forming an acute angle (69° in the isocyanides). Reduction of **1** and **2** with Zn dust in acetonitrile occurs under mild reflux, but the reduction promotes loss of a chelate ligand to ultimately yield $[Mo(CO)_4(S_2CNR_2)]^-$.

The low ν_{MoF} stretching frequency and the Mo–F bond distance suggest a weak M–F interaction relative to that in higher oxidation state metal fluoride complexes where fluoride π donation to the metal can strengthen the Mo–F bond. Verification of no significant F pπ–Mo dπ interaction was gleaned from inspection of proper orbitals in the EHMO calculation. An absence of π donation in 18-electron fluoride complexes has been observed by Crabtree.[33]

In summary, this work exploits the structure of a seven-coordinate dicarbonyl fluoride of Mo(II) to suggest a frontier-controlled ligand substitution mechanism in saturated Mo(II) and W(II) systems and to decipher ligand properties responsible for determining the final geometry. We have also probed factors promoting acute angles in bis chelate dicarbonyl halides with capped-trigonal-prismatic geometries through a theoretical (EHMO) study of fluoride complex **1**.

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Registry No. **1**, 96394-35-3; **2a**, 96394-37-5; **2b**, 96427-14-4; **3**, 96394-39-7; **4**, 96394-41-1; $Mo(CO)_2(S_2CNMe_2)_2$, 80664-77-3; $Mo(CO)_2(S_2CNEt_2)_2$, 74807-43-5; $[Et_4N][Mo(CO)_5I]$, 14781-00-1; $Mo(CO)_6$, 13939-06-5; $[Et_4N][W(CO)_5I]$, 14781-01-2; $W(CO)_6$, 14040-11-0; $W(CO)_3(S_2CNMe_2)_2$, 72881-01-7; $W(CO)_3(S_2CNEt_2)_2$, 72827-54-4; $W(CO)_2(S_2CNMe_2)_2$, 69916-43-4; $W(CO)_2(S_2CNEt_2)_2$, 82284-90-0; $Mo(CO)_2(S_2CNH_2)_2$, 80004-29-1; $[Mo(CO)_2(S_2CNH_2)_2F]^-$, 96427-15-5.

Supplementary Material Available: Tables of thermal parameters, calculated hydrogen positions, and observed and calculated structure factors (Tables VII, VIII, and IX, respectively) (21 pages). Ordering information is given on any current masthead page.

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(34) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Contribution from the Dipartimento di Chimica dell'Università,
Istituto ISSECC, CNR, 50132 Firenze, Italy

Synthesis and Characterization of Dinuclear Metal Complexes with the P_2S and As_2S Heteroatomic Inorganic Rings as Bridging Units. Crystal and Molecular Structure of $[(triphos)Rh(As_2S)Rh(triphos)](BPh_4)_2\cdot 2(CH_3)_2CO$ [triphos = 1,1,1-Tris((diphenylphosphino)methyl)ethane]

MASSIMO DI VAIRA, FABRIZIO MANI, SIMONETTA MONETI, MAURIZIO PERUZZINI, LUIGI SACCONI, and PIERO STOPPIONI*

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The cobalt complexes $[(triphos)Co(E_2S)]BF_4$ [triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane; E = As, P], containing the heterocyclic diphosphorus–sulfur and diarsenic–sulfur units η^3 coordinated to the metal atom, react with a rhodium(I) complex or with cobalt(II) tetrafluoroborate in the presence of triphos, yielding compounds with the general formula $[(triphos)M(E_2S)M'(triphos)]Y_2$ (E = As, P; M = M′ = Co or M = Co and M′ = Rh, Y = BF_4; M = M′ = Rh, Y = BPh_4). The crystal structure of $[(triphos)Rh(As_2S)Rh(triphos)](BPh_4)_2\cdot 2(CH_3)_2CO$ has been elucidated through a complete X-ray analysis: triclinic, $a = 19.344$ (9) Å, $b = 18.887$ (9) Å, $c = 19.581$ (10) Å, $\alpha = 122.93$ (9)°, $\beta = 93.56$ (8)°, $\gamma = 95.09$ (8)°, space group $P\bar{1}$, $Z = 2$, $R = 0.083$, 4727 reflections. The complex has a triple-decker sandwich structure with the As_2S unit bridging the two Rh(triphos) moieties. Such an internal unit, affected by orientational disorder, has the shape of a triangle with two sides [2.34 (1), 2.52 (1) Å] in the range of normal bond lengths and a very long [3.10 (1) Å] side. The same sort of structure is assigned to all of the complexes on the basis of conductivity, spectrophotometric, and magnetic measurements.

Introduction

The cobalt complexes of formula $[(triphos)Co(E_2S)]BF_4$ [triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane; E = As, P], containing the heterocyclic diphosphorus–sulfur or diarsenic–sulfur units η^3 coordinated to the metal atom, have been synthesized and characterized.[1,2] These compounds have provided the first examples of inorganic heteroatomic three-membered rings π bonded to a metal atom. Such cationic compounds are isoelectronic with the neutral $[(triphos)M(P_3)]$ (M = Co, Rh, Ir) complexes,[3,4] which contain the homocyclic triphosphorus unit. The latter complexes have been found to be capable of reacting with appropriate metal–ligand moieties, affording homo- and heterometallic sandwich complexes of formula $[(triphos)M(P_3)M'(triphos)]Y_2$ (M = Co, Rh; M′ = Co, Ni, Rh, Ir, Y = BF_4, PF_6, BPh_4),[5,6] in which the *cyclo*-triphosphorus unit bridges two metal atoms.

With the aim to investigate possible effects on the reactivity of the cationic complexes due to the presence of the heteroatom in the triatomic E_2S ring, the $[(triphos)Co(E_2S)]BF_4$ (E = As, P) compounds have been reacted with $Co(BF_4)_2\cdot 6H_2O$ and $[RhCl(cod)]_2$ (cod = cycloocta-1,5-diene) in the presence of triphos. Dinuclear homo- and heterometallic derivatives of formula $[(triphos)M(E_2S)M'(triphos)]Y_2$ (E = As, P; M = M′ = Co or M = Co and M′ = Rh, Y = BF_4; M = M′ = Rh, Y = BPh_4) have been obtained. These complexes, which crystallize with two molecules of acetone, have been characterized by means of magnetic, spectrophotometric, and conductivity measurements.

