The last of these integrals is identically zero and the next to the last is simply the value of the overlap when the configuration is perfectly eclipsed. Hence the overlap depends on the twist angle χ according to the value of cos 2χ. For $\chi = 30°$ the δ overlap is reduced by a factor of 0.5 from its maximum value.

While it is an oversimplification to regard bond energy as a linear function of overlap, the two are related in approximately this way and thus we conclude that even for a twist of 30° the δ bond still retains about half of its maximum possible strength. It is worth pointing out that from 30 to 45° the value of cos 2χ drops sharply to zero so that a twist angle much greater than 30° would probably be inconsistent with retention of the δ bond. The value of $\chi = 39°$ found in the rhenium analogue of this structure allows only 21% of the maximum δ overlap.

The reduction by 0.5 of the δ bond strength would not be expected to affect the Mo–Mo bond distance very much since the δ component makes only a minor contribution to the total bond energy. In the case of $[Mo_2(SO_4)_4]^{4-}$ vs. $[Mo_2(SO_4)_4]^{3-}$ where the δ bond order changes from 1.0 to 0.5 the Mo–Mo distance increases by about 0.05 Å.[11] Unfortunately, there is no structure for an eclipsed $Mo_2Br_4(PR_3)_4$ molecule available for comparison with that of Mo_2Br_4(arphos). The most similar molecule available is probably $Mo_2Cl_4(SEt_2)_4$, which has an Mo–Mo distance of 2.144 (1) Å.[12] It has been reported[13] that the electronic spectra of $Mo_2Cl_4(SEt_2)_4$ and $Mo_2Cl_4(PBu_3)_4$ are very similar, so that the bond length in the latter may also be about 2.144 Å. Thus, the twisting in Mo_2Br_4(arphos)$_2$ may have caused a lengthening of the Mo–Mo bond by ca. 0.03 Å, which seems a reasonable magnitude.

Attempts to determine the Mo–Mo stretching frequency in Mo_2Br_4(arphos)$_2$ have been unsuccessful. The Raman spectrum recorded on a Cary 82 spectrometer using excitation from the argon laser line at 524.5 nm displayed no features significantly greater than the base line noise. The electronic spectra of a KBr pellet recorded at 5 K on a Cary 17D displayed no vibrational fine structure on any of the broad bands centered at about 795, 622, and 493 nm.

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Supplementary Material Available: A table of observed and calculated structure factors (11 pages). Ordering information is given on any current masthead page.

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cyclo-Triphosphorus and *cyclo*-Triarsenic as Ligands in "Double Sandwich" Complexes of Cobalt and Nickel

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Abstract: The reaction of white phosphorus or yellow arsenic with cobalt and nickel tetrafluoroborate in the presence of the tri(tertiary phosphine) 1,1,1-tris(diphenylphosphinomethyl)ethane, $CH_3C(CH_2PPh_2)_3$, triphos, gives a series of metal complexes each containing the novel cyclic P_3 or As_3 group. These compounds have the general formula $[M_2(D_3)(\text{triphos})_2]Y_n$ (M = Co, Ni; D = P, As; $Y^- = BF_4^-, BPh_4^-$; $n = 1, 2$). The X-ray structure determinations performed on the complexes $[Ni(P_3)(\text{triphos})_2](BPh_4)_2\cdot 2.5(CH_3)_2CO$, $[Co,Ni(P_3)(\text{triphos})_2](BPh_4)_2\cdot 2(CH_3)_2CO$, and $[Co_2(As_3)(\text{triphos})_2](BPh_4)_2$ have shown that the compounds are of double-sandwich structure with two molecules of triphos as external "slices". The internal layer in each complex is formed by an unprecedented *cyclo*-triphosphorus or *cyclo*-triarsenic unit acting as a 3π system which connects the two metal atoms. These double-decker $[(\text{triphos})M\text{-}\mu\text{-}(\eta^3\text{-}D_3)M(\text{triphos})]Y_n$ complexes are air stable. The number of valence electrons ranges from 31 to 34 along the series of complexes. The number of unpaired electrons, calculated on the basis of the magnetic moments, varies from zero to two electrons for the dinuclear complex cation. This is rationalized by a qualitative MO approach.

Introduction

In recent years much interest has been roused by polynuclear metal complexes having multiple-sandwich structure.[1] The ring systems acting as layers in the "sandwich" metal complexes so far described are delocalized "pure" carbocyclic groups, heterocyclic groups containing boron, nitrogen, or sulfur as heteroatoms, or borazine-type rings.

We have found two new non-carbon-containing ring systems capable of functioning as internal layers in "double sandwich" metal complexes: they are the *cyclo*-triphosphorus, η^3-P_3, and the *cyclo*-triarsenic, η^3-As_3, groups. These molecular units are capable of bridging two metal atoms in complexes and act as 3π systems. The external "slices" of such double-decker compounds are formed by two molecules of the tri(tertiary phosphine) 1,1,1-tris(diphenylphosphinomethyl)ethane, $CH_3C(CH_2PPh_2)_3$, triphos.

The complexes obtained have the general formula $[(\text{triphos})M\text{-}\mu\text{-}(\eta^3\text{-}D_3)M(\text{triphos})]Y_n$, where M = Co, Ni; D = P, As; $Y^- = BF_4^-, BPh_4^-$; $n = 1, 2$. The compounds with $n = 2$ are obtained by reaction of THF solutions of white phos-

