"Triple-Decker" Sandwich Complexes of *cyclo*-Triphosphorus with 4d and 5d Metals

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Abstract: Several homo- and heterometal triple-decker sandwich complexes (**1**–**7**) of rhodium and iridium containing the *cyclo*-triphosphorus unit as a η^3 ligand, with the general formula $[(\text{triphos})M_1\text{-}\mu\text{-}(\eta^3\text{-}P_3)M_2(\text{triphos})]Y_n$ (triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane; M_1 = Co, Ni, Rh; M_2 = Rh, Ir; Y = BF_4, BPh_4; n = 1,2 and generally crystallizing with solvent molecules included in the lattice), have been synthesized. The structures of these complexes have been elucidated through complete X-ray analysis of the derivatives $[(\text{triphos})\text{Co-}\mu\text{-}(\eta^3\text{-}P_3)\text{Rh}(\text{triphos})](BPh_4)_2\cdot 2(CH_3)_2CO$ (**2**) and $[(\text{triphos})\text{Ni-}\mu\text{-}(\eta^3\text{-}P_3)\text{Rh}(\text{triphos})](BF_4)_2\cdot C_4H_8O$ (**4**): **2**, triclinic, a = 17.550 (7) Å, b = 15.900 (7) Å, c = 13.815 (6) Å, α = 111.47 (5)°, β = 91.15 (5)°, γ = 115.44 (5)°, space group $P1$, Z = 1, R = 0.079, 3765 reflections; **4**, triclinic, a = 20.023 (7) Å, b = 15.720 (7) Å, c = 16.333 (8) Å, α = 126.58 (6)°, β = 91.00 (5)°, γ = 93.46 (5)°, space group $P\bar{1}$, Z = 2, R = 0.064, 4450 reflections. The complexes that are assigned 31 valence electrons (**1**, **2**, **6**) are paramagnetic with magnetic moments corresponding to one unpaired electron, analogously to the isoelectronic compounds formed by first-row transition metals. On the other hand, the complexes with 32 valence electrons are diamagnetic (**7**) or exhibit a small residual paramagnetism (**3**, **4**, **5**), at variance with the isoelectronic 3d derivatives already described, which have spin triplet ground states. This is rationalized in terms of the distortion from axial symmetry that has been detected for compound **4**.

Introduction

In previous papers several "double sandwich" complexes of 3d metals containing the *cyclo*-triphosphorus, η^3-P_3, group have been reported.[1,2] This new molecular unit behaves as a η^3 ligand and is capable of functioning as the internal layer in complexes of the above type. Since the properties of the *cyclo*-triphosphorus group and those of the complexes in which it is involved were not yet explored exhaustively, we attempted to synthesize double-sandwich *cyclo*-P_3 derivatives of second- and third-row transition metals such as rhodium and iridium. By reaction of white phosphorus with the tripod-like tri(tertiary phosphine) 1,1,1-tris((diphenylphosphino)methyl)ethane (triphos) and with appropriate complexes of rhodium or iridium, the mononuclear *cyclo*-triphosphorus derivatives $[(\text{triphos})\text{Rh}(\eta^3\text{-}P_3)]$ and $[(\text{triphos})\text{Ir}(\eta^3\text{-}P_3)]$ were obtained.[3] These complexes were then reacted with $[\text{Rh}(C_2H_4)_2\text{Cl}]_2$, $[\text{Co}(H_2O)_6](BF_4)_2$, or $[\text{Ni}(H_2O)_6](BF_4)_2$ in the presence of triphos. In this manner several homo- and heterometal dinuclear complexes were obtained, having the general formula $[(\text{triphos})M_1\text{-}\mu\text{-}(\eta^3\text{-}P_3)M_2(\text{triphos})]Y_n\cdot xS$ (M_1 = Co, Ni, Rh; M_2 = Rh, Ir; Y = BF_4, BPh_4; n = 1,2; S = CH_2Cl_2, $(CH_3)_2CO$, C_4H_8O). All of these complexes have a triple-decker sandwich structure with the internal layer formed by the *cyclo*-triphosphorus unit. They have been characterized by means of magnetic, spectrophotometric, and conductivity measurements. Complete X-ray structural investigations have been carried out on the compounds $[(\text{triphos})\text{CO-}\mu\text{-}(\eta^3\text{-}P_3)\text{Rh}(\text{triphos})](BPh_4)_2\cdot 2(CH_3)_2CO$ and $[(\text{triphos})\text{Ni-}\mu\text{-}(\eta^3\text{-}P_3)\text{Rh}(\text{triphos})](BF_4)_2\cdot C_4H_8O$. A preliminary account of part of this work has already been given.[4]

Experimental Section

Reagents. The ligand triphos[5] and the complexes $[\text{Rh(CO)}_2\text{Cl}]_2$,[6] $[\text{Rh}(C_2H_4)_2\text{Cl}]_2$,[7] $[(\text{triphos})\text{Rh}(\eta^3\text{-}P_3)]$,[3] and $[(\text{triphos})\text{Ir}(\eta^3\text{-}P_3)]$[3] were prepared according to published procedures. All other chemicals were reagent grade and were used without further purification.