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0020-1669/85/1324-2230$01.50/0

Table I. Physical Constants and Analytical Data

compd	Λ_M,[a] Ω^{-1} cm^2 M^{-1}	anal.[b] % C	% H	% Co	% Rh	μ_{eff},[c] μ_B
$[(triphos)Co(P_2S)Co(triphos)](BF_4)_2 \cdot 2(CH_3)_2CO$[d]	132	60.21 (60.36)	5.25 (5.18)	6.60 (6.73)		1.35
$[(triphos)Co(P_2S)Rh(triphos)](BF_4)_2 \cdot 2(CH_3)_2CO$[e]	150	58.49 (58.89)	5.19 (5.05)	3.17 (3.28)	5.59 (5.73)	1.50
$[(triphos)Rh(P_2S)Rh(triphos)](BPh_4)_2 \cdot 2(CH_3)_2CO$[f]	129	70.85 (70.90)	5.74 (5.69)		8.84 (8.93)	1.42
$[(triphos)Co(As_2S)Co(triphos)](BF_4)_2 \cdot 2(CH_3)_2CO$[g]	143	57.49 (57.48)	4.99 (4.93)	6.30 (6.41)		1.27
$[(triphos)Co(As_2S)Rh(triphos)](BF_4)_2 \cdot 2(CH_3)_2CO$[h]	150	56.02 (56.14)	5.01 (4.82)	3.09 (3.13)	5.39 (5.47)	1.14
$[(triphos)Rh(As_2S)Rh(triphos)](BPh_4)_2 \cdot 2(CH_3)_2CO$[i]	136	68.28 (68.30)	5.61 (5.48)		8.57 (8.61)	1.45

[a] Molar conductance of ca. 10^{-3} M nitroethane solution at ca. 20 °C. [b] Calculated values in parentheses. [c] Room temperature. [d] Anal. Found (calcd): P, 14.03 (14.15); S, 1.79 (1.83). [e] Anal. Found (calcd): P, 1367 (13.80); S, 1.78 (1.79). [f] Anal. Found (calcd): P, 10.60 (10.75); S, 1.34 (1.39). [g] Anal. Found (calcd): P, 10.02 (10.10). [h] Anal. Found (calcd): As, 7.84 (7.96). [i] Anal. Found (calcd): As, 6.24 (6.27); P, 7.66 (7.77); S, 1.32 (1.34).

A complete X-ray structural investigation has been carried out on the compound $[(triphos)Rh(As_2S)Rh(triphos)](BPh_4)_2 \cdot 2(CH_3)_2CO$.

Experimental Section

All solvents were reagent grade and were appropriately dried and freed of molecular oxygen prior to use.[7] All reactions were performed under a nitrogen atmosphere. Electronic spectra and conductivity measurements were obtained as previously described.[8] Magnetic susceptibilities were measured by the Faraday method.[9] The ligand 1,1,1-tris((diphenylphosphino)methyl)ethane (triphos)[10] and the complexes $[(triphos)Co(P_2S)]BF_4$,[1] $[(triphos)Co(As_2S)]BF_4$,[2] and $[RhCl(cod)]_2$[11] (cod = cycloocta-1,5-diene) were prepared according to published procedures. All the compounds were collected on a sintered-glass frit, in a closed system, and washed with ethanol and light petroleum (bp 40–70 °C) in turn before being dried under a stream of nitrogen. They were recrystallized from acetone–ethanol. Analytical data (Table I) for the complexes which crystallize with two molecules of acetone (ν(CO) ca. 1710 cm^{-1}) are in good agreement with the proposed formulas.

Preparation of Complexes. $[(triphos)Co(E_2S)Co(triphos)](BF_4)_2$ (E = As, P). The appropriate complex $[(triphos)Co(E_2S)]BF_4$ (E = As, P) (0.5 mmol) dissolved in acetone (20 mL) was added at room temperature to a solution obtained by mixing $Co(BF_4)_2 \cdot 6H_2O$ (0.5 mmol) in ethanol (10 mL) and triphos (0.5 mmol) in acetone (20 mL). After addition of ethanol (20 mL) a stream of nitrogen was passed through the solution until dark red crystals separated; yield 45%.

$[(triphos)Co(E_2S)Rh(triphos)](BF_4)_2$ (E = As, P). $AgBF_4$ (1.1 mmol) dissolved in acetone (10 mL) was added to a solution of $[RhCl(cod)]_2$ (0.5 mmol) in the same solvent (30 mL). The resulting mixture was refluxed with magnetic stirring for 30 min and filtered to eliminate AgCl. The yellow filtrate solution was added to triphos (1 mmol) in acetone (20 mL) and then to the stoichiometric amount of $[(triphos)Co(E_2S)]BF_4$ (E = As, P) in acetone (20 mL). Red-orange needles of the complexes were obtained after addition of $(NBu_4)BF_4$ (1 mmol) in ethanol (20 mL) and evaporation of the solvent at ca. 50 °C; yield 80%.

$[(triphos)Rh(E_2S)Rh(triphos)](BPh_4)_2$ (E = As, P). Method A. The appropriate $[(triphos)Co(E_2S)]BF_4$ derivative (E = As, P) (0.3 mmol) dissolved in acetone (20 mL) was added to a solution of $[RhCl(cod)]_2$ (0.8 mmol) in acetone (35 mL) that had been treated with $AgBF_4$ (1.6 mmol) and triphos (1.6 mmol) as described for the synthesis of the $[(triphos)Co(E_2S)Rh(triphos)](BF_4)_2$ complexes. The resulting solution was refluxed for 10 min, and $NaBPh_4$ (1.8 mmol) in ethanol (30 mL) was added. Dark red crystals of the complexes were obtained by slowly evaporating the solvent at ca. 40 °C; yield 85%.

Method B. The $[(triphos)Co(E_2S)Rh(triphos)](BPh_4)_2$ compound (E = As, P) (0.2 mmol) dissolved in acetone (40 mL) was reacted with $[RhCl(cod)]_2$ (0.3 mmol), $AgBF_4$ (0.6 mmol), and triphos (0.6 mmol) by the procedure described above. Dark red crystals of the complexes were obtained by adding to the resulting solution $NaBPh_4$ (1.4 mmol) in ethanol (40 mL) and slowly evaporating the solvent at room temperature; yield 90%.

Crystallographic Data Collection and Refinement of the Structure of $[(triphos)Rh(As_2S)Rh(triphos)](BPh_4)_2 \cdot 2(CH_3)_2CO$. Crystals of the compounds listed in Table I are generally affected by twinning and/or provide poorly diffracting material for x-ray work. Crystals of moderately good quality could be found for the above dirhodium compound although the rather rapid attenuation of intensities with θ was indicative of some degree of disorder in the structure. Cell parameters for the compound were obtained by least-squares refinement of the setting angles of 20 reflections with $18° < 2\theta < 24°$. Crystal data for $[(triphos)Rh(As_2S)Rh(triphos)](BPh_4)_2 \cdot 2(CH_3)_2CO$ ($C_{136}H_{130}As_2B_2P_6Rh_2S$): mol wt 2391.7, triclinic, a = 19.344 (9) Å, b = 18.887 (9) Å, c = 19.581 (10) Å, α = 122.93 (9)°, β = 93.56 (8)°, γ = 95.09 (8)°, V = 5928.5 $Å^3$, Z = 2, d_{calcd} = 1.34 g cm^{-3}, μ(Mo Kα) = 9.72 cm^{-1}; space group $P\bar{1}$, initially chosen and later confirmed by the analysis. Diffraction data were collected from an elongated crystal with dimensions 0.20 × 0.30 × 0.60 mm. A Philips PW 1100 automated diffractometer and graphite-monochromated Mo Kα radiation (λ = 0.71069 Å) were used for all operations. The intensities of 11 015 symmetry-independent reflections were measured by the θ–2θ scan method in the interval $5° < 2\theta < 40°$, with a symmetric scan range of $(1.10 + 0.30 \tan \theta)°$ and a scan speed of 6°/min in 2θ. the intensities of three standard reflections monitored every 90 min showed a smooth decay with 20% overall decrease. The raw intensity data were rescaled for such decay and were corrected for absorption effects by a numerical procedure,[12a] the transmission coefficients ranging from 0.75 to 0.83. After correction for Lorentz and polarization effects, 4727 reflections with $I > 3\sigma(I)$ were used for structure solution and refinement. The principal computer programs used in the crystallographic calculations are listed in ref 12. The structure was solved by a combination of heavy-atom methods and direct methods, which provided the positions of the Rh atoms and of two ring sites. A series of Fourier maps yielded the positions of the other non-hydrogen atoms in the structure, except for those of the solvent molecules, which were located later from ΔF maps. Least-squares refinement was based on minimization of the function $\sum w(|F_o| - |F_c|)^2$ with weights $w = (\sigma^2 F_0 + 0.0005 F_0{}^2)^{-1}$. The As_2S group, having the shape of a triangle with a very long side (ca. 3.10 Å), was found to be affected by orientational disorder, similar to that found in the structure of the parent $[(triphos)Co(As_2S)]BF_4$[2] as well as in those of related compounds.[1] Two models were tested, as described below, in order to determine the As/S occupancy factors of the ring sites. In either refinement anisotropic thermal parameters were assigned to the Rh and P atoms as well as to the sites of the As_2S ring, whereas isotropic thermal parameters were assigned to the other atoms. All phenyl rings in the structure were refined as rigid groups with idealized geometry (C–C = 1.395 Å), each group being separately assigned an overall temperature factor. Hydrogen atoms, except those of the solvent molecules, were introduced at calculated positions (C–H = 1.00 Å) with the methyl groups treated as rigid tetrahedral fragments. The CH_2 and CH_3 H atoms were given a fixed (U = 0.06 $Å^2$) temperature factor whereas each of the phenyl H atoms was assigned a temperature factor 20% larger than that of the respective C atom. Each solvent molecule was assigned an overall temperature factor. The C–O and C–C bond lengths within each acetone molecule were linked to one parameter whose value was refined. The scattering factors for the neutral atoms[13] were used, and the anomalous dispersion corrections for Rh and As[14a] were included.