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

no.	compd		%C	%H	%Co	%Ni	%P	%As	μ_B[a]	ΛM,[b] cm^2/Ω mol
I	$[Co_2(P_3)(triphos)_2](BF_4)_2$	calcd	60.28	4.81	7.21		17.06		2.20	156
		found	59.54	5.23	6.70		16.92			
II	$[Co_2(P_3)(triphos)_2](BPh_4)_2 \cdot 2(CH_3)_2CO$	calcd	73.61	5.94	5.35		12.65		2.02	103
		found	73.54	6.03	5.06		12.59			
III	$[Co_2(As_3)(triphos)_2](BF_4)_2$	calcd	55.78	4.45	6.68		10.53	12.73	2.10	160
		found	55.30	4.74	6.45		10.46	12.69		
IV	$[Co_2(As_3)(triphos)_2](BPh_4)_2 \cdot 2(CH_3)_2CO$	calcd	69.45	5.61	5.05		7.96	9.63	2.22	106
		found	69.78	5.76	4.75		7.52	9.38		
V	$[Co_2(P_3)(triphos)_2](BPh_4)$	calcd	71.55	5.55	6.62		15.66		3.13	42
		found	72.06	5.57	6.55		15.87			
VI	$[Co_2(As_3)(triphos)_2](BPh_4)$	calcd	66.61	5.17	6.17		9.72	11.76	3.29	55
		found	66.85	5.35	6.00		9.67	11.71		
VII	$[CoNi(P_3)(triphos)_2](BPh_4)_2 \cdot 2(CH_3)_2CO$	calcd	73.62	5.95	2.68	2.67	12.66		3.14	104
		found	73.46	6.16	2.59	2.58	13.09			
VIII	$[Ni_2(P_3)(triphos)_2](BF_4)_2$	calcd	60.30	4.81		7.19			2.09	150
		found	60.00	5.14		6.95				
IX	$[Ni_2(P_3)(triphos)_2](BPh_4)_2 \cdot 2.5(CH_3)_2CO$	calcd	73.61	5.93		5.23	12.42		2.00	96
		found	73.61	6.47		5.15	12.92			
X	$[Ni_2(As_3)(triphos)_2](BF_4)_2$	calcd	55.78	4.45		6.65	10.53	12.73	2.01	158
		found	55.39	4.50		6.58	10.60	12.28		
XI	$[Ni_2(As_3)(triphos)_2](BPh_4)_2 \cdot 2(CH_3)_2CO$	calcd	69.47	5.61		5.03	7.96		2.20	107
		found	69.86	5.84		4.88	8.67			
XII	$[Ni_2(P_3)(triphos)_2](BPh_4) \cdot (CH_3)CO$	calcd	71.27	5.71		6.39	15.17		0	45
		found	71.63	5.89		6.25	15.95			
XIII	$[Ni_2(As_3)(triphos)_2](BPh_4)$	calcd	66.62	5.17		6.15	9.73	11.76	0	47
		found	66.27	5.19		6.03	9.86	11.71		

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

phosphorus or yellow arsenic with cobalt(II) or nickel(II) tetrafluoroborate in the presence of triphos. The derivatives with $n = 1$ are formed by reaction of the former complexes with $NaBH_4$.

Complete X-ray structural analyses have been carried out for the compounds $[(triphos)Ni\text{-}\mu\text{-}(\eta^3\text{-}P_3)Ni(triphos)](BPh_4)_2 \cdot 2.5(CH_3)_2CO$, $[(triphos)Co\text{-}\mu\text{-}(\eta^3\text{-}P_3)Ni(triphos)](BPh_4)_2 \cdot 2(CH_3)_2CO$, and $[(triphos)Co\text{-}\mu\text{-}(\eta^3\text{-}As_3)Co(triphos)](BPh_4)_2$.

A preliminary account of part of this work has already been published.[2]

Experimental Section

Reagents. The ligand triphos was prepared by the method previously described.[3] Yellow arsenic was prepared by an improved (see below) Erdmann and von Unruh method.[4] All other chemicals were reagent grade and were used without further purification.

Preparation of the Complexes. All the reactions were carried out under dry nitrogen, using deoxygenated solvents, and the complexes were dried in a stream of dry nitrogen. The yields were generally more than 60%.

$[(triphos)M\text{-}\mu\text{-}(\eta^3\text{-}P_3)M(triphos)](BF_4)_2$ (M = Co, Ni). $[Ni(H_2O)_6](BF_4)_2$ (or $[Co(H_2O)_6](BF_4)_2$) (0.34 g, 1 mmol) in 15 mL of ethanol was added to a solution of 0.62 g (1 mmol) of triphos in 20 mL of THF; 0.12 g (1 mmol) of white phosphorus in 30 mL of THF was added to the resulting solution at room temperature. After ca. 1 h the solution was filtered in air and concentrated at room temperature. The crystals so formed were filtered off and washed with ethanol and light petroleum. The complex was recrystallized from acetone/1-butanol.

$[(triphos)M\text{-}\mu\text{-}(\eta^3\text{-}As_3)M(triphos)](BF_4)_2$ (M = Co, Ni). Gray arsenic (7 g) was heated for ca. 90 min at 560–580 °C as previously described,[4] and the vapors of yellow arsenic were absorbed at ca. 0 °C by 250 mL of THF. The solution was filtered off and then concentrated to 150 mL in the dark, at room temperature. To this solution 0.68 g (2 mmol) of $[Ni(H_2O)_6](BF_4)_2$ (or $[Co(H_2O)_6](BF_4)_2$) in 20 mL of ethanol and 1.25 g (2 mmol) of the ligand in 30 mL of acetone were added. The resulting mixture was heated in the dark on a water bath under a nitrogen stream for 20 min, then concentrated in the light to ca. 30 mL in a stream of nitrogen. The crystals so formed were filtered off, washed with THF and light petroleum, and dried in vacuo.

$[(triphos)M\text{-}\mu\text{-}(\eta^3\text{-}D_3)M(triphos)](BPh_4)_2 \cdot 2(CH_3)_2CO$ (M = Co, Ni; D = P, As). A typical procedure is outlined for D = P, M = Ni. The complex $[(triphos)Ni\text{-}\mu\text{-}(\eta^3\text{-}P_3)Ni(triphos)](BF_4)_2$ (18 g, 1 mmol) was dissolved in 50 mL of acetone. To this solution 0.32 g (1 mmol) of $NaBPh_4$ dissolved in 40 mL of 1-butanol was added. After ca. 2 h dark crystals precipitated. They were filtered off, washed with butanol and light petroleum, and dried in vacuo.

$[(triphos)M\text{-}\mu\text{-}(\eta^3\text{-}D_3)M(triphos)]BPh_4$ (M = Co, Ni; D = P, As). A typical procedure is outlined for D = P, M = Ni. To a solution of the $[(triphos)Ni\text{-}\mu\text{-}(\eta^3\text{-}P_3)Ni(triphos)](BPh_4)_2 \cdot 2(CH_3)_2CO$ complex (1.1 g, 0.5 mmol) in 50 mL of acetone, 19 mg (0.5 mmol) of sodium tetrahydroborate dissolved in 20 mL of ethanol was added dropwise, at room temperature. The solution was then concentrated in a stream of nitrogen. The crystals which precipitated were filtered off and washed with alcohol, water, alcohol again, and then light petroleum before being dried in a current of nitrogen. The complex $[(triphos)Ni\text{-}\mu\text{-}(\eta^3\text{-}P_3)Ni(triphos)]BPh_4$ crystallizes with one molecule of acetone.