Preparation of the Complexes. All reactions and manipulations were routinely performed in an atmosphere of dry nitrogen by using deoxygenated solvents. The complexes were collected on a sintered-glass frit, in a closed system, and washed with ethanol and petroleum ether in turn before being dried in a stream of dry nitrogen. The yields were generally more than 60%.

$[(\text{triphos})\text{Co-}\mu\text{-}(\eta^3\text{-}P_3)\text{Rh}(\text{triphos})](BF_4)_2\cdot 0.75CH_2Cl_2$ (1). A solution of $[(\text{triphos})\text{Rh}(\eta^3\text{-}P_3)]$ (0.41 g, 0.5 mmol) in 40 mL of CH_2Cl_2 was added, at room temperature, to a mixture of $[\text{Co}(H_2O)_6](BF_4)_2$ (0.17 g, 0.5 mmol) in ethanol (15 mL) and triphos (0.31 g, 0.5 mmol) in CH_2Cl_2 (20 mL). The resulting solution was concentrated and the brown crystals so formed were recrystallized from CH_2Cl_2/ethanol.

$[(\text{triphos})\text{Co-}\mu\text{-}(\eta^3\text{-}P_3)\text{Rh}(\text{triphos})](BPh_4)_2\cdot 2(CH_3)_2CO$ (2). This derivative was obtained by addition of $NaBPh_4$ (0.34 g, 1 mmol) in ethanol (15 mL) to the above solution of **1** and recrystallized from acetone/ethanol.

$[(\text{triphos})\text{Ni-}\mu\text{-}(\eta^3\text{-}P_3)\text{Rh}(\text{triphos})](BF_4)_2$ (3). This dark red complex was prepared by the same procedure as the above cobalt compounds except for substitution of $[\text{Ni}(H_2O)_6](BF_4)_2$ for the cobalt analogue.

$[(\text{triphos})\text{Ni-}\mu\text{-}(\eta^3\text{-}P_3)\text{Rh}(\text{triphos})](BF_4)_2\cdot C_4H_8O$ (4). The complex $[(\text{triphos})\text{Rh}(\eta^3\text{-}P_3)]$ (0.41 g, 0.5 mmol) in 80 mL of THF was added, at room temperature, to a mixture of $[\text{Ni}(H_2O)_6](BF_4)_2$ (0.17 g, 0.5 mmol) in ethanol (30 mL) and triphos (0.31 g, 0.5 mmol) in THF (10 mL). The resulting mixture was concentrated to 40 mL under reduced pressure. After one night dark red crystals had separated.

$[(\text{triphos})\text{Ni-}\mu\text{-}(\eta^3\text{-}P_3)\text{Rh}(\text{triphos})](BPh_4)_2\cdot CH_2Cl_2$ (5). This complex was prepared by the same procedure as **3** except for addition of $NaBPh_4$.

$[(\text{triphos})\text{Co-}\mu\text{-}(\eta^3\text{-}P_3)\text{Ir}(\text{triphos})](BF_4)_2\cdot CH_2Cl_2$ (6). This red-brown complex was prepared by the same procedure as the cobalt-rhodium derivative by using the compound $[(\text{triphos})\text{Ir}(\eta^3\text{-}P_3)]$ (0.45 g, 0.5 mmol) instead of the rhodium analogue.

$[(\text{triphos})\text{Rh-}\mu\text{-}(\eta^3\text{-}P_3)\text{Rh}(\text{triphos})](BPh_4)\cdot(CH_3)_2CO$ (7). A solution of $[(\text{triphos})\text{Rh}(\eta^3\text{-}P_3)]$ (0.41 g, 0.5 mmol) in 40 mL of CH_2Cl_2 was added to a mixture of $[\text{Rh}(C_2H_4)_2\text{Cl}]_2$ (or $[\text{Rh(CO)}_2\text{Cl}]_2$) (0.12 g, 0.3 mmol) and triphos (0.38 g, 0.6 mmol) in 20 mL of CH_2Cl_2. On addition of $NaBPh_4$ (0.18 g, 0.5 mmol) in 30 mL of ethanol and slow evaporation of the solvent, red orange crystals were obtained, which were recrystallized from acetone/ethanol.

Physical Measurements. Infrared and electronic spectra, conductivity measurements, and magnetic susceptibilities were recorded using previously described methods.[8]

The analytical, magnetic, and conductivity data of the complexes are reported in Table I. Table II lists the electronic spectral data for four representative complexes.

Collection and Reduction of X-ray Intensity Data. The compounds described in this paper generally have been found not to provide good quality crystals for X-ray investigations. Suitable crystals for structural analysis could only be obtained for the cobalt–rhodium derivative **2** and for the nickel–rhodium complex **4** (compounds are numbered as in Table I). The former has 31 electrons in its valence shell analogous to the cases for **1** and **6**, whereas the latter is representative of the complexes (**3**–**5**,