In the first model used for the disordered As_2S group the population parameters in the ring were assigned by imposing the requirement that the equivalent isotropic temperature factors of the three sites should be close to each other. Such a procedure, which had already been followed in the refinement of similarly disordered structures,[1,2] led to an As oc-

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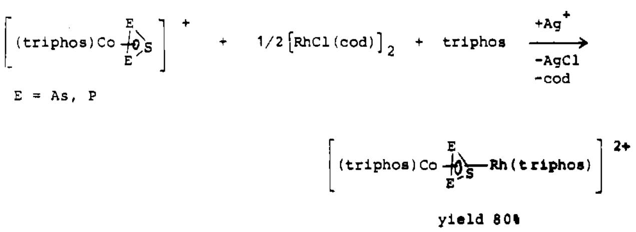
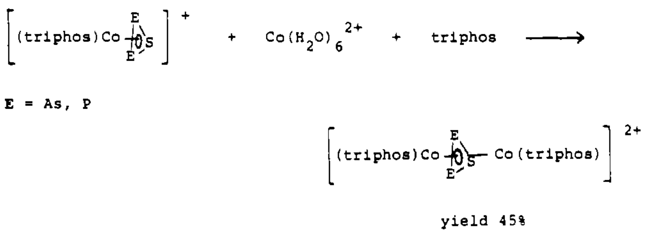
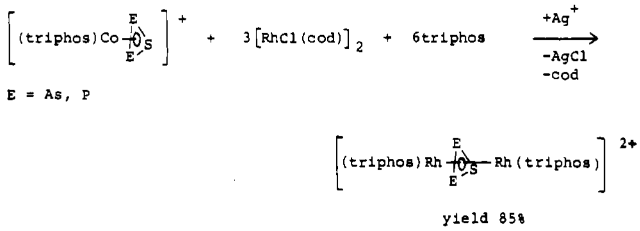
Scheme I



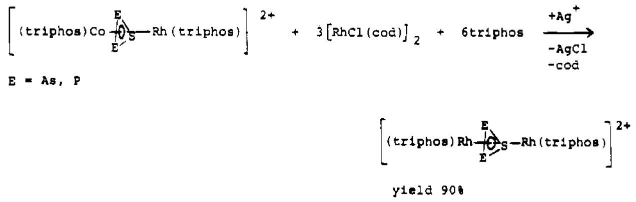
Scheme II



Scheme III



Scheme IV



cupancy factor close to unity (subsequently assumed equal to 1.00 for simplicity) for the As(2) site lying opposite the elongated bond in the triangle. The As occupancies for the other two positions were 0.70 and 0.30, respectively, for sites labeled As(1) and S, with complementary values for the sulfur occupancy factors. With a total of 322 parameters such refinement converged at $R = 0.084$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.086$. According to the alternative procedure of refinement of the disordered As_2S group the set of occupancy factors was used that allowed us to reproduce the trend in values of the difference density integrated over the three peaks in the As_2S region of a ΔF Fourier map calculated without ring atom contributions. It was verified that such a trend closely agreed (within 1%) with that obtained from a set of three ΔF maps computed with exclusion of one ring atom at a time. The parameters for the other two ring sites in each of the latter calculations were taken from the refinement of the alternative model, previously described. The peaks in these ΔF maps were rather broad and approximately spherical, so they did not provide any indication of the amount of displacement between the S and As positions at each vertex of the triangular As_2S unit. The 0.89:1.00:0.66 ratios between the integrated difference densities at the positions respectively labeled As(1), As(2), and S were fitted by assigning the following As occupancy factors: 0.74, 0.95, and 0.31 to the three sites in the above order, with complementary S population parameters. Such values were close to those of the first model. They were not allowed to change in the least-squares cycles whereas the positional and thermal parameters for the ring were refined without constraints. This refinement converged at $R = 0.083$ and $R_w = 0.085$. The final difference Fourier maps from either refinement showed no features greater than 0.7 e Å^{-3}. The temperature factors of the metal sites were in the normal range, indicating that Co had been completely replaced by Rh, consistent with the analytical data reported in Table I. The values of corresponding parameters from the two sets of refinements generally agreed within 1σ; only a few components of the thermal ellipsoids of the ring sites differed by 2σ and those of As(2) by 5σ. The substantial uniformity of U_{iso} values for the ring, which was assumed with the first model but found for the second one, may be due to a balance between larger substitutional disorder in the As(1) and S sites and larger thermal motion in the As(2) position, which lies at comparatively longer distances from the metal atoms. The rather high R values are ascribed to the poor quality of the data, caused in turn by the disorder in the orientation of the As_2S ring and by high thermal motion or disorder in the positions of the solvent molecules and of a phenyl group [C(31)–C(36)], whose temperature factor reached a high value. Results from the refinement on the second model are reported here because of the small but statistically[14b] significant improvement in R and of the physically more convincing procedure for assignment of the fractional population parameters. The positional parameters for the non-hydrogen atoms are given in Table II. Values of selected bond distances and angles are collected in Table III. It should be noted that the esd's on all entries for the As_2S ring sites in the above two tables are underestimated by the least squares due to the disorder. Such esd values are used here in the absence of unambiguous alternative choices, but it should be clear that irrespective of the error estimates adopted the geometrical parameters of the ring cannot be compared with usual chemical standards. Lists of the temperature factors, H atom coordinates, bond distances and angles, and observed and calculated structure amplitudes are available as supplementary data.[15]