$[(triphos)Co\text{-}\mu\text{-}(\eta^3\text{-}P_3)Ni(triphos)](BPh_4)_2 \cdot 2(CH_3)_2CO$. The complex $[(triphos)Co(\eta^3\text{-}P_3)]$[2] (0.77 g, 1 mmol) in 150 mL of CH_2Cl_2 was added, at room temperature, to a solution obtained by mixing 0.62 g (1 mmol) of triphos in CH_2Cl_2 (15 mL) and 0.34 g (1 mmol) of $[Ni(H_2O)_6](BF_4)_2$ in ethanol (20 mL). Solid $NaBPh_4$ (0.64 g, 2 mmol) was then added to the resultant red-brown solution. A brisk stream of nitrogen was passed through the solution until sufficient methylene chloride had evaporated and crystallization was initiated. The crystalline product was filtered off and washed with ethanol and light petroleum ether. The complex was recrystallized from acetone/1-butanol mixture.

The $[(triphos)Co\text{-}\mu\text{-}(\eta^3\text{-}P_3)Co(triphos)](BPh_4)_2$ complex can also be prepared by reacting $[(triphos)Co(\eta^3\text{-}P_3)]$[2] with equimolar amounts of $[Co(H_2O)_6](BF_4)_2$ and triphos.

Physical Measurements. Infrared and electronic spectra, conductivity measurements, and magnetic susceptibilities were recorded by previously described methods.[5] The EPR spectra were recorded on a Varian E9 apparatus.

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

Collection and Reduction of X-ray Intensity Data. The investigation of the structure of the "mixed" double-sandwich compound VII (the

Table II. Electronic Spectra

no.	compd		absorption max,[a] cm^{-1} (ϵ_M for soln)
II	[$Co_2(P_3)(triphos)_2](BPh_4)_2$	a	9500 sh, 14 300, 18 200, 23 800
	$\cdot 2(CH_3)_2CO$	b	13 800 (5200), 18 000 (15 300), 23 500 (12 500), 26 600 sh
IV	[$Co_2(As_3)(triphos)_2](BPh_4)_2$	a	11 800 sh, 13 800, 17 200, 22 700, 26 700
	$\cdot 2(CH_3)_2CO$	b	13 800 (4600), 17 000 (13 000), 22 200 (11 000), 28 600 sh
V	[$Co_2(P_3)(triphos)_2](BPh_4)$	a	10 500, 17 500, 24 100, 27 400
		b	9300 sh, 10 300 (919), 17 200 (12 240), 24 400 sh
VI	[$Co_2(As_3)(triphos)_2](BPh_4)$	a	9800, 16 400, 22 700, 26 700
		b	9700 (771), 16 100 (9987), 22 500 (11 968), 26 800 (24 986)
VII	[$CoNi(P_3)(triphos)_2](BPh_4)_2$	a	8200 sh, 10 500, 18 200, 23 500
	$\cdot 2(CH_3)_2CO$	b	8300 sh, 10 500 (2360), 18 500 (11 045), 22 700 (11 270)
IX	[$Ni_2(P_3)(triphos)_2](BPh_4)_2$	a	10 000, 16 700, 19 200, 22 700
	$\cdot 2.5(CH_3)_2CO$	b	9700 (700), 15 600 (2110), 19 000 sh, 22 200 (24 200)
XI	[$Ni_2(As_3)(triphos)_2](BPh_4)_2$	a	9000, 18 200, 22 200, 26 700
	$\cdot 2(CH_3)_2CO$	b	9300 (320), 14 900 (1420), 18 200 sh, 21 500 (19 000)
XII	[$Ni_2(P_3)(triphos)_2](BPh_4)$	a	17 900, 22 200, 26 700
	$\cdot (CH_3)_2CO$	b	17 500 (3520), 22 200 (32 380), 27 800 (27 400)
XIII	[$Ni_2(As_3)(triphos)_2](BPh_4)$	a	16 400, 20 800, 25 000
		b	16 100 (3025), 20 800 (24 919), 26 700 (23 518)

[a] Key: a, solid; b, 1,2-dichloroethane solution.

Table III. Summary of Crystal Data, Intensity Collection, and Refinement for [(triphos)Ni-μ-(η^3-P_3)Ni(triphos)]$(BPh_4)_2 \cdot 2.5(CH_3)_2CO$ (IX), [(triphos)Co-μ-(η^3-P_3)Ni(triphos)]$(BPh_4)_2 \cdot 2(CH_3)_2CO$ (VII), and [(triphos)Co-μ-(η^3-As_3)Co(triphos)]$(BPh_4)_2$ (IV)

	IX	VII	IV
formula	$C_{137.5}H_{133}B_2Ni_2O_{2.5}P_9$	$C_{136}H_{130}B_2Co_1Ni_1O_2P_9$	$C_{130}H_{118}As_3B_2Co_2P_6$
formula weight	2243.4	2214.6	2230.5
a, Å	17.532 (7)	17.550 (8)	17.576 (11)
b, Å	15.860 (6)	15.859 (7)	15.832 (10)
c, Å	13.880 (5)	13.833 (5)	13.751 (9)
α, deg	111.77 (4)	111.65 (4)	111.33 (6)
β, deg	91.22 (4)	91.17 (4)	91.20 (6)
γ, deg	115.35 (4)	115.29 (4)	115.26 (6)
V, Å^3	3163.6	3162.0	3152.2
Z	1	1	1
density, g cm^{-3}	1.177 (calcd) 1.20 (obsd)	1.163 (calcd) 1.18 (obsd)	1.175 (calcd) *a*
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
crystal dimensions, mm	0.40 × 0.20 × 0.15	0.10 × 0.20 × 0.30	0.10 × 0.20 × 0.20
crystal shape	flat prism with six well-formed faces	flat crystal with eight irregularly developed faces	flat crystal with eight irregularly developed faces
temp, °C	22	22	22
radiation	Mo Kα (λ 0.7107 Å), graphite monochromatized	Mo Kα	Mo Kα
μ, cm^{-1}	4.6	4.4	11.6
transmission factors	0.866-0.922	*b*	*b*
scan speed, 2ϑ deg/min	6.0	4.5	4.5
scan range, deg	1.0, symmetric	1.0	1.0
background	$t_{b1} = t_{b2} = \frac{1}{2}t_s$[c]	$t_{b1} = t_{b2} = \frac{1}{2}t_s$	$t_{b1} = t_{b2} = \frac{1}{2}t_s$
2ϑ limits, deg	4.0-46.0	4.0-40.0	4.0-40.0
unique data used ($F_o^2 > 3\sigma(F_o^2)$)	5758	4235	2233
final no. of variables	417	403	235
R	0.071	0.089	0.137
R_w	0.088	0.107	0.162
error in observation of unit wt, electrons	1.81	1.16	1.72