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Table I. Analytical, Magnetic, and Conductivity Data for the Complexes

no.	compd		% C	% H	% Co	% Ni	% Rh	% Ir	% P	μ_B[a]	Λ_M,[b] cm^2/Ω mol
1	$[CoRh(P_3)(triphos)_2](BF_4)_2 \cdot 0.75CH_2Cl_2$	calcd	57.08	4.60	3.38		5.91		16.00	2.09	150
		found	57.01	4.08	3.37		5.32		15.58		
2	$[CoRh(P_3)(triphos)_2](BPh_4)_2 \cdot 2(CH_3)_2CO$	calcd	72.32	5.80	2.61		4.55		12.34	2.20	102
		found	72.28	5.75	2.54		4.20		12.80		
3	$[NiRh(P_3)(triphos)_2](BF_4)_2$	calcd	58.70	4.69		3.50	6.13		16.61	1.05	140
		found	58.43	4.77		3.30	5.80		16.80		
4	$[NiRh(P_3)(triphos)_2](BF_4)_2 \cdot C_4H_8O$	calcd	59.04	4.95		3.35	5.88		15.93	1.50	145
		found	58.06	5.00		3.19	5.95		15.50		
5	$[NiRh(P_3)(triphos)_2](BPh_4)_2 \cdot CH_2Cl_2$	calcd	70.64	5.43		2.64	4.62		12.51	1.64	99
		found	70.80	5.59		2.62	4.74		12.74		
6	$[CoIr(P_3)(triphos)_2](BF_4)_2 \cdot CH_2Cl_2$	calcd	53.80	4.35	3.18			10.37	15.05	1.95	139
		found	54.49	4.78	3.18			9.50	14.40		
7	$[Rh_2(P_3)(triphos)_2](BPh_4) \cdot (CH_3)_2CO$	calcd	67.99	5.44			10.68		14.47	0	42
		found	66.70	5.52			10.20		14.72		

[a] Room temperature. [b] Nitroethane solution.

Table II. Reflectance Spectra of Representative Complexes

no.	compd	absorption max, cm^{-1}
1	$[CoRh(P_3)(triphos)_2](BF_4)_2 \cdot 0.75CH_2Cl_2$	9900, 13 900, 21 100–23 500
3	$[NiRh(P_3)(triphos)_2](BF_4)_2$	7300, 14 700, 18 200 sh, 24 000
6	$[CoIr(P_3)(triphos)_2](BF_4)_2 \cdot CH_2Cl_2$	10 700, 15 200, 25 600–28 500
7	$[Rh_2(P_3)(triphos)_2](BPh_4) \cdot (CH_3)_2CO$	10 700, 20 000 sh, 22 500 sh, 25 600

Table III. Summary of Crystal Data, Intensity Collection, and Refinement for $[(triphos)Co\text{-}\mu\text{-}(\eta^3\text{-}P_3)Rh(triphos)](BPh_4)_2 \cdot 2CO(CH_3)_2$ (**2**) and $[(triphos)Ni\text{-}\mu\text{-}(\eta^3\text{-}P_3)Rh(triphos)](BF_4)_2 \cdot C_4H_8O$ (**4**)

	2	4
formula	$C_{136}H_{130}B_2Co_1O_2P_9Rh_1$	$C_{86}H_{86}B_2F_8Ni_1O_1P_9Rh_1$
fw	2258.8	1749.6
a, Å	17.550 (7)	20.023 (7)
b, Å	15.900 (7)	15.720 (7)
c, Å	13.815 (6)	16.333 (8)
α, deg	111.47 (5)	126.58 (6)
β, deg	91.15 (5)	91.00 (5)
γ, deg	115.44 (5)	93.46 (5)
V, $Å^3$	3166.8	4111.4
Z	1	2
density, g cm^{-3}	1.184 (calcd) 1.22 (obsd)	1.413 (calcd) 1.42 (obsd)
space group	$P1$	$P\bar{1}$
cryst dimens, mm	0.20 × 0.25 × 0.30	0.05 × 0.18 × 0.40
cryst shape	prism with six well-formed faces	elongated plate
temp, °C	23	23
radiatn	Mo Kα (λ 0.7107 Å), graphite monochromatized	Mo Kα
μ, cm^{-1}	4.17	6.61
transmission factors	0.89–0.97	0.86–0.97
scan speed, 2θ deg/min	6.0	6.0
scan range, deg	1.10 + 0.30 tan θ	1.00
background	$t_{b1} = t_{b2} = {}^1/_2 t_s$[a]	$t_{b1} = t_{b2} = {}^1/_2 t_s$
2θ limits, deg	4.0–46.0	4.0–40.0
unique data used, ($F_o^2 > 3.5\sigma(F_o^2)$)	3765	4450
final no. of variables	398	371
R	0.079	0.064
R_w	0.103	0.078
error in observn of unit wt, electrons	2.03	1.50

[a] t_{b1}, t_{b2} = background count times; t_s = total scan time.

7) with 32 valence electrons.[9] Data sets for both complexes were collected by using a Philips PW 1100 automated diffractometer and monochromated Mo Kα radiation (λ 0.7107 Å). Details on crystal data, intensity collection, and refinement are reported in Table III. Lattice constants were determined by least-squares refinement of the angular positions of 24 reflections for each compound. The intensities of three standard reflections measured every 100 min during data collection showed small oscillations (≤4%) about their mean values but failed to reveal any significant trends. Data sets were rescaled and processed by using a value of 0.05 for *p* in the calculation of the $\sigma(I)$'s.[10] Corrections for absorption were applied. The principal computer programs used for the crystallographic calculations have been described.[11]