Results and Discussion

The isoelectronic [(triphos)M(E_2S)M′(triphos)]Y_2 complexes (E = As, P; M = M′ = Co or M = Co and M′ = Rh, Y = BF_4; M = M′ = Rh, Y = BPh_4) have been synthesized by reacting the mononuclear [(triphos)Co(E_2S)]BF_4 [E = As (**1**), P (**2**)] compounds with cobalt(II) tetrafluoroborate hydrate or with the rhodium(I) dimeric complex [RhCl(cod)]$_2$ in the presence of triphos. In particular, the heterometallic [(triphos)Co(E_2S)Rh(triphos)](BF_4)$_2$ complexes have been obtained (Scheme I) by simple addition of the [Rh(triphos)]$^+$ unit, which is formed by treating rhodium cycloocta-1,5-diene chloride dimer with a silver salt in the presence of the triphos ligand, to the mononuclear cobalt derivative **1** or **2**. The homometallic cobalt derivatives of formula [(triphos)Co(E_2S)Co(triphos)](BF_4)$_2$ have been obtained by reacting the **1** or **2** cationic complexes (Scheme II) with cobalt(II) tetrafluoroborate hydrate and triphos in a 1:1 ratio. In this process the sum of the oxidation numbers of the two metal atoms involved decreases by one unit. The homometallic rhodium derivatives of formula [(triphos)Rh(E_2S)Rh(triphos)](BPh_4)$_2$ have been obtained by reacting compounds **1** and **2** with a large excess of [RhCl(cod)]$_2$, triphos, and $AgBF_4$ (Scheme III). In such a reaction the Co(triphos) moiety in the parent compounds is replaced by the isoelectronic Rh(triphos) one. The same sort of replacement takes place in the alternative route to these dirhodium complexes summarized in Scheme IV. The latter reaction, in particular, shows that the dimetal sandwich complexes may act as suitable intermediates allowing transferability of the E_2S units between isoelectronic cobalt and rhodium moieties.

The compounds are stable under nitrogen both in the solid state and in solution but quickly decompose in the air. The complexes are soluble in dichloromethane, acetone, nitroethane, and acetonitrile. In nitroethane solution all of the compounds behave as 1:2 electrolytes (Table I).[16]

All complexes here reported exhibited a feeble paramagnetism, which is temperature dependent. The room-temperature magnetic moment values per dimetal unit range from 1.14 to 1.50 μ_B (Table I); they smoothly decrease to 0.6–0.7 μ_B at ca. 80 K.

The structure of the compound [(triphos)Rh(As_2S)Rh(triphos)](BPh_4)$_2$·2(CH_3)$_2$CO consists of dinuclear [(triphos)Rh(As_2S)Rh(triphos)]$^{2+}$ cations, BPh_4^- anions, and solvate acetone molecules. The cation has a triple-decker structure with the As_2S unit bridging the two metal atoms and the two triphos ligands forming the external layers (Figure 1). Each metal atom is coordinated by the atoms of the triatomic As_2S group and by the three P atoms of the polyphosphine. The cation does not exhibit

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(15) See the paragraph at the end of the paper dealing with the supplementary material.

(16) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

Table II. Positional Parameters (×10⁴) for [(triphos)Rh(As_2S)Rh(triphos)]$(BPh_4)_2$·$2(CH_3)_2CO$[a]

atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Rh(1)	2674 (1)	3699 (1)	1539 (1)	C(102)	866 (5)	5412 (8)	877 (8)
Rh(2)	1841 (1)	5643 (1)	2882 (1)	C(103)	937 (5)	5292 (8)	118 (8)
As(1)[b]	2439 (2)	4589 (2)	2937 (2)	C(104)	1216 (5)	5975 (8)	79 (8)
As(2)[b]	1420 (1)	4041 (2)	1824 (2)	C(105)	1423 (5)	6777 (8)	800 (8)
S[b]	2167 (3)	4832 (3)	1505 (3)	C(106)	1352 (5)	6897 (8)	1559 (8)
P(1)	2850 (3)	2557 (4)	1655 (4)	C(111)	2822 (5)	7338 (7)	2894 (7)
P(2)	2522 (3)	2701 (4)	84 (4)	C(112)	3016 (5)	6772 (7)	2124 (7)
P(3)	3858 (3)	3951 (4)	1552 (4)	C(113)	3179 (5)	7052 (7)	1616 (7)
P(4)	1321 (3)	6051 (4)	4066 (4)	C(114)	3148 (5)	7898 (7)	1879 (7)
P(5)	1018 (3)	6311 (4)	2570 (4)	C(115)	2955 (5)	8464 (7)	2650 (7)
P(6)	2594 (3)	6910 (4)	3526 (4)	C(116)	2792 (5)	8184 (7)	3157 (7)
C(1)	3745 (10)	2133 (11)	398 (11)	C(121)	3439 (7)	7030 (7)	4056 (7)
C(2)	3612 (10)	2100 (12)	1165 (11)	C(122)	3508 (7)	6832 (7)	4645 (7)
C(3)	3067 (10)	1872 (11)	−171 (11)	C(123)	4161 (7)	7003 (7)	5091 (7)
C(4)	4126 (10)	2999 (10)	659 (11)	C(124)	4744 (7)	7372 (7)	4949 (7)
C(5)	4240 (10)	1462 (12)	−73 (12)	C(125)	4674 (7)	7570 (7)	4360 (7)
C(6)	1389 (10)	7699 (11)	4241 (11)	C(126)	4021 (7)	7399 (7)	3913 (7)
C(7)	989 (10)	7081 (11)	4458 (11)	C(131)	6615 (5)	2589 (7)	722 (6)
C(8)	1116 (11)	7451 (11)	3374 (11)	C(132)	6106 (5)	2485 (7)	126 (6)
C(9)	2211 (9)	7750 (11)	4382 (11)	C(133)	5877 (5)	3198 (7)	194 (6)
C(10)	1211 (10)	8568 (11)	4863 (11)	C(134)	6158 (5)	4014 (7)	857 (6)
C(11)	2981 (7)	2791 (6)	2683 (8)	C(135)	6667 (5)	4118 (7)	1453 (6)
C(12)	3652 (7)	2795 (6)	2992 (8)	C(136)	6896 (5)	3405 (7)	1386 (6)
C(13)	3784 (7)	2988 (6)	3788 (8)	C(141)	6580 (6)	851 (6)	−264 (7)
C(14)	3244 (7)	3177 (6)	4276 (8)	C(142)	6898 (6)	649 (6)	−956 (7)
C(15)	2573 (7)	3173 (6)	3967 (8)	C(143)	6586 (6)	−29 (6)	−1732 (7)
C(16)	2442 (7)	2980 (6)	3170 (8)	C(144)	5955 (6)	−505 (6)	−1815 (7)
C(21)	2121 (7)	1689 (7)	1217 (6)	C(145)	5636 (6)	−303 (6)	−1122 (7)
C(22)	1435 (7)	1858 (7)	1207 (6)	C(146)	5949 (6)	375 (6)	−347 (7)
C(23)	877 (7)	1196 (7)	890 (6)	C(151)	6547 (5)	1591 (7)	1362 (7)
C(24)	1005 (7)	365 (7)	582 (6)	C(152)	6711 (5)	912 (7)	1408 (7)
C(25)	1692 (7)	197 (7)	592 (6)	C(153)	6451 (5)	791 (7)	1992 (7)
C(26)	2250 (7)	858 (7)	909 (6)	C(154)	6028 (5)	1349 (7)	2530 (7)
C(31)	1650 (9)	2140 (10)	−382 (8)	C(155)	5864 (5)	2028 (7)	2484 (7)
C(32)	1514 (9)	1265 (10)	−782 (8)	C(156)	6123 (5)	2149 (7)	1900 (7)
C(33)	739 (9)	922 (10)	−1116 (8)	C(161)	7761 (7)	1916 (6)	823 (7)
C(34)	254 (9)	1454 (10)	−1050 (8)	C(162)	8155 (7)	1812 (6)	1375 (7)
C(35)	467 (9)	2329 (10)	−650 (8)	C(163)	8884 (7)	1998 (6)	1495 (7)
C(36)	1166 (9)	2672 (10)	−315 (8)	C(164)	9218 (7)	2289 (6)	1062 (7)
C(41)	2727 (6)	3082 (7)	−582 (7)	C(165)	8823 (7)	2393 (6)	510 (7)
C(42)	3163 (6)	2695 (7)	−1189 (7)	C(166)	8095 (7)	2207 (6)	390 (7)
C(43)	3298 (6)	3003 (7)	−1680 (7)	C(171)	2552 (7)	2216 (8)	5654 (6)
C(44)	2997 (6)	3699 (7)	−1565 (7)	C(172)	3243 (7)	2581 (8)	6007 (6)
C(45)	2561 (6)	4086 (7)	−959 (7)	C(173)	3447 (7)	3452 (8)	6373 (6)
C(46)	2426 (6)	3778 (7)	−467 (7)	C(174)	2959 (7)	3959 (8)	6384 (6)
C(51)	4217 (6)	4810 (7)	1438 (8)	C(175)	2268 (7)	3594 (8)	6031 (6)
C(52)	4054 (6)	4799 (7)	728 (8)	C(176)	2064 (7)	2722 (8)	5665 (6)
C(53)	4362 (6)	5455 (7)	667 (8)	C(181)	2925 (7)	678 (8)	5205 (7)
C(54)	4832 (6)	6124 (7)	1316 (8)	C(182)	3461 (7)	674 (8)	4759 (7)
C(55)	4995 (6)	6136 (7)	2027 (8)	C(183)	3994 (7)	184 (8)	4654 (7)
C(56)	4688 (6)	5479 (7)	2088 (8)	C(184)	3990 (7)	−301 (8)	4994 (7)
C(61)	4436 (6)	4178 (6)	2466 (7)	C(185)	3453 (7)	−296 (8)	5440 (7)
C(62)	5097 (6)	3919 (6)	2382 (7)	C(186)	2921 (7)	193 (8)	5545 (7)
C(63)	5557 (6)	4168 (6)	3076 (7)	C(191)	1958 (6)	705 (8)	4212 (8)
C(64)	5358 (6)	4674 (6)	3856 (7)	C(192)	1571 (6)	−109 (8)	3789 (8)
C(65)	4697 (6)	4932 (6)	3941 (7)	C(193)	1370 (6)	−548 (8)	2944 (8)
C(66)	4237 (6)	4684 (6)	3246 (7)	C(194)	1556 (6)	−171 (8)	2522 (8)
C(71)	1839 (5)	6208 (7)	4978 (7)	C(195)	1943 (6)	644 (8)	2945 (8)
C(72)	2053 (5)	5477 (7)	4884 (7)	C(196)	2143 (6)	1082 (8)	3790 (8)
C(73)	2453 (5)	5533 (7)	5534 (7)	C(201)	1651 (6)	1200 (6)	5795 (7)
C(74)	2638 (5)	6319 (7)	6278 (7)	C(202)	943 (6)	895 (6)	5490 (7)
C(75)	2423 (5)	7050 (7)	6372 (7)	C(203)	463 (6)	945 (6)	6012 (7)
C(76)	2024 (5)	6994 (7)	5722 (7)	C(204)	690 (6)	1300 (6)	6839 (7)
C(81)	564 (6)	5343 (7)	3974 (6)	C(205)	1397 (6)	1605 (6)	7145 (7)
C(82)	563 (6)	4463 (7)	3501 (6)	C(206)	1878 (6)	1555 (6)	6623 (7)
C(83)	−17 (6)	3915 (7)	3420 (6)	B(1)	6883 (13)	1700 (14)	633 (14)
C(84)	−596 (6)	4248 (7)	3813 (6)	B(2)	2267 (13)	1197 (14)	5198 (14)
C(85)	−595 (6)	5128 (7)	4285 (6)	O(1)	4573 (10)	1834 (10)	8272 (10)
C(86)	−15 (6)	5675 (7)	4366 (6)	C(211)	4748 (14)	1311 (9)	7646 (9)
C(91)	85 (6)	5911 (7)	2451 (6)	C(212)	4877 (15)	1505 (14)	7006 (11)
C(92)	−137 (6)	5089 (7)	2249 (6)	C(213)	5023 (14)	547 (11)	7562 (13)
C(93)	−849 (6)	4804 (7)	2152 (6)	O(2)	−475 (11)	2023 (13)	3564 (14)
C(94)	−1339 (6)	5343 (7)	2256 (6)	C(221)	67 (10)	1797 (15)	3584 (14)
C(95)	−1118 (6)	6165 (7)	2457 (6)	C(222)	100 (16)	997 (14)	3572 (19)
C(96)	−406 (6)	6449 (7)	2555 (6)	C(223)	574 (13)	1747 (19)	3011 (16)
C(101)	1073 (5)	6214 (8)	1598 (8)				

[a] Estimated standard deviations in the least significant figure(s) are in parentheses. Atoms Rh(1)–C(126) belong to the cation, atoms C(131)–B(2) to the anions, and atoms O(1)–C(223) to the acetone solvate molecules. [b] These sites have occupancies: As(1) (0.74 As, 0.26 S); As(2) (0.95 As, 0.05 S); S (0.31 As, 0.69 S).

Table III. Selected Bond Lengths (Å) and Angles (deg) for the Structure of [(triphos)Rh(As_2S)Rh(triphos)]$(BPh_4)_2$·2$(CH_3)_2CO$

Rh(1)-P(1)	2.340 (6)	Rh(2)-P(4)	2.338 (6)
Rh(1)-P(2)	2.391 (7)	Rh(2)-P(5)	2.360 (7)
Rh(1)-P(3)	2.294 (6)	Rh(2)-P(6)	2.305 (6)
Rh(1)-As(1)	2.410 (4)	Rh(2)-As(1)	2.437 (4)
Rh(1)-As(2)	2.582 (3)	Rh(2)-As(2)	2.578 (3)
Rh(1)-S	2.461 (5)	Rh(2)-S	2.430 (5)
As(1)-As(2)	2.521 (5)	As(2)-S	2.336 (5)
As(1)-S	3.099 (6)	Rh(1)···Rh(2)	3.750 (3)