[a] Not measured owing to experimental difficulties. [b] Correction for absorption not applied (see text): transmission factors range estimated to be less than that for compound IX. [c] t_{b1}, t_{b2} = background count times; t_s = total scan time.

numbering of compounds is as in Table I) was undertaken, after the structure of compound IX had been solved,[2] in order to know whether the approach that had been adopted in rationalizing the properties of the "homonuclear" compounds could be safely extended to the case of the "mixed" one. Crystals of the η^3-As_3 derivatives were generally unsuitable for X-ray investigation as their diffraction pattern consisted of broad, low-intensity peaks. After repeated attempts several sets of (poor quality) data were collected for the cobalt compound IV. Results obtained using the "best" set of data are reported here. It was assumed that even inaccurate results for the structure of compound IV would be of interest, in view of the novelty of these *cyclo*-triarsenic compounds.

Data were collected following essentially the same procedure for the three compounds IV, VII, and IX. A Philips PW 1100 automated diffractometer and monochromated Mo Kα radiation (λ 0.7107) were used for all operations. Details on crystal data, intensity collection, and refinement are reported in Table III. The three compounds are isomorphous to each other. Lattice constants were determined by least-squares refinement of the angular positions of 24 reflections for each compound. Those of compound IV were observed to change

Table IV. Atomic Parameters for the Structure of $[(\text{triphos})\text{Ni-}\mu\text{-}(\eta^3\text{-P}_3)\text{Ni}(\text{triphos})](\text{BPh}_4)_2\cdot 2.5(\text{CH}_3)_2\text{CO}$[a] (All Quantities $\times 10^4$)

atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ni1[b]	1145	46	51	320 (11)	367(11)	426 (12)	185 (9)	77 (9)	156 (9)
Ni2	−1179 (1)	−79 (2)	−84 (2)	308 (11)	362 (11)	419 (12)	188 (9)	89 (9)	156 (9)
P1	1422 (3)	−995 (3)	−1337 (3)	368 (22)	391 (23)	422 (25)	214 (19)	84 (19)	112 (19)
P2	2320 (3)	1506 (3)	304 (3)	343 (22)	387 (23)	518 (27)	164 (19)	86 (19)	217 (21)
P3	1778 (3)	−212 (3)	1257 (3)	373 (22)	410 (24)	445 (25)	187 (19)	31 (19)	185 (20)
P4	−2381 (3)	−1535 (3)	−1082 (3)	350 (22)	387 (23)	454 (25)	160 (19)	69 (19)	155 (20)
P5	−1768 (3)	260 (3)	1351 (3)	431 (23)	483 (26)	419 (25)	264 (21)	140 (19)	180 (21)
P6	−1464 (3)	917 (3)	−682 (3)	338 (22)	423 (24)	548 (27)	211 (19)	118 (19)	243 (21)
P7	324 (3)	939 (3)	358 (4)	366 (25)	438 (26)	939 (37)	213 (21)	61 (24)	187 (26)
P8	−219 (3)	−562 (4)	−971 (4)	422 (25)	660 (31)	523 (28)	337 (24)	65 (21)	108 (24)
P9	−180 (3)	−422 (4)	648 (4)	420 (25)	837 (34)	693 (32)	400 (25)	205 (23)	425 (28)
F rel, scale factor = 21 498									

[a] In the tables of atomic parameters standard deivations on the last significant digits are given in parentheses. Anisotropic temperature factors are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + \ldots + 2U_{12}hka^*b^* + \ldots)$; this form is used throughout. [b] Positional parameters of this atom not refined (see text).

slightly between crystals chosen from different batches. The intensities of three standard reflections measured every 100 min revealed an overall linear decrease of ca. 15 (IX), 5 (VII), and 9% (IV) in intensities. Data sets, properly rescaled to account for the small amount of decomposition, were processed in the usual way, a value of 0.04 for p being used in the calculation of the $\sigma(I)$'s.[6] A correction for absorption was applied to the intensities of compound IX but not to those of the other two compounds, owing to the irregular shape of the crystals and, in the case of compound IV, to the overall bad quality of the data. The principal computer programs used for the crystallographic calculations have been described.[7]

Determination and Refinement of the Structures. The structure of compound IX was solved by standard heavy-atom techniques. The positions of all nonhydrogen atoms were determined from Fourier syntheses. In the full-matrix least-squares refinement the function $\Sigma w(|F_o| - |F_c|)^2$ was minimized with weights $w = 1/\sigma^2(F_o)$. The atomic scattering factors were taken from ref 8 and anomalous dispersion terms for the nickel and phosphorus atoms were included in F_c.[9] The agreement factors are defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2}$. 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 $P1$ space group is undefined. A ΔF Fourier calculated at $R = 0.12$ showed four groups of three to four diffuse peaks, with heights 0.6–1.2 e Å^{-3} in different parts of the unit cell. Such peaks were attributed to acetone molecules in highly disordered positions; presence of the solvent in the lattice was also indicated by the IR, elemental analysis, and density data. The disorder affecting the position of each molecule was predominantly, but not only, threefold: from examination of the difference synthesis it was impossible to distinguish between the positions of the oxygen and of the methyl carbon atoms. Rigid group refinement in which three properly weighted models of the acetone molecule, rotated by ca. 120° with respect to each other, were introduced into the same region of space failed owing to the high correlations between the parameters. The model which was finally adopted for each solvent molecule consisted of a regular triangular arrangement of carbon atoms about a central carbon atom (C–C = 1.44 Å, weighted average of the C–C and C–O distances in the acetone molecule). Rigid group refinement was performed on four such "molecules" applying an overall temperature factor and imposing a damping factor on all parameter shifts. This refinement slowly converged, yielding positions which agreed with those of the highest peaks in the difference Fourier. The occupancy factors of the solvent sites were refined in separate sets of cycles. Their values are consistent with estimates of the overall electron density in the appropriate regions of the difference Fourier and their sum, of 2.5, reasonably accounts for the density and elemental analysis data for this compound. Parameters from the above refinement of the solvent were used without further change in the final set of cycles. The fixed contribution of the solvent to the F_c produces an improvement of ca. 0.009 in R. Hydrogen atoms bonded to the cation and to the anion carbon atoms were introduced in calculated positions (C–H = 1.00 Å) by the procedure described previously[7] and their fixed contribution was added to the F_c. The idealized positions of the methyl hydrogen atoms were calculated by least-squares fitting to the positions observed in a ΔF Fourier. Refinement converged to the R value of 0.071. A final ΔF Fourier showed few diffuse peaks with heights $\leq$0.4 e Å^{-3} in the regions occupied by the solvent. A refinement performed on the structure of the enantiomer did not produce a significant change in R or in the atomic coordinates (shifts $\leq$3). Results are reported for the model which gave (slightly) better agreement with the expected values for the bond distances and angles about the nongroup carbon atoms.