Determination and Refinement of the Structures. Since compound **2** is isomorphous with the complexes previously investigated containing two 3d metal atoms in the dinuclear cation,[2] its structure was refined by using as the initial values of the atomic coordinates those determined for one of the latter compounds. It was soon apparent that the position of the heterometal cation in the structure of **2** was affected by twofold orientational disorder, analogous to that detected in the case of the compound $[(triphos)Co\text{-}\mu\text{-}(\eta^3\text{-}P_3)Ni(triphos)](BPh_4)_2 \cdot 2(CH_3)_2CO$ (**8**),[2] each metal site being statistically occupied by the two metal atoms, with equal probability. The average of the scattering factors of cobalt and rhodium was therefore assigned to each one of the metal sites. Anisotropic thermal parameters were used for the metal and phosphorus atoms and isotropic parameters for the boron and carbon atoms. Phenyl groups were refined as rigid bodies with idealized geometry. The coordinates of one heavy atom were not allowed to change in the least-squares cycles as the position of the origin in the *P*1 space group is undefined. The atomic scattering factors were taken from ref 12, and anomalous dispersion terms for the metal and phosphorus atoms were included in F_c.[13] The mean values both of the real and of the imaginary parts of the corrections to the cobalt and rhodium form factors were used. In the full-matrix least-squares refinement the function $\sum w(|F_o| - |F_c|)^2$ was minimized with weights $w = 1/\sigma^2(F_o)$. The agreement factors are defined as $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2)^{1/2}$. A Δ*F* Fourier calculated at *R* = 0.11 showed residual density (peak heights ca. 1 e $Å^{-3}$) in two regions which were occupied by solvent molecules in the structures of the isomorphous compounds.[2] The presence of acetone molecules in the structure of compound **2** was also revealed by its IR spectrum. Two solvent molecules were considered to be present in the cell, consistent with the aspect of the difference synthesis and in reasonable agreement with the elemental analysis and density data. The model previously adopted,[2] consisting of a regular triangular arrangement of carbon atoms about a central carbon atom, was used also in this case for the very disordered solvent molecules. Rigid group refinement, applying an overall temperature factor, was performed on such "molecules" separately from the refinement on the other parameters of the structure. Hydrogen atoms, including those of the methyl groups of the triphos ligands but obviously not those of the "solvent molecules", were introduced in calculated positions (C–H = 0.95 Å) by the procedure described previously,[2,14] and their fixed contribution was added to the F_c. Re-

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(9) The criteria for assigning electrons to the valence shell of each complex have been described in a previous paper.[2]

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Table IV. Positional and Thermal Parameters for the Metal and Phosphorus Atoms in the Structure of $[(\text{triphos})\text{Co-}\mu\text{-}(\eta^3\text{-P}_3)\text{Rh}(\text{triphos})](\text{BPh}_4)_2\cdot2(\text{CH}_3)_2\text{CO}^a$ (All Quantities $\times10^4$)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
M1[b]	1099	45	39	604 (21)	530 (19)	655 (23)	275 (16)	125 (17)	173 (17)
M2	−1151 (2)	−74 (3)	−89 (3)	523 (19)	547 (19)	625 (23)	284 (16)	122 (16)	188 (17)
P1	1401 (4)	−984 (4)	−1301 (5)	301 (38)	277 (37)	225 (44)	136 (30)	41 (30)	6 (31)
P2	2282 (4)	1464 (5)	271 (5)	321 (38)	273 (37)	400 (48)	148 (31)	77 (32)	160 (34)
P3	1758 (4)	−193 (5)	1227 (5)	434 (43)	279 (40)	361 (49)	159 (34)	67 (35)	108 (35)
P4	−2353 (4)	−1488 (4)	−1090 (5)	366 (40)	208 (37)	362 (48)	130 (31)	49 (33)	102 (33)
P5	−1765 (4)	222 (5)	1299 (5)	380 (41)	387 (42)	292 (48)	195 (34)	106 (34)	127 (35)
P6	−1453 (4)	921 (5)	−629 (5)	264 (37)	326 (39)	353 (47)	174 (31)	131 (32)	153 (34)
P7	314 (4)	929 (5)	208 (6)	372 (45)	410 (45)	822 (66)	271 (37)	163 (41)	183 (43)
P8	−273 (4)	−680 (5)	−963 (6)	370 (42)	586 (49)	339 (51)	281 (39)	30 (35)	0 (39)
P9	−144 (5)	−312 (6)	745 (6)	467 (48)	729 (56)	494 (57)	377 (43)	187 (40)	334 (45)
F rel scale factor = 31 860									

[a] Parameters for the other atoms in the structure of $[(\text{triphos})\text{Co-}\mu\text{-}(\eta^3\text{-P}_3)\text{Rh}(\text{triphos})](\text{BPh}_4)_2\cdot2(\text{CH}_3)_2\text{CO}$ are listed in Tables V–VII (supplementary material). In the tables of atomic parameters standard deviations on the last significant digits are given in parentheses. Anisotropic temperature factors are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^* + \cdots)]$; this form is used throughout. [b] Metal sites M1 and M2 have 50% Co and Rh occupancy factors; positional parameters of M1 not refined (see text).