P(1)-Rh(1)-P(2)	87.1 (2)	P(4)-Rh(2)-P(5)	87.6 (2)
P(1)-Rh(1)-P(3)	88.7 (2)	P(4)-Rh(2)-P(6)	92.7 (2)
P(1)-Rh(1)-As(1)	93.5 (2)	P(4)-Rh(2)-As(1)	94.0 (2)
P(1)-Rh(1)-As(2)	109.1 (2)	P(4)-Rh(2)-As(2)	108.0 (2)
P(1)-Rh(1)-S	164.2 (2)	P(4)-Rh(2)-S	163.4 (2)
P(2)-Rh(1)-P(3)	90.8 (2)	P(5)-Rh(2)-P(6)	87.7 (2)
P(2)-Rh(1)-As(1)	162.2 (2)	P(5)-Rh(2)-As(1)	163.3 (2)
P(2)-Rh(1)-As(2)	102.5 (2)	P(5)-Rh(2)-As(2)	103.4 (2)
P(2)-Rh(1)-S	95.8 (2)	P(5)-Rh(2)-S	94.8 (2)
P(3)-Rh(1)-As(1)	107.0 (2)	P(6)-Rh(2)-As(1)	108.8 (2)
P(3)-Rh(1)-As(2)	158.1 (2)	P(6)-Rh(2)-As(2)	156.7 (2)
P(3)-Rh(1)-S	106.7 (2)	P(6)-Rh(2)-S	103.8 (2)
As(1)-Rh(1)-As(2)	60.5 (1)	As(1)-Rh(2)-As(2)	60.3 (1)
As(1)-Rh(1)-S	79.0 (2)	As(1)-Rh(2)-S	79.1 (2)
As(2)-Rh(1)-S	55.1 (1)	As(2)-Rh(2)-S	55.5 (1)
Rh(1)-As(1)-As(2)	63.1 (1)	Rh(2)-As(1)-As(2)	62.6 (1)
Rh(1)-As(1)-S	51.2 (1)	Rh(2)-As(1)-S	50.4 (1)
Rh(1)-As(1)-Rh(2)	101.4 (1)	As(2)-As(1)-S	47.8 (1)
Rh(1)-As(2)-As(1)	56.3 (1)	Rh(2)-As(2)-As(1)	57.1 (1)
Rh(1)-As(2)-S	59.8 (1)	Rh(2)-As(2)-S	59.0 (1)
Rh(1)-As(2)-Rh(2)	93.2 (1)	As(1)-As(2)-S	79.2 (2)
Rh(1)-S-As(1)	49.8 (1)	Rh(2)-S-As(1)	50.5 (1)
Rh(1)-S-As(2)	65.1 (2)	Rh(2)-S-As(2)	65.5 (2)
Rh(1)-S-Rh(2)	100.1 (2)	As(1)-S-As(2)	53.0 (1)

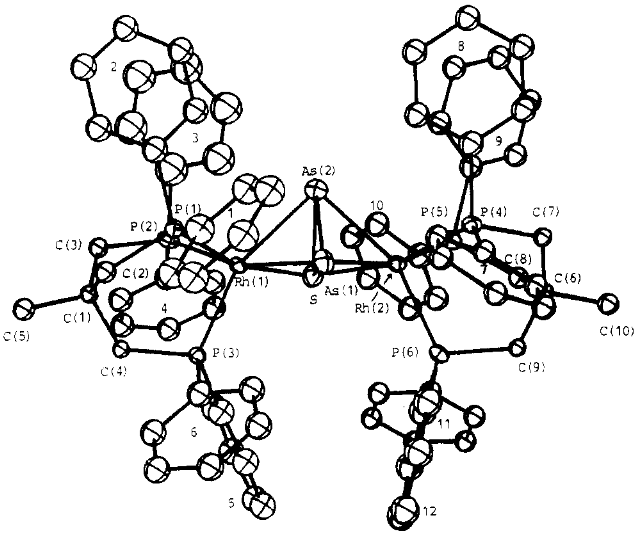

Figure 1. Perspective view of the [(triphos)Rh(As_2S)Rh(triphos)]$^{2+}$ cation with 20% probability ellipsoids. Phenyl groups are numbered consistently with the first figure(s) in the labels of their carbon atoms.

the pseudothreefold symmetry that has been found for most of the triple-decker complexes having the triangular cyclo-triphosphorus unit as internal slice.[17] The lower symmetry of the present cation is due both to the irregular shape of its As_2S group and to the position that such a group occupies with respect to the metal atoms. One side of the As_2S ring is so long [As(1)-S = 3.099 (6) Å] that it should involve no bonding interaction, whereas the other two sides are shorter but are of different lengths [As(1)-As(2) = 2.521 (5) Å, As(2)-S = 2.336 (5) Å]. It should be noted that due to the orientational disorder in the ring (see the Experimental Section and footnote *b* to Table II) the above As/S labels have been assigned on the basis of predominant site occupancy. Moreover, the positional parameters obtained from the least-squares refinement for the ring sites are averaged over those of the As and S occupants of each site so that no precise chemical significance may be attached to the values of distances in the ring quoted above, irrespective of the error estimates provided by the least squares. It is, however, possible to state that (a) the bond undergoing cleavage has predominant As-S character since it lies opposite the As(2) site having As occupancy close to 1.0 and (b) the lengths of the other two edges, As(1)-As(2) > As(2)-S, correlate with the As contents of the unshared As(1) and S sites: 0.74 and 0.31, respectively. The last two edges are longer in the mean (2.43 Å) than those of the disordered As_2S group in the parent cobalt compound [(triphos)Co(As_2S)]BF_4, which span the 2.26-2.34-Å range.[2] The triangular As_2S unit is approximately perpendicular to the line joining the metal atoms and lies with its long edge close to that line: the deviations of the As(1), S, Rh(1), and Rh(2) atoms from their least-squares plane are indeed all <0.05 Å. The above four atoms form the base of a sort of square pyramid having As(2) in the apical position (Figure 2a,b). The latter site forms with the metal atoms longer distances [2.58 (1) Å, mean] than those formed by the basal sites (2.41-2.46 Å). The Rh(1)···Rh(2) separation, 3.750 (3) Å, is shorter than the metal-metal distance in any of the *cyclo*-triphosphorus or *cy-*