The structure of the "mixed" compound VII was refined following the same procedure as for compound IX, using as initial values of the atomic coordinates those from the structure of the latter compound. Special consideration was required for the metal atom and solvent contributions. Attempts to assign the cobalt and the nickel atom positions were based mainly on (a) comparison between values of the thermal factors of the two metal sites at the end of refinements in which these were assigned identical form factors, (b) refinements in which the scattering factor of cobalt was assigned to one metal site and that of nickel to the other site, the two alternative assignments being made in separate refinements, (c) refinement, imposing appropriate constraints, of the cobalt and nickel population parameters for both metal sites. The alternative models gave identical results and no difference could be detected between the two sites, which appear to be statistically occupied by both metal atoms, with equal probability, in the solid. Therefore, in the following refinement the average of the scattering factors of cobalt and nickel was assigned to each one of the metal sites. The essential identity of the temperature factors of the two "metals" and that of the dimensions of the coordination about the two metal centers later confirmed that this model was correct. No anomalous dispersion correction was applied. A ΔF Fourier calculated at $R = 0.098$ showed two sets of diffuse peaks with heights ca. 1.0 e Å^{-3} and a third set of peaks with lower heights in three regions which were occupied by the solvent in the structure of compound IX. The model described above was used for the solvent also in this case and refinement converged yielding acceptable positions for two solvent "molecules". The position of the third one, which corresponded to the set of lower peaks in the map, was affected by large esd's and it oscillated during the refinement so that the molecule formed short contact distances with other parts of the structure. In view of these difficulties and of the fact that the occupancy of that solvent site was probably low, such molecule was excluded from the refinement. The population parameters of the other two sites were slightly less than one and were rounded to an integer in the final calculations. The number of two acetone molecules per unit cell agrees with the density and elemental analysis data. Although the model adopted for the solvent in compounds IX and VII is not very accurate, it may be considered satisfactory enough to derive the desired chemical information. The fixed contribution of the hydrogen atoms was calculated as for compound IX. A difference Fourier calculated at $R = 0.090$ showed residual density ($\leq$0.6 e Å^{-3}) in the position of the acetone molecule that had been excluded from the model and few additional peaks close of the positions of the other two solvent molecules and to those of the metal atoms. Refinement converged to the R value of 0.089.

The structure of the *cyclo*-triarsenic derivative IV was refined using a very simplified model in view of the small number and bad quality of the data. Anisotropic thermal factors were assigned to the arsenic atoms. Individual isotropic thermal parameters were assigned to the cobalt and phosphorus atoms. As the temperature factors of few light atoms tended to assume negative values, the following constraints were imposed: $U(\mathrm{B1}) = U(\mathrm{B2})$, $U(\mathrm{C}_i) = U(\mathrm{C}_j)$ (C_i, C_j = nonphenyl carbon atoms). Phenyls were refined as rigid groups with an overall U value for each group. A damping factor of 0.5 was applied to all parameters shifts. Anomalous dispersion terms were included for arsenic, cobalt, and phosphorus. The hydrogen atoms contribution was added. A ΔF Fourier calculated at $R = 0.14$ showed few peaks with height 1.0-1.5 e Å^{-3} close to the heavy-atom positions and residual density in three regions which are occupied by the solvent in the structure of compound IX. Attempts to include the solvent in the model of the structure failed owing to the existence of several short contacts and to oscillations in values of the parameters during the refinement. Therefore, in spite of the evidence from the IR and elemental analysis data for presence of the solvent in the structure, this was not considered further; indeed the model was already oversimplified. For this reason the solvent is not included in the formula of compound IV where reference to the structure of that compound is made. The final R value is 0.137.

The final positional and thermal parameters appear in Tables IV-XV.[10] A listing of the observed and calculated structure amplitudes is available.[10]

Results and Discussion

All the complexes are air stable both in the solid state and in solution. They are soluble in methylene chloride, acetone, nitroethane, and acetonitrile. In the last solvent the nickel derivatives undergo rapid decomposition. In nitroethane solution the compounds $[\mathrm{M_2(D_3)(triphos)_2}]\mathrm{Y_2}$ and $[\mathrm{M_2(D_3)(triphos)_2}]\mathrm{Y}$ behave as 1:2 and 1:1 electrolytes, respectively.

The room temperature effective magnetic moments of the dinuclear complexes (Table I) are in the ranges 3.13-3.29 (compounds V, VI, and VII), 2.00-2.20 (compounds I, II, III, IV, VIII, IX, X, and XI) and 0.0 μ_B (compounds XII and XIII), corresponding to triplet, doublet, or singlet ground states, respectively. The μ_B values of the paramagnetic compounds do not vary with the temperature in the range 293-84 K.