Table VIII. Positional and Thermal Parameters for the Metal and Phosphorus Atoms in the Structure of $[(\text{triphos})\text{Ni-}\mu\text{-}(\eta^3\text{-P}_3)\text{Rh}(\text{triphos})](\text{BF}_4)_2\cdot\text{C}_4\text{H}_8\text{O}^a$ (All Quantities $\times10^4$)

atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
M1	2178 (1)	1811 (1)	−2174 (1)	404 (9)	307 (9)	245 (8)	51 (7)	64 (7)	144 (7)
M2	2533 (1)	2080 (1)	418 (1)	408 (9)	311 (8)	258 (8)	27 (6)	39 (6)	147 (7)
P1	1235 (2)	2402 (3)	−2473 (2)	444 (24)	351 (23)	261 (20)	83 (19)	82 (18)	149 (19)
P2	2856 (2)	2617 (3)	−2624 (3)	420 (24)	344 (23)	346 (22)	28 (18)	34 (18)	195 (19)
P3	2160 (2)	285 (3)	−3803 (2)	498 (25)	349 (23)	248 (20)	75 (18)	77 (18)	135 (18)
P4	1795 (2)	2008 (3)	1438 (3)	500 (26)	421 (24)	299 (22)	39 (20)	75 (19)	181 (20)
P5	3012 (2)	3564 (3)	1816 (3)	542 (27)	371 (24)	351 (22)	−8 (20)	13 (19)	190 (20)
P6	3226 (2)	950 (3)	449 (3)	482 (25)	351 (23)	348 (22)	63 (19)	19 (19)	189 (20)
P7	2002 (2)	2678 (3)	−413 (3)	662 (29)	503 (26)	293 (22)	216 (22)	118 (20)	219 (21)
P8	2886 (2)	1635 (3)	−1160 (3)	501 (26)	595 (28)	372 (23)	152 (22)	120 (20)	300 (22)
P9	1877 (2)	974 (3)	−1324 (3)	847 (36)	520 (30)	621 (30)	−168 (26)	164 (26)	206 (25)
F rel scale factor = 55 073									

[a] Parameters for the other atoms in the structure of $[(\text{triphos})\text{Ni-}\mu\text{-}(\eta^3\text{-P}_3)\text{Rh}(\text{triphos})](\text{BF}_4)_2\cdot\text{C}_4\text{H}_8\text{O}$ are listed in Tables IX–XI (supplementary material). Occupancy factors of metal sites: M1, 45% Rh and 55% Ni; M2, 55% Rh and 45% Ni.

finement converged to the *R* value of 0.079. A final ΔF Fourier showed as the most prominent features two peaks with heights ≤0.6 e Å^{-3} in regions that were not occupied by atoms included in the model.

The structure of compound **4** was solved by standard heavy-atom techniques. The positions of all nonhydrogen atoms were determined from Fourier syntheses. Since the position of the cation was found to be affected by twofold orientational disorder, essentially as in the case of compounds **2** and **8**, the average of the scattering factors of nickel and rhodium, properly corrected for anomalous dispersion effects, was (initially) used for the metal atom contributions to the F_c. Anisotropic temperature factors were used for the metal, phosphorus, and fluorine atoms and isotropic thermal factors were applied to the carbon and boron atoms. The refinement procedure was closely similar to that described for compound **2**. A ΔF Fourier calculated at $R = 0.080$ clearly showed the tetrahydrofuran molecule in the asymmetric unit. The position of the THF oxygen atom could be identified with reasonable confidence on the basis of the peak heights. The geometry of the molecule was idealized (C–C = 1.48 Å, C–O = 1.44 Å, C–O–C = 100°), assuming slightly shorter (by ca. 0.02 Å) bond distances than those reported for coordinating THF.[15] Such shortening, assumed in order to allow partly for the effects of thermal motion, was consistent with the aspect of the ΔF Fourier. Rigid-group refinement using an overall temperature factor was performed on the solvent molecule, separately from the refinement on the rest of the structure. Hydrogen atom contributions were calculated as described above but, in this case, were also applied to the THF molecule. When the refinement was almost completed, significant differences existing between the thermal parameters of the two "metal atoms" and small differences between the mean values of their M–P bond lengths suggested that the nickel and the rhodium atoms were probably not distributed with equal frequency between the two metal centers. This could be due to the distortion from linearity of the dication in the structure of **4** (see below) causing the two orientations of the heterometal cation not to be equiprobable. Separate sets of refinements were then performed, in which different occupancy factors were assigned to the two metal sites, by using properly weighted combinations of the nickel and rhodium form factors. The model with 55% Rh and 45% Ni character assigned to that metal center which was found to form longer M–P bonds gave the lowest *R* value (0.001 improvement with respect to the model with 0.5 population parameters for nickel and rhodium) and closely similar temperature factors for the two metal centers. Bond lengths were not affected. Such a model was used in the final refinement, which converged at *R* 0.064.

