the metal atom [12]. The chemical shift is smaller for each cationic complex than for the neutral compound formed by the metal atom of the same transition row. In sharp contrast the $P(\eta^3-P_3)$ values do not vary smoothly within each group of compounds, although they exhibit similar trends for the neutral and the cationic complexes. The resonances of the latter compounds are considerably downfield shifted with respect to those of the former. Remarkably, the $^1J(M-P_{\eta^3-P_3})$ coupling constants, of 13 and 171 Hz for $M = Rh$ and Pt , respectively (Table 5), are more than one order of magnitude smaller than the $^1J(M-P_{\text{triphos}})$ ones, which in turn are in the usual range for the phosphine complexes of such metals [13]. A comparable reduction in the coupling constant has been found for $^1J(M-^{13}C)$ on going from complexes containing $M-C \sigma$ bonds to complexes containing $M-C \pi$ bonds with olefins [14].

The crystal structures of the two $[(\text{triphos})M(\eta^3-P_3)]BF_4 \cdot C_2H_5OH$ ($M = Ni, Pt$) isomorphous complexes consist of $[(\text{triphos})M(\eta^3-P_3)]^+$ cations, BF_4^- anions, and interposed ethanol molecules. The metal atom in each cation is six-coordinated by

TABLE 6

SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR THE STRUCTURES OF $[(\text{triphos})Ni(\eta^3-P_3)]BF_4 \cdot C_2H_5OH$ (I) AND $[(\text{triphos})Pt(\eta^3-P_3)]BF_4 \cdot C_2H_5OH$ (II)^a

	I	II
M-P(1)	2.240(2)	2.332(2)
M-P(2)	2.241(2)	2.337(2)
M-P(3)	2.247(2)	2.349(2)
M-P(4)	2.301(2)	2.430(3)
M-P(5)	2.311(2)	2.437(3)
M-P(6)	2.307(2)	2.433(3)
P(4)-P(5)	2.117(3)	2.153(4)
P(4)-P(6)	2.124(3)	2.147(4)
P(5)-P(6)	2.124(3)	2.165(4)
P(1)-M-P(2)	95.2(1)	92.3(1)
P(1)-M-P(3)	95.5(1)	92.6(1)
P(1)-M-P(4)	150.2(1)	151.9(1)
P(1)-M-P(5)	105.2(1)	105.3(1)
P(1)-M-P(6)	96.1(1)	101.6(1)
P(2)-M-P(3)	90.4(1)	87.7(1)
P(2)-M-P(4)	100.8(1)	105.7(1)
P(2)-M-P(5)	155.1(1)	156.8(1)
P(2)-M-P(6)	109.7(1)	109.5(1)
P(3)-M-P(4)	109.1(1)	109.1(1)
P(3)-M-P(5)	101.5(1)	106.1(1)
P(3)-M-P(6)	155.7(1)	156.9(1)
P(4)-M-P(5)	54.7(1)	52.5(1)
P(4)-M-P(6)	54.9(1)	52.4(1)
P(5)-M-P(6)	54.8(1)	52.8(1)

^a $M = Ni$ (I), $M = Pt$ (II).

TABLE 7
STRUCTURAL DATA FOR THE COMPLEXES^a

Compound	M-P(triphos)	M-P(η^3 -P ₃)	P-P	P-M-P ^b	P-M-P ^c	Ref.
[(triphos)Co(η^3 -P ₃)]	2.186(1)	2.301(1)	2.141(2)	93.55(4)	55.43(5)	1
[(triphos)Rh(η^3 -P ₃)]	2.294(1)	2.418(2)	2.152(2)	91.25(4)	52.86(5)	2
[(triphos)Ir(η^3 -P ₃)]	2.277(2)	2.436(2)	2.159(4)	91.22(7)	52.60(8)	2
[(triphos)Ni(η^3 -P ₃)]BF ₄	2.243(4)	2.306(5)	2.122(4)	94(3)	54.8(1)	this work
[(triphos)Pd(η^3 -P ₃)]BF ₄	2.37(1)	2.412(8)	2.115(8)	91(2)	52.0(1)	3
[(triphos)Pt(η^3 -P ₃)]BF ₄	2.339(8)	2.433(5)	2.155(9)	91(1)	52.6(3)	this work