The crystal structures of the three isomorphous compounds $[\mathrm{(triphos)Ni}\text{-}\mu\text{-}(\eta^3\text{-}\mathrm{P_3})\mathrm{Ni(triphos)}](\mathrm{BPh_4})_2{\cdot}2.5(\mathrm{CH_3})_2\mathrm{CO}$ (IX), $[\mathrm{(triphos)Co}\text{-}\mu\text{-}(\eta^3\text{-}\mathrm{P_3})\mathrm{Ni(triphos)}](\mathrm{BPh_4})_2{\cdot}2(\mathrm{CH_3})_2\mathrm{CO}$ (VII), and $[\mathrm{(triphos)Co}\text{-}\mu\text{-}(\eta^3\text{-}\mathrm{As_3})\mathrm{Co(triphos)}](\mathrm{BPh_4})_2$ (IV), determined by X-ray diffraction, consist of dinuclear complex cations of type $[\mathrm{(triphos)M}\text{-}\mu\text{-}(\eta^3\text{-}\mathrm{D_3})\mathrm{M'(triphos)}]^{2+}$ and of tetraphenylborate anions. There are, in addition, acetone molecules of crystallization interspersed in the lattice. The geometries of the complex cations are essentially the same in the three compounds. Each metal atom is bonded to the three phosphorus atoms of one triphos ligand and to the three atoms of the bridging (η^3-$\mathrm{D_3}$) group in a very distorted six-coordinate arrangement. The same double-sandwich structure may be assigned to the other complexes described in this paper, on the basis of their physical properties. Values of bond distances and angles in the coordination sphere for the complexes IV, VII, and IX are reported in Table XVI. Figure 1 shows a perspective view of the $[\mathrm{(triphos)Ni}\text{-}\mu\text{-}(\eta^3\text{-}\mathrm{P_3})\mathrm{Ni(triphos)}]^{2+}$ cation. The inner skeleton of the $[\mathrm{(triphos)Co}\text{-}\mu\text{-}(\eta^3\text{-}\mathrm{As_3})\mathrm{Co(triphos)}]^{2+}$ cation is shown in Figure 2.

The arrangement of the phosphorus donor atoms about the two metal centers in each complex is slightly different, as the triphos and the (η^3-$\mathrm{D_3}$) ligands are rotated by different amounts with respect to each other in the two parts of the double sandwich about the axis passing through the two metal atoms. Such asymmetry is clearly revealed by the values of the P(triphos)-M-P(ring) angles (Table XVI) and can be ascribed to steric effects which impose an overall low symmetry on the coordination shell; the idealized symmetry is C_3. The M-P(triphos) bond distances in the three compounds are within the range usually found for the M-P bonds formed by this ligand.[11] The M-P(ring) bond distances in compounds VII and IX, which range from 2.32 to 2.38 Å, are longer than those of 2.30-2.32 Å found in the mononuclear $[\mathrm{(triphos)Co}(\eta^3\text{-}\mathrm{P_3})]$ and $[\mathrm{(np_3)Co}(\eta^3\text{-}\mathrm{P_3})]$ ($\mathrm{np_3} = \mathrm{N(CH_2CH_2PPh_2)_3}$) complexes;[2,12] this is probably due to steric interactions between the two triphos ligands in the dinuclear compounds. The Co-As average distance of 2.42 (2) Å in IV is close to that of 2.439 (5) Å found in the compound $\mathrm{As_3Co(CO)_3}$.[13] The mean value of the P-P bond distances [2.164 (10) Å] within the *cyclo*-triphosphorus unit is identical for compounds VII and IX. It is smaller than the value of 2.21 Å found in the $\mathrm{P_4}$ molecule[14] and is slightly longer than the 2.13-2.14 Å values found in the monomeric cobalt compounds.[2,12] The mean value of the As-As distance, 2.43 (2) Å, in compound IV matches that in the $\mathrm{As_4}$ molecule[14] as well as that found in a recently determined organo-*cyclo*-triarsane.[15] On the other hand it is longer than the 2.372 (5) Å found in $\mathrm{As_3Co(CO)_3}$.[13]

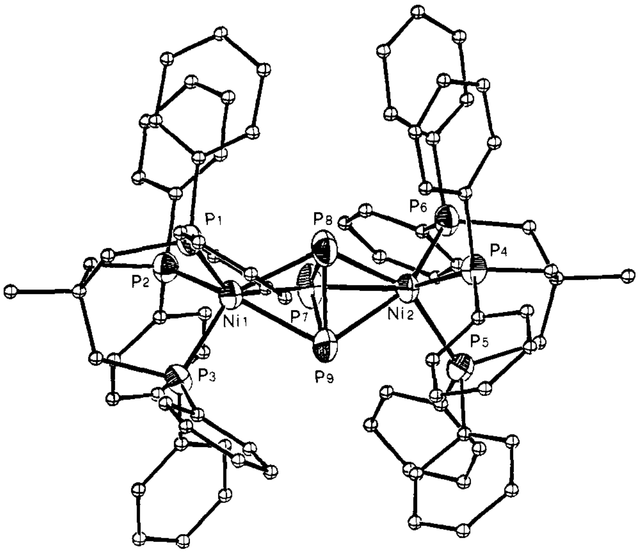

Figure 1. Perspective view of the $[\mathrm{(triphos)Ni}\text{-}\mu\text{-}(\eta^3\text{-}\mathrm{P_3})\mathrm{Ni(triphos)}]^{2+}$ cation.

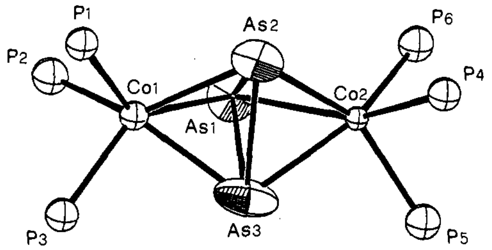

Figure 2. Inner skeleton of the $[\mathrm{(triphos)Co}\text{-}\mu\text{-}(\eta^3\text{-}\mathrm{As_3})\mathrm{Co(triphos)}]^{2+}$ cation.

This is the first time that the *cyclo*-$\mathrm{P_3}$ and *cyclo*-$\mathrm{As_3}$ units have been found as internal layers in double-sandwich metal complexes. Up to now only two mononuclear complexes have been reported where a $\mathrm{Co(CO)_3}$ group is substituting for a P or As atom at the apex of a $\mathrm{P_4}$ or $\mathrm{As_4}$ tetrahedron.[13,16]

The bonding as well as the gross features of the physicochemical properties of these complexes may be rationalized by an extension of the MO model devised by Hoffmann for analogous sandwich compounds.[17] It is expedient to proceed by fragment analysis, considering first the effect of the interactions within the two (triphos)M and the (η^3-$\mathrm{D_3}$) moieties which constitute the complex cations. The expected trend of energies of the molecular orbitals forming the valence shell of one (triphos)M fragment is shown on the left side of Figure 3

Table XVI. Bond Lengths (Å) and Angles (deg) within the Coordination Polyhedron of [(triphos)Ni-μ-(η^3-P_3)Ni(triphos)]$(BPh_4)_2$·$2.5(CH_3)_2CO$ (IX), [(triphos)Co-μ-(η^3-P_3)Ni(triphos)]$(BPh_4)_2$·$2(CH_3)_2CO$ (VII), and [(triphos)Co-μ-(η^3-As_3)Co(triphos)]$(BPh_4)_2$ (IV)