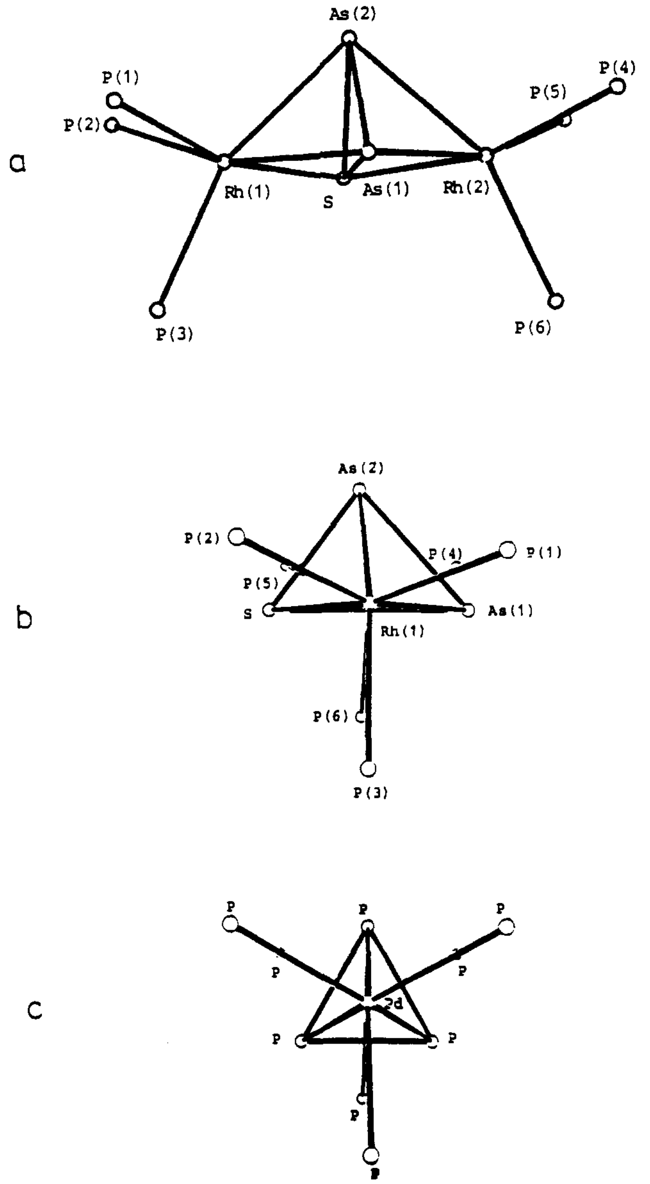

Figure 2. (a) Inner skeleton of the [(triphos)Rh(As_2S)Rh(triphos)]$^{2+}$ cation. (b) Skeleton of the [(triphos)Rh(As_2S)Rh(triphos)]$^{2+}$ cation viewed along the metal-metal direction. (c) View as in (b) of the core of the [(triphos)Pd(P_3)Pd(triphos)]$^{2+}$ cation[18] having approximate D_{3h} symmetry.

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Table IV. Absorption Maxima and Extinction Coefficients for the Electronic Spectra of the Complexes

compd	sample[a]	λ_{max}, nm (ϵ, M^{-1} cm^{-1})
$[(triphos)Co(P_2S)Co(triphos)](BF_4)_2\cdot 2(CH_3)_2CO$	a	460 (sh), 380
	b	470 (sh, ~2200), 370 (10 200)
$[(triphos)Co(P_2S)Rh(triphos)](BF_4)_2\cdot 2(CH_3)_2CO$	a	460 (sh), 380
	b	460 (sh, ~2400), 370 (9800)
$[(triphos)Rh(P_2S)Rh(triphos)](BPh_4)_2\cdot 2(CH_3)_2CO$	a	460 (sh), 380
	b	460 (sh, ~2150), 370 (10 100)
$[(triphos)Co(As_2S)Co(triphos)](BF_4)_2\cdot 2(CH_3)_2CO$	a	950, 480 (sh), 380
	b	950 (680), 480 (sh, ~2250), 380 (9200)
$[(triphos)Co(As_2S)Rh(triphos)](BF_4)_2\cdot 2(CH_3)_2CO$	a	750 (sh), 480 (sh), 380
	b	740 (sh, ~700), 480 (sh, ~2130), 380 (8700)
$[(triphos)Rh(As_2S)Rh(triphos)](BPh_4)_2\cdot 2(CH_3)_2CO$	a	740, 470 (sh), 380
	b	730 (720), 470 (sh, ~2050), 380 (8950)

[a] Key: a, solid; b, nitroethane solution.

clo-triarsenic complexes previously investigated,[17] mainly as a consequence of the lengthening of one side of the internal triatomic ring. The same sort of structure may be assigned to the other complexes reported here, on the basis of the similarities in their magnetic and spectral properties (Table I and IV).

The arrangement of the inner skeleton of the present cation, which may be assigned the idealized C_{2v} symmetry if we ignore that the As_2S ring is heteroatomic (Figure 2a,b), could be considered to originate from the more regular arrangement possessed by most triple-decker *cyclo*-triphosphorus complexes,[17] which approaches the D_{3h} geometry (Figure 2c),[18] through a distortion involving the simultaneous (a) lengthening of one side of the internal triatomic ring, (b) shift of such a group along the direction going from the bond being cleaved to the opposite vertex, and (c) bending of the axes of the triphos ligands, which follow the shift of the internal slice. The conformations at both ends of such an idealized $D_{3h} \rightarrow C_{2v}$ distortion path are compared in parts c (D_{3h})[18] and b (C_{2v}) of Figure 2. An intermediate conformation along such a path is that found for the $[(triphos)Ni(P_3)Rh(triphos)]^{2+}$ cation.[6] That cation has the same 32-valence-electron count[17] as the present complexes and exhibits quite similar magnetic properties. No significant distortion from the threefold symmetry, on the other hand, was detected for the isoelectronic, but high-spin, $[(triphos)Co(P_3)Ni(triphos)]^{2+}$ complex.[5] Actually, these 32-electron triple-decker complexes should have, in the description of an electrostatic one-electron Hamiltonian, a spin triplet and orbitally degenerate ground state, stabilized by exchange, associated with the C_3 or higher effective symmetry of their inner skeleton. They may, however, also gain stability by undergoing a distortion to an arrangement with C_{2v} effective symmetry as described above: this removes the orbital degeneracy, producing a singlet ground state. It was suggested that the tendency of *cyclo*-triphosphorus complexes to distort increases with increasing interactions between the (triphos)M moieties and the internal triatomic unit.[6,17]

In order to test this hypothesis further, with inclusion in the considerations of the triple-decker complexes formed by heteroatomic rings, extended Hückel calculations[19,20] with values of parameters from the literature[21-24] have been performed on idealized $[(PH_3)_3M(E_2E')M(PH_3)_3]^{n+}$ 32-valence-electron models [M = Co, Rh; E = E' = P, As; E = P, E' = S; E = As, E' = S; n = 1 (E' = S), 2 (E' = P, As); both homoatomic and heteroatomic bond cleavage tested for the P_2S and As_2S models]. The φ, ϑ, and δ parameters shown in Figure 3 were varied in order to reproduce as closely as possible the distortion experimentally found; details are given with the supplementary material.[15] In spite of the limitations of the method and of the simplifying assumptions necessarily involved in the model[15] the following general indications provided by the calculations should be meaningful. The trends in the sums of orbital energies for the models with M = Co are grossly similar to each other, as are those for the models with M = Rh, the two sets being distinctly different. The representative trends shown in Figure 3 suggest that the distortion is favored when 3d metal atoms are replaced by 4d metal atoms in the cation. A similar conclusion is drawn from inspection of trends in the energy of the highest occupied molecular orbital (not shown), which are all decreasing, those for M = Rh more steeply than those for M = Co. The following mechanism for distortion is