The final positional and thermal parameters appear in Tables IV–XI. Listings of the observed and calculated structure amplitudes are available.[16]

Results and Discussion

All the complexes are quite air stable in the solid state but are rather unstable in solution, where the nickel–rhodium derivatives (**3**–**5**) undergo decomposition, even in an inert atmosphere. They are soluble in dichloromethane, acetone, nitroethane, and acetonitrile. In nitroethane solution the compounds **1**–**6** behave as 1:2 electrolytes, whereas **7** is a 1:1 electrolyte (Table I). The complexes **1**, **2**, and **6** are paramagnetic, with room-temperature magnetic moments (Table I) corresponding to a doublet ground state. Compound **7** is essentially diamagnetic at room temperature, whereas **3**, **4**, and **5** have low μ_{eff} values that depend on temperature and are somewhat sensitive to the nature of the counterion and of the solvent in the lattice. Such μ_{eff} values, ranging from 1.1 to 1.6 μ_B at room temperature (Table I), decrease smoothly to 0.7–0.8 μ_B at ca. 130 K and level off at lower temperatures. It should be pointed out that the magnetic properties of the complexes (**1**, **2**, **6**) having 31 electrons in their valence shell[9] match those of the isoelectronic 3d complexes previously investigated, whereas the magnetic behavior of the 32-electron complexes (**3**–**5**, **7**) differs markedly from that of the isoelectronic 3d compounds. In fact, the latter have been found to possess a triplet ground state.[2] The determination of the structure of a nickel–rhodium derivative (**4**)

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(15) Sarma, R.; Ramirez, F.; McKeever, B.; Chaw, Y. F.; Marecek, J. F.; Nierman, D.; McCaffery, T. M. *J. Am. Chem. Soc.* **1977**, *99*, 5289.

(16) See paragraph at the end of paper regarding supplementary material.

Table XII. Selected Bond Lengths (Å) and Angles (Deg) for [(triphos)Co-μ-(η^3-P_3)Rh(triphos)]$(BPh_4)_2 \cdot 2(CH_3)_2CO$ (**2**)

M1-P1	2.225 (7)	M2-P4	2.224 (6)
M1-P2	2.219 (7)	M2-P5	2.217 (8)
M1-P3	2.220 (9)	M2-P6	2.214 (10)
M1-P7	2.317 (10)	M2-P7	2.298 (7)
M1-P8	2.314 (8)	M2-P8	2.294 (10)
M1-P9	2.337 (9)	M2-P9	2.327 (11)
P7-P8	2.206 (10)	P8-P9	2.195 (12)
P7-P9	2.198 (13)		
P1-M1-P2	95.2 (2)	P4-M2-P5	92.2 (3)
P1-M1-P3	91.8 (3)	P4-M2-P6	94.1 (3)
P2-M1-P3	91.1 (3)	P5-M2-P6	93.0 (3)
P7-M1-P8	56.9 (3)	P7-M2-P8	57.4 (3)
P7-M1-P9	56.4 (4)	P7-M2-P9	56.7 (3)
P8-M1-P9	56.3 (3)	P8-M2-P9	56.7 (3)
P1-M1-P7	136.1 (3)	P4-M2-P7	149.7 (3)
P1-M1-P8	89.4 (3)	P4-M2-P8	93.2 (3)
P1-M1-P9	129.8 (2)	P4-M2-P9	115.8 (3)
P2-M1-P7	88.7 (3)	P5-M2-P7	116.8 (3)
P2-M1-P8	130.4 (3)	P5-M2-P8	149.6 (4)
P2-M1-P9	134.6 (3)	P5-M2-P9	94.2 (3)
P3-M1-P7	131.9 (3)	P6-M2-P7	93.2 (3)
P3-M1-P8	138.2 (3)	P6-M2-P8	116.4 (4)
P3-M1-P9	92.8 (3)	P6-M2-P9	149.0 (3)

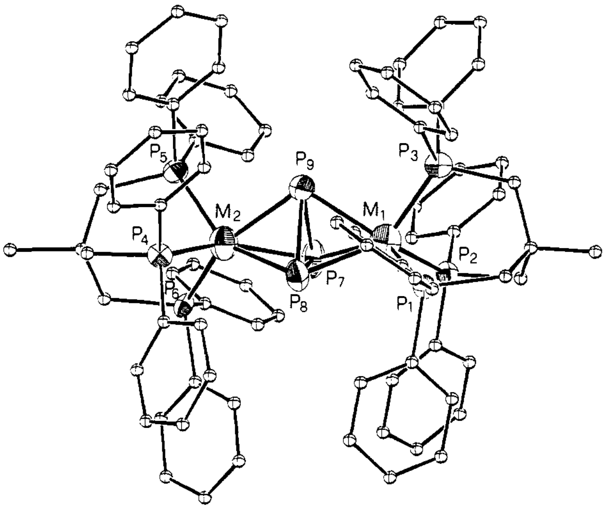

Figure 1. Perspective view of the [(triphos)Co-μ-(η^3-P_3)Rh(triphos)]$^{2+}$ cation.

Table XIII. Selected Bond Lengths (Å) and Angles (Deg) for [(triphos)Ni-μ-(η^3-P_3)Rh(triphos)]$(BF_4)_2 \cdot C_4H_8O$ (**4**)