XI		VII		IV	
Ni1-P1	2.245 (5)	M1-P1	2.241 (7)	Co1-P1	2.24 (3)
Ni1-P2	2.238 (4)	M1-P2	2.245 (6)	Co1-P2	2.23 (3)
Ni1-P3	2.240 (6)	M1-P3	2.217 (9)	Co1-P3	2.16 (4)
Ni1-P7	2.363 (7)	M1-P7	2.327 (10)	Co1-As1	2.40 (2)
Ni1-P8	2.352 (5)	M1-P8	2.328 (7)	Co1-As2	2.42 (2)
Ni1-P9	2.386 (5)	M1-P9	2.337 (8)	Co1-As3	2.40 (2)
Ni1-P4	2.243 (4)	M2-P4	2.248 (6)	Co2-P4	2.24 (2)
Ni2-P5	2.257 (5)	M2-P5	2.228 (8)	Co2-P5	2.24 (3)
Ni2-P6	2.249 (7)	M2-P6	2.252 (10)	Co2-P6	2.20 (4)
Ni2-P7	2.340 (4)	M2-P7	2.322 (8)	Co2-As1	2.41 (1)
Ni2-P8	2.328 (6)	M2-P8	2.334 (10)	Co2-As2	2.40 (2)
Ni2-P9	2.355 (7)	M2-P9	2.325 (11)	Co2-As3	2.44 (2)
P7-P8	2.169 (6)	P7-P8	2.169 (9)	As1-As2	2.45 (1)
P7-P9	2.151 (8)	P7-P9	2.150 (14)	As1-As3	2.42 (2)
P8-P9	2.171 (7)	P8-P9	2.173 (11)	As2-As3	2.45 (2)
P1-Ni1-P2	96.6 (2)	P1-M1-P2	94.9 (3)	P1-Co1-P2	94 (1)
P1-Ni1-P3	94.4 (2)	P1-M1-P3	92.1 (3)	P1-Co1-P3	93 (1)
P2-Ni1-P3	93.2 (2)	P2-M1-P3	92.3 (3)	P2-Co1-P3	91 (1)
P7-Ni1-P8	54.8 (2)	P7-M1-P8	55.5 (3)	As1-Co1-As2	61.2 (6)
P7-Ni1-P9	53.9 (2)	P7-M1-P9	54.9 (3)	As1-Co1-As3	60.6 (6)
P8-Ni1-P9	54.5 (2)	P8-M1-P9	55.5 (3)	As2-Co1-As3	61.2 (6)
P1-Ni1-P7	138.3 (2)	P1-M1-P7	134.9 (3)	P1-Co1-As1	135.1 (10)
P1-Ni1-P8	89.7 (2)	P1-M1-P8	89.4 (3)	P1-Co1-As2	86.4 (8)
P1-Ni1-P9	125.5 (2)	P1-M1-P9	130.2 (2)	P1-Co1-As3	131.2 (8)
P2-Ni1-P7	89.1 (2)	P2-M1-P7	88.7 (3)	P2-Co1-As1	86.8 (1.0)
P2-Ni1-P8	124.9 (2)	P2-M1-P8	128.8 (3)	P2-Co1-As2	130.7 (1.2)
P2-Ni1-P9	136.7 (2)	P2-M1-P9	134.0 (3)	P2-Co1-As3	135.1 (1.0)
P3-Ni1-P7	126.7 (2)	P3-M1-P7	132.7 (3)	P3-Co1-As1	131.8 (9)
P3-Ni1-P8	141.0 (2)	P3-M1-P8	138.6 (3)	P3-Co1-As2	137.8 (9)
P3-Ni1-P9	93.1 (2)	P3-M1-P9	94.2 (3)	P3-Co1-As3	89.4 (9)
P4-Ni2-P5	93.6 (2)	P4-M2-P5	92.9 (3)	P4-Co2-P5	91 (1)
P4-Ni2-P6	95.3 (2)	P4-M2-P6	94.8 (3)	P4-Co2-P6	93 (1)
P5-Ni2-P6	95.3 (2)	P5-M2-P6	93.6 (3)	P5-Co2-P6	90 (1)
P7-Ni2-P8	55.4 (2)	P7-M2-P8	55.5 (3)	As1-Co2-As2	61.4 (4)
P7-Ni2-P9	54.5 (2)	P7-M2-P9	55.1 (3)	As1-Co2-As3	59.8 (5)
P8-Ni2-P9	55.2 (2)	P8-M2-P9	55.6 (3)	As2-Co2-As3	60.8 (6)
P4-Ni2-P7	151.4 (2)	P4-M2-P7	148.4 (3)	P4-Co2-As1	150.9 (9)
P4-Ni2-P8	96.1 (2)	P4-M2-P8	93.6 (3)	P4-Co2-As2	90.9 (9)
P4-Ni2-P9	111.3 (2)	P4-M2-P9	115.4 (4)	P4-Co2-As3	116.3 (1.0)
P5-Ni2-P7	111.5 (2)	P5-M2-P7	116.8 (3)	P5-Co2-As1	117.4 (6)
P5-Ni2-P8	151.4 (3)	P5-M2-P8	149.5 (4)	P5-Co2-As2	151.6 (1.2)
P5-Ni2-P9	96.2 (2)	P5-M2-P9	94.9 (3)	P5-Co2-As3	93.1 (1.0)
P6-Ni2-P7	95.7 (2)	P6-M2-P7	93.2 (3)	P6-Co2-As1	93.0 (8)
P6-Ni2-P8	110.5 (2)	P6-M2-P8	114.5 (4)	P6-Co2-As2	118.4 (1.0)
P6-Ni2-P9	150.2 (2)	P6-M2-P9	147.7 (3)	P6-Co2-As3	150.5 (7)