^a Means over sets of chemically equivalent bond distances (Å) and angles (°) are reported; e.s.d.'s, shown in parentheses, are calculated by the formula $[\sum_i |\Delta_i|^2 / (n-1)]^{1/2}$, where n is the number of observations and Δ_i are deviations of individual values from the mean. ^b Angle involving P atoms of triphos. ^c Angle involving *cyclo*-P₃ atoms.

the triphos P atoms and by those of the cyclo-P₃ group in a distorted octahedral environment, similar to that existing in the Pd isomorph [3] as well as in the neutral complexes of the cobalt group [1,2]. A view of the [(triphos)Ni(η^3 -P₃)]⁺ cation is shown in Fig. 2. Values of bond distances and angles about the metal atom in each structure are listed in Table 6. Mean values of important bond lengths and angles in the three neutral and in the three cationic complexes so far investigated are presented in Table 7. The M–P(η^3 -P₃) distances are comparable for pairs of compounds belonging to the same transition row, whereas the M–P(triphos) distances are consistently longer, by 0.06–0.07 Å, in the cationic complex of each pair (Table 7). Both the M–P(η^3 -P₃) and the M–P(triphos) bond lengths increase significantly on going from the 3*d* to the 4*d* derivative, in the cobalt as well as in the nickel group. Although such bond lengths vary much less from the 4*d* to the 5*d* complex as a consequence of the lanthanide contraction, they do exhibit significant variations with consistent trends for the two groups of compounds: the M–P(η^3 -P₃) bonds lengthen slightly in the 5*d* derivative whereas the M–P(triphos) ones shorten by a comparable amount. Finally, variations of the P–P distances in the cyclo-P₃ group are not strictly parallel for the two sets of compounds (Table 7). However, the deviations, which must arise from specific requirements of individual metal atom, are small.

Although numerous factors may contribute to the main trends described above, a decisive role is probably played by the amount of mixing of the metal (*n* + 1)*s* and (*n* + 1)*p* virtual orbitals in the occupied MO's of the complex. Such mixing is controlled by the energies of the empty metal orbitals, which do not vary regularly along a group [15]. Moreover, as indicated by iterative calculations to self-consistency in charge and configuration at the extended-Hückel level [4], such mixing is different in the sets of MO's contributing to the different M–P bonds: it is large with distinct bonding character in the high-energy orbitals of the complex, which essentially provide the M–P(η^3 -P₃) bond density, whereas it is smaller and less bonding, or even antibonding, in the lower-energy orbitals which correspond to the phosphine "lone pairs". This may cause the opposing trends, from the second transition row downward, in the two sets of M–P bond distances as well as the overall lengthening of the M–P(triphos) bonds in the cationic complexes, where the virtual orbitals of the metal atom are stabilized so that they interact more strongly with those of the donor atoms.

A rationalization of the NMR data for the complexes may be sought along similar lines, bearing in mind in particular that resonances due to the bare cyclo-P₃ phosphorus atoms, involved in the formation of high-energy molecular orbitals with large metal orbitals participation, should be more sensitive than those of the phosphine donor atoms to modifications in the geometry or in the electronic structure going from compound to compound. The irregularly varying admixture of metal empty orbitals along a group may be therefore at the origin of the nonlinear trends in the ³¹P chemical shifts of the cyclo-P₃ atoms (Fig. 1), being at the same time compatible with the smoother trends in the P(triphos) δ values. For analogous reasons signals due to the cyclo-P₃ group should be more sensitive to variations in the molecular charge, as is actually observed. Failure to detect downfield shifts in the P(triphos) resonances on going from the neutral to the cationic complexes may be tentatively ascribed to an overriding effect due to the lengthening of the M–P(triphos) bonds which occurs in the same sense. Finally, the unusually low values of the

$^1J(M-P)$ coupling constants to atoms of the cyclic unit may be principally traced to the low $M-P(\eta^3-P_3)$ bond order, which is 2–3 times smaller than that of $M-P$ (phosphine) bonds [4]. Although the s -orbitals bond order (not reliably provided by the semi-empirical calculations) rather than the total bond order is of predominant importance here [16], it is conceivable that values of the former do not deviate considerably from trends calculated for the latter. Since the coupling constant depends on the second power of the bond order, it should be drastically reduced as a consequence of the decrease in the values of the latter quantity.

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