M1-P1	2.322 (5)	M2-P4	2.295 (5)
M1-P2	2.219 (5)	M2-P5	2.208 (3)
M1-P3	2.283 (3)	M2-P6	2.343 (5)
M1-P7	2.383 (4)	M2-P7	2.334 (6)
M1-P8	2.311 (5)	M2-P8	2.368 (5)
M1-P9	2.476 (7)	M2-P9	2.558 (5)
P7-P8	2.315 (6)	P8-P9	2.152 (6)
P7-P9	2.147 (6)		
P1-M1-P2	92.1 (2)	P4-M2-P5	87.6 (2)
P1-M1-P3	94.8 (1)	P4-M2-P6	91.9 (2)
P2-M1-P3	89.0 (2)	P5-M2-P6	95.5 (2)
P7-M1-P8	59.1 (2)	P7-M2-P8	59.0 (2)
P7-M1-P9	52.4 (2)	P7-M2-P9	51.8 (2)
P8-M1-P9	53.3 (2)	P8-M2-P9	51.6 (2)
P1-M1-P7	94.2 (2)	P4-M2-P7	109.1 (2)
P1-M1-P8	153.2 (2)	P4-M2-P8	154.0 (2)
P1-M1-P9	110.3 (2)	P4-M2-P9	102.5 (2)
P2-M1-P7	119.5 (1)	P5-M2-P7	103.0 (2)
P2-M1-P8	102.6 (2)	P5-M2-P8	116.7 (2)
P2-M1-P9	155.9 (2)	P5-M2-P9	154.7 (2)
P3-M1-P7	149.7 (2)	P6-M2-P7	152.3 (2)
P3-M1-P8	107.6 (2)	P6-M2-P8	94.3 (2)
P3-M1-P9	97.5 (2)	P6-M2-P9	107.1 (2)

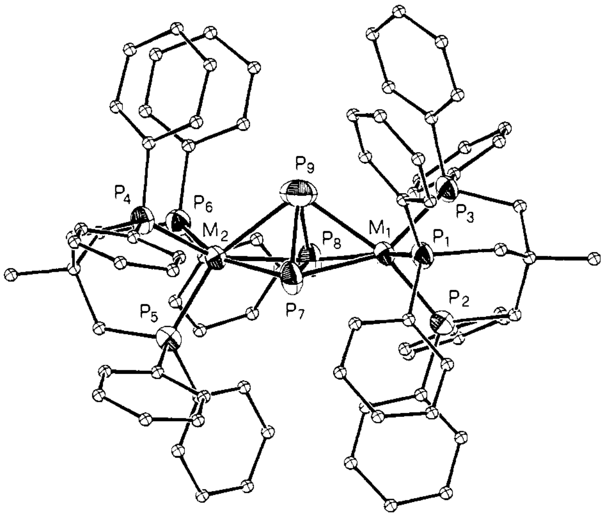

Figure 2. Perspective view of the [(triphos)Ni-μ-(η^3-P_3)Rh(triphos)]$^{2+}$ cation.

has proved to be of crucial importance, as discussed below, for an understanding of the factors which are responsible for such a discrepancy.

The structure of the dinuclear cation in the complex [(triphos)Co-μ-(η^3-P_3)Rh(triphos)]$(BPh_4)_2 \cdot 2(CH_3)_2CO$ (**2**) is similar to that existing in the complexes [(triphos)Co-μ-(η^3-P_3)Ni(triphos)]$(BPh_4)_2 \cdot 2(CH_3)_2CO$ (**8**) and [(triphos)Ni-μ-(η^3-P_3)Ni(triphos)]$(BPh_4)_2 \cdot 2.5(CH_3)_2CO$ (**9**) previously investigated.[2] The two triphos ligands form the external slices of the "triple-decker sandwich" while the *cyclo*-triphosphorus group is the internal layer. Each metal atom is bonded to the three phosphorus atoms of the bridging *cyclo*-P_3 group in a very distorted six-coordinate arrangement. Bond distances and angles in the coordination sphere of complex **2** are reported in Table XII. Figure 1 shows a perspective view of the cation. The mean values of the metal-phosphorus bond distances are lower than those existing in the dications of both complexes **8** and **9**,[2] in spite of the fact that the latter contain only 3d metal atoms: in particular, the M-P(triphos) distances average 2.22 Å (**2**), 2.24 Å (**8**), and 2.25 Å (**9**) and the M-P(η^3-P_3) distances 2.31 Å (**2**), 2.33 Å (**8**), and 2.35 Å (**9**). On the contrary, the P-P bond lengths in the triangular η^3-P_3 unit in complex **2** are larger (average 2.20 Å) than those found in compounds **8** and **9** (average 2.16 Å). Such features of the structure of complex **2** are indicative of stronger metal-ligand interactions in that compound. Finally, the M···M distance of 3.869 (6) Å in **2** is smaller than the metal-metal separations of 3.93 and 3.99 Å in complexes **8** and **9**, respectively. A structure analogous to that of compound **2** may be assigned to the complex [(triphos)Co-μ-(η^3-P_3)Ir(triphos)]$(BF_4)_2 \cdot CH_2Cl_2$ (**6**) on the basis of the close similarity of all their properties.

The structure of the dication in the complex [(triphos)Ni-μ-(η^3-P_3)Rh(triphos)]$(BF_4)_2 \cdot C_4H_8O$ (**4**) is grossly similar to those of the other dinuclear complexes (**2**, **8**, **9**), although it is less regular than the latter. Selected values of bond distances and angles appear in Table XIII, and a perspective view of the cation is shown in Figure 2. While the dinuclear complexes **2**, **8**, and **9** have idealized C_3 symmetry, the *cyclo*-triphosphorus group in complex **4** is shifted away from the line through the two metal centers along the plane normal to that line. In such an unsymmetrical setting the *cyclo*-P_3 group attains an irregular geometry, one of the P-P distances in the cycle (P_7-P_8 = 2.31 Å) being much larger than the other two (average 2.15 Å). The mean values of the M-P(triphos) and M-P(η^3-P_3) bond lengths in **4**, of 2.28 and 2.40 Å, respectively, are definitely larger than the corresponding values in **2**. Also the metal-metal distance of 4.041 (3) Å in **4** is much larger than that of 3.869 (6) Å in compound **2**.