(C_3 symmetry labels are used throughout). Predominant contributions to these molecular orbitals arise from the atomic functions bearing the P(triphos) lone pairs and from the metal d set. For electron-counting purposes the levels shown in this part of the diagram may be formally allocated the six electrons of the donor-atoms lone pairs and the electrons belonging to the d shell of the metal. The interaction between two (triphos)M fragments placed at a large distance from each other, as occurs in these complexes, is very weak: this is schematically shown in the figure. The molecular orbitals of the (η^3-D_3) group, which may interact significantly with those of the other fragments, are essentially formed by the phosphorus or arsenic pπ orbitals which are normal to the plane of the ring. Their energies are given on the right side of Figure 3. Such orbitals are assigned three electrons, so that the (η^3-D_3) group acts as a three-electron donor. In fact, all the other electrons in the valence shell of the (η^3-D_3) fragment fill in the "essentially s" and the bonding combinations of the in-plane p orbitals. All these molecular orbitals should have comparatively low energies and are not shown in the figure. By allowing the three fragments to interact with each other, the molecular orbitals in the valence shell of the complex are obtained; the proposed ordering of the energies is shown in the figure. The levels up to the 5e are filled in all of the complexes. The 6e level is occupied by one electron in the [(triphos)Co-μ-(η^3-D_3)Co(triphos)]$^{2+}$ complexes and becomes completely filled in the [(triphos)Ni-μ-(η^3-D_3)Ni(triphos)]$^+$ complexes. The number of valence electrons in all of these compounds falls within the range of 30–34 electrons that has been indicated as necessary for the existence of stable double-sandwich compounds.[17]

The spin states of the complexes are rationalized to the bonding by the above approach. In order to make this evident, the values of the magnetic moments together with the numbers of valence electrons, of unpaired electrons, and of the electrons populating the uppermost (twofold degenerate) 6e orbital for representative complexes are listed in Table XVII. The ground state of the [(triphos)Co-μ-(η^3-P_3)Ni(triphos)]$^{2+}$ derivative is the same as that of the homonuclear 32-electron species, as would be expected in view of the similarity of the structures. There is an implicit indication from the values of the magnetic moments of the 32-electron complexes and from their temperature independence that the degeneracy of the 6e orbital

Table XVII

compd	number of valence electrons	μ_B	number of unpaired electrons	number of electrons in the highest orbital
$[Co_2(P_3)(triphos)_2](BPh_4)_2$	31	2.02	1	1
$[Co_2(P_3)(triphos)_2]BPh_4$	32	3.13	2	2
$[Co,Ni(P_3)(triphos)_2](BPh_4)_2$	32	3.14	2	2
$[Ni_2(P_3)(triphos)_2](BPh_4)_2$	33	2.00	1	3
$[Ni_2(P_3)(triphos)_2]BPh_4$	34	0	0	4

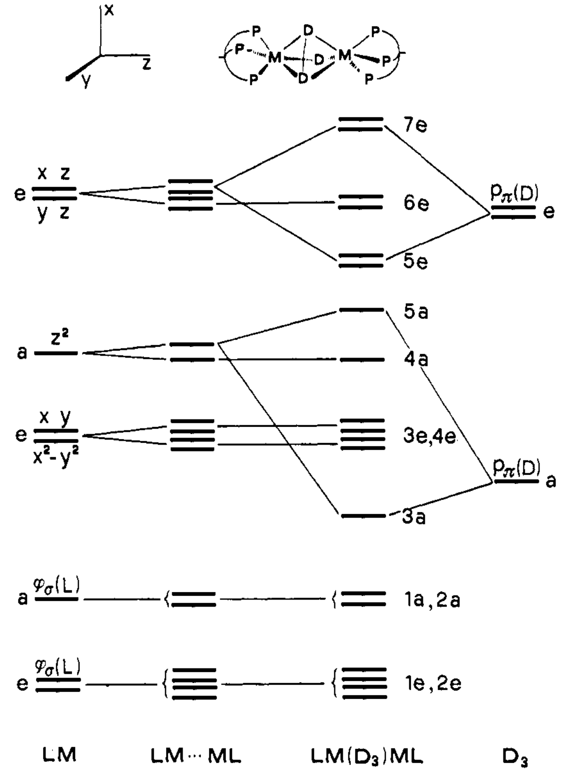

Figure 3. Energy level diagram for the $[(triphos)M\text{-}\mu\text{-}(\eta^3\text{-}D_3)M(triphos)]^{n+}$ complexes. On the left are sketched the energies of the valence orbitals of one (triphos)M moiety (LM) and of two such weakly interacting moieties (LM···ML). The energies of the valence orbitals of the η^3-D_3 group are sketched on the right (D_3). The molecular orbitals of the complex ($LM(D_3)ML$) are formed through interaction of the LM···ML and D_3 fragments. The complex has C_3 symmetry; see text.

is not substantially lifted by the deviations in the coordination geometry from the idealized C_3 symmetry, in the solid state.

The visible-UV absorption spectrum of each compound is essentially similar to the corresponding reflectance spectrum. There is a set of broad and intense bands, with grossly similar structure in all the spectra, at frequencies above 16 000-18 000 cm^{-1} (η^3-P_3 derivatives) or above 15 000-17 000 cm^{-1} (η^3-As_3 derivatives). No band is present at lower energies in the spectra of the 34-electron complexes, whereas an additional weaker band is found at 9000-10 000 cm^{-1} in the spectra of the 33- and 32-electron complexes or at 13 000-14 000 cm^{-1} in those of the 31-electron compounds. With reference to the energy level diagram (Figure 3), the intense high-energy bands may be assigned to the spin-allowed transitions associated with the one-electron excitations from the 6e to the 7e and to higher energy levels. The small low-energy shift of the first band of this set on going from the *cyclo*-triphosphorus to the *cyclo*-triarsenic derivatives may be due to weaker metal-ligand interactions in the latter compounds and to the consequent decrease in the separation between nonbonding and antibonding levels. The band at 9000-10 000 cm^{-1} could be due to a 5e → 6e transition. If this assignment is maintained for the band at 13 000-14 000 cm^{-1} in the spectra of the 31-electron complexes, the shift toward higher energies is tentatively attributed to the fact that on approaching the stable 30-electron configuration, electron transfers from the bonding to the nonbonding orbitals should be disfavored.

The EPR powder spectra of the compounds with doublet ground state do not change significantly with temperature and are indicative of an essentially isotropic g factor. Its value is ca. 2.1 and is consistently slightly larger for the nickel compounds than for the cobalt ones. The powder spectra of the compounds with triplet ground state are almost featureless at room temperature. At 4 K they show complicated, not readily interpretable, structures. In no case was hyperfine splitting observed.

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Supplementary Material Available: Tables V-XV, atomic parameters for compounds IV, VII, and IX, and listings of structure factor amplitudes (71 pages). Ordering information is given on any current masthead page.

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