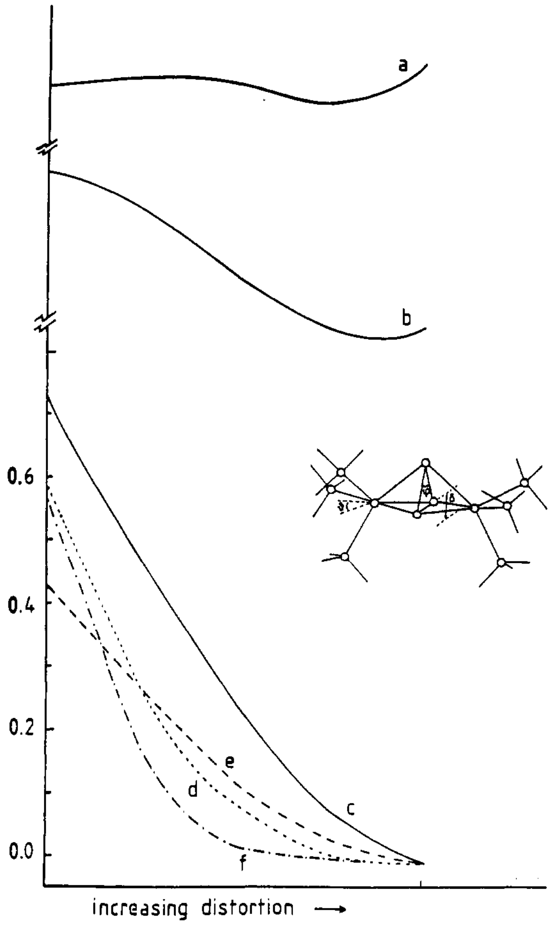

Figure 3. Representative trends in total energy (curve a and b; eV markings, arbitrary origin) and in bond overlap population (curves c–f) from extended Hückel calculations on $[(PH_3)_3M(EE'E'')M(PH_3)_3]^{n+}$ models (notation EE'E'' used here to specify the position of the hetero atom in E_2S rings) as a function of the distortion produced by linear increase in the φ and ϑ angles and δ elevation.[15] The amount of distortion approximately corresponding to that found in the As_2S complex is indicated by a marking on the abscissas. E_{tot} trends are shown for models with E = E'' = As, E' = S and with (a) M = Co or (b) M = Rh. Overlap population trends, for the E···E' bond, are all for models with M = Rh and (c) E = E' = E'' = P, (d) E = E' = E'' = As, (e) E = E' = As, E'' = S, and (f) E = E'' = As, E' = S (present case).

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indicated: a moderate deformation imposed on the E$_3$ rings or the inherent asymmetry of the heteroatomic E$_2$E′ rings favors mixing of high-energy empty orbitals of the triatomic fragment into the HOMO of the cation, producing a substantial antibonding contribution to one of the bonds in the ring. The extent of such mixing increases with increasing interactions between the internal slice and the other moieties in the complex, *i.e.* with the larger interfragment overlaps when Co is replaced by Rh and with the better availability of low-energy empty orbitals of the triatomic fragment when P is replaced by As. It is probably less safe to conclude from the above trends in overlap population and availability of virtual orbitals that the heteroatomic As–S bond in the As$_2$S ring should cleave rather than the homoatomic As–As one, because moderate perturbations, such as small deformations of the ring or shifts of the undistorted As$_2$S unit with respect to the M···M axis, are sufficient to switch the antibonding contribution from one bond to the other. It should moreover be noted in this connection that the type of distortion presently found brings as As, rather than S, atom in the site which lies farthest from the metal atoms, with the least decrease in overlap population. The As(1)···S overlap population at the experimental geometry practically vanishes.

It should be noted that the distortion toward a square-pyramidal arrangement of the inner skeleton in the present compounds is rationalized also by Wade's rules.[25] In fact, such an arrangement corresponds to the geometry of the nido species based on the octahedron, expected for a cluster of five atoms with seven skeletal bonding electron pairs.

The low magnetic moments of the compounds (Table I), which decrease with temperature, are tentatively attributed to TIP contribution to a singlet ground state, in analogy with the rationalization already proposed for the magnetic behavior of the isoelectronic *cyclo*-triphosphorus complexes.[6] The electronic spectra of all compounds (Table IV) exhibit two intense bands in the 370–480-nm range, whose positions are remarkably insensitive to changes in the nature of the metal and/or ring atoms. Both are shifted to frequencies higher than the two intense bands in the spectra of the isoelectronic *cyclo*-triphosphorus derivatives previously investigated.[6] Such a shift is probably related to the larger distortion existing in the present compounds since these bands should originate from transitions between states in the HOMO–LUMO region and should therefore be sensitive to changes in geometry. A lower feature at 730–950 nm is present in the spectra of the As$_2$S derivatives but not in those of the P$_2$S ones, where it may be masked by the intense bands. Alternatively, such a band may originate from a spin-forbidden transition which gains intensity in the spectra of the As$_2$S derivatives due to the presence of a larger number of heavy atoms in those compounds.

Finally, two aspects of the reactivity of these compounds are worthy of note. First, the formation, in rather low yields, of the dicobalt complexes from the [(triphos)Co(E$_2$S)]BF$_4$ parents and the Co(BF$_4$)$_2$ salt involves a decrease in the average oxidation number of the metal atoms, at variance with the formation of the 31-electron *cyclo*-triphosphorus [(triphos)Co(P$_3$)Co(triphos)]$^{2+}$ complex,[5] which does not involve any reduction although it takes place through the analogous reaction of [(triphos)Co(P$_3$)] with Co(BF$_4$)$_2$. Presumably, 31-electron dinuclear intermediates are formed also in the present cases but, being reactive due to their 3+ charge and to the presence of the heteroatomic ring, they undergo reduction, transforming to the diamagnetic distorted species. Second, the transferability of the triatomic unit between metal–ligand moieties, never detected for *cyclo*-triphosphorus derivatives, suggests that cleavage of bonds between the metal and ring atoms is easier when the ring is heteroatomic.

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Registry No. [(triphos)Co(P$_2$S)Co(triphos)](BF$_4$)$_2$, 96212-91-8; [(triphos)Co(P$_2$S)Rh(triphos)](BF$_4$)$_2$, 96212-93-0; [(triphos)Rh(P$_2$S)-Rh(triphos)](BPh$_4$)$_2$, 96212-95-2; [(triphos)Co(As$_2$S)Co(triphos)](BF$_4$)$_2$, 96212-97-4; [(triphos)Co(As$_2$S)Rh(triphos)](BF$_4$)$_2$, 96212-99-6; [(triphos)Rh(As$_2$S)Rh(triphos)](BPh$_4$)$_2$·2(CH$_3$)$_2$CO, 96213-02-4; [(triphos)-Co(As$_2$S)]BF$_4$, 88887-22-3; [(triphos)Co(P$_2$S)]BF$_4$, 84070-49-5; [RhCl(cod)]$_2$, 12092-47-6; [(PH$_3$)$_3$Co(As$_2$P)Co(PH$_3$)$_3$]$^+$, 96213-03-5; [(PH$_3$)$_3$Co(P$_2$As)Co(PH$_3$)$_3$]$^+$, 96213-04-6; [(PH$_3$)$_3$Rh(P$_2$As)Rh-(PH$_3$)$_3$]$^+$, 96213-05-7; [(PH$_3$)$_3$Rh(As$_2$P)Rh(PH$_3$)$_3$]$^+$, 96213-06-8; [(PH$_3$)$_3$Co(As$_2$S)Co(PH$_3$)$_3$]$^{2+}$, 96213-07-9; [(PH$_3$)$_3$Co(P$_2$S)Co-(PH$_3$)$_3$]$^{2+}$, 96213-08-0; [(PH$_3$)$_3$Rh(As$_2$S)Rh(PH$_3$)$_3$]$^{2+}$, 96213-09-1; [(PH$_3$)$_3$Rh(P$_2$S)Rh(PH$_3$)$_3$]$^{2+}$, 96245-23-7.

Supplementary Material Available: Tables of thermal parameters, hydrogen atom coordinates, bond distances and angles, and calculated and observed structure factor amplitudes for [(triphos)Rh(As$_2$S)Rh-(triphos)](BPh$_4$)$_2$·2(CH$_3$)$_2$CO and details on EH models (41 pages). Ordering information is given on any current masthead page.

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(25) Wade, K. In "Transition Metal Clusters"; Johnson, B. F. G., Ed.; Wiley: New York, 1980.