The difference in size between the cations in compounds **2** and **4** should be mainly related to electronic factors. The importance of these factors is seen by a comparison of the isostructural complexes **2**, **8**, and **9**. In fact, the size of the cation, as indicated by the values of the M–P and M···M distances quoted above, increases from compound **2** (which has 31 electrons in its valence shell) through **8** (which has 32 valence electrons) up to **9** (which has 33 electrons). That is, the size increases with the number of valence electrons. Such effect accounts in part for the large difference between the dimensions of the cations in compounds **2** and **4** (the latter being a 32-electron compound). Also the loss of axial symmetry in **4**, which is caused by the electronic factors discussed below, may play a role in determining the above differences. The distribution of electron density in the valence shell of these complexes probably has so large stereochemical effects because the highest-occupied molecular orbitals (labeled 6e in ref 2) are predominantly formed by metal d orbitals directed toward the phosphorus atoms.

Turning to a consideration of the magnetic properties of these complexes, the discrepancy between the magnetic behavior of the present 32-electron compounds and that of the isoelectronic compounds containing only 3d metals has been pointed out above. This discrepancy can be rationalized on the basis of the results of the structural investigation of compound **4** using the approach that has been applied previously to the bonding in all of these triple-decker complexes.[2]

According to that model, the highest occupied molecular orbital, which is doubly degenerate in idealized C_3 symmetry, is allocated 1, 2, or 3 electrons in the complexes having 31, 32, or 33 valence electrons, respectively. Hence all of the 31–33-electron systems would be expected to undergo a distortion of Jahn–Teller type, tending to remove the orbital degeneracy. Consequently the largest energy gain by such a mechanism should occur for the 32-electron compounds since the orbital which is stabilized in the course of the distortion may then be occupied by two electrons (at the expense of some spin-pairing energy) leaving its destabilized partner unoccupied. In spite of this, approximate C_3 symmetry has been found for complexes **8** and **9** and is likely to exist for all of the other dinuclear complexes formed by two 3d metal atoms: the 32-electron complexes, in particular, having a triplet ground state, must possess effective C_3 symmetry. As shown by the structure of compound **4**, however, the replacement of at least one 3d metal atom in a 32-electron cation by a heavier transition metal is followed by loss of the axial symmetry. The factors that tip the balance in favor of the singlet state and of the distorted geometry associated with it may be identified with the higher strength of the ligand field and with the higher spin–orbit coupling constants of the heavier transition-metal atoms compared with those of the 3d metals. Such factors indeed magnify the degenerate levels splitting that are caused by distortions from axial symmetry, so that the energy gain by the mechanism described above becomes predominant, at least in the favorable case of the 32-electron complexes. The peculiar magnetic behavior of nickel–rhodium complexes **3**–**5** in the 100–300 K temperature range may be due to the fact that the higher lying triplet state is thermally accessible or that such state and the spin singlets from the lowest excited configurations provide substantial TIP contributions to the susceptibility of the compounds. On the other hand, the diamagnetism of the rhodium–rhodium derivative **7** is indicative of a larger single–triplet separation for that compound and is consistent with the fact that the trend toward distortion from axial symmetry should be strengthened by the presence of two 4d metal atoms in the cation. This latter view is supported by the comparison between the spectra of compounds **4** and **7** (see below).

The electronic spectra of the cobalt–rhodium complexes **1** and **2** are practically identical with each other and are similar to that of cobalt–iridium complex **6** (Table II). They are also similar to the spectra previously recorded for the analogous 3d complexes with 31 electrons in the valence shell, so that they may be assigned correspondingly.[2] An overall high energy shift of the bands is observed on going from the 3d metal derivatives through the rhodium to the iridium one, which is consistent with the expected increase in field strength.

The reflectance spectra of the complexes **3**–**5** are all similar to each other and to that of **7**, except for an overall shift and compression of the bands toward higher energies in the spectrum of the latter compound (Table II). At variance with the case of the 31-electron compounds, the absorption spectra of these 32-electron complexes differ dramatically from the corresponding solid-state spectra. Indeed the compounds are unstable in solution. The band at 7300 cm^{-1} in the reflectance spectra of **3**–**5** is at an unusually low frequency for compounds that are practically diamagnetic and may be assigned to a transition between the two components of the degenerate 6e level, which is split as a result of the distortion from C_3 symmetry. The shift toward higher energies of this band, as well as of all the others, in the spectrum of complex **7** is consistent with the overall increase of field strength in the presence of two rhodium atoms. Finally, the existence of a low-lying excited state and the distorted geometry of complex **4** may account for its instability in solution.

Acknowledgment. Thanks are expressed to Mr. F. Cecconi for technical assistance and to Mr. F. Nuzzi and Mr. G. Vignozzi for microanalyses.

Supplementary Material Available: Tables V–VII and IX–XI, atomic parameters for compounds **2** and **4**, and listings of structure factor amplitudes (46 pages). Ordering information is given on any current masthead page.