$Fe(CO)_5$ to give the trimetallic species **2**; it is hoped that $^{\bullet}Re(CO)_5$ generated in this fashion will react with other coordinatively unsaturated metal centers to form new metal–metal bonds. We are also investigating the reactivity of **1** toward a variety of two-electron ligands as a preparative route to other Re(0) radicals.

Acknowledgment. We thank Dr. J. W. Faller for his assistance in solving the crystal structure of **1**. We are grateful to the donors of the Petroleum Research Fund, administered by the American Chemistry Society, for their support of this research. B.M.M. acknowledges the receipt of a PRF Summer Research Fellowship. L.S.C. is grateful for a Connecticut High Technology Graduate Scholarship. The receipt of a Cottrell Grant from the Research Corp. is gratefully acknowledged.

Supplementary Material Available: For **1** and **2** summaries of the complete X-ray analyses, including tables of positional parameters, distances, angles, and thermal parameters, and for **2** perspective drawings of its two crystallographically independent molecules (34 pages); listings of F_o and F_c for **1** and **2** (34 pages). Ordering information is given on any current masthead page.

Contribution from the Dipartimento di Chimica, Università di Firenze, Via Maragliano 77, 50144 Florence, Italy,
and Department of Chemistry, University of Sheffield, Sheffield S3 7HF, England

Reactivity of Tetraphosphorus Trichalcogenides with Rhodium(I)- and Iridium(I)-Triphosphane Fragments. Synthesis and Characterization of Mixed-Metal and Unsubstituted-Main-Group-Element Cluster Compounds. Crystal and Molecular Structures of $[(\text{triphos})M(P_3X_3)]\cdot C_6H_6$ (M = Rh, X = S, Se; M = Ir, X = S)

Massimo Di Vaira,[†] Brian E. Mann,[‡] Maurizio Peruzzini,[§] and Piero Stoppioni[*,†]

Received February 19, 1988

The reaction of tetraphosphorus trisulfide or tetraphosphorus triselenide with $[MCl(cod)]_2$ (M = Rh, Ir; cod = cycloocta-1,5-diene) in the presence of triphos [triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane, $CH_3C(CH_2PPh_2)_3$] yields the compounds $[(\text{triphos})M(P_3X_3)]\cdot C_6H_6$ [M = Rh, X = S (**1**), Se (**2**); M = Ir, X = S (**3**), Se (**4**)]. The crystal structures of **1**–**3** have been elucidated through complete X-ray analyses. The compounds crystallize in the orthorhombic $P2_1nb$ space group with $Z = 4$ and the following unit-cell dimensions: **1**, $a = 19.109$ (5) Å, $b = 19.445$ (5) Å, $c = 12.319$ (4) Å; **2**, $a = 19.277$ (7) Å, $b = 19.608$ (9) Å, $c = 12.398$ (6) Å; **3**, $a = 19.131$ (9) Å, $b = 19.451$ (9) Å, $c = 12.293$ (6) Å. The compounds contain the (triphos)M system replacing a basal P atom of the cage molecule. ^{31}P NMR data for the compounds, which form systems having six (**3**, **4**) and seven (**1**, **2**) magnetically active nuclei, are reported.

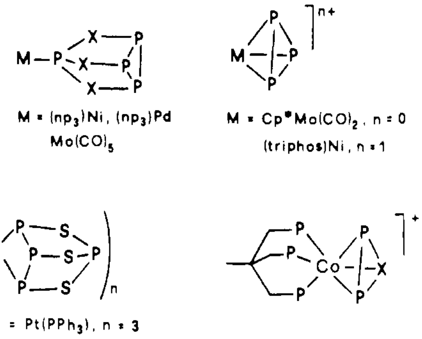
Introduction

Some effort has been recently devoted to elucidating the reactivity of main-group clusters toward transition-metal fragments.[1–6] Among the numerous neutral and ionic species containing unsubstituted main-group elements, the chalcogenides of group V elements, E_4X_3 (E = P, As; X = S, Se), are receiving considerable attention because different types of atoms are present in the cage molecules of these compounds and atoms of the same chemical type have different environments (e.g. apical vs basal pnicogens).

In particular, the intact P_4X_3 (X = S, Se) molecules have been found to coordinate to a metal fragment through the apical P atom in the four-coordinate complexes $[(np_3)M(P_4X_3)]$ [np_3 = tris(2-diphenylphosphinoethyl)amine; M = Ni, Pd; X = S,[7] Se[8]] and in the hexacoordinate complex $[Mo(P_4S_3)(CO)_5]$[9] (Chart I). P_4S_3 reacts with $[IrCl(CO)(PPh_3)_2]$ and $[Pt(C_2H_4)(PPh_3)_2]$ to give di-[10] and trimetallic[11] compounds through the insertion of a metal–ligand fragment into a P–P bond of the cage. Substantial cleavage of the cage molecules, on the other hand, occurs in the reactions with $[Cp^*Mo(CO)_2]_2$ (Cp^* = pentamethylcyclopentadienyl) and with cobalt(II) and nickel(II) tetrafluoroborates in the presence of triphos [triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane]. The molybdenum[12,13] and nickel[14] derivatives contain the cyclo-P_3 unit η^3-bound to the metal fragment, whereas the cobalt compounds[15] incorporate the heterocyclic P_2X units (X = S, Se) η^3-bound to the cobalt moiety. These processes have recently been summarized.[16]

We have investigated the reactions of P_4X_3 (X = S, Se) with the $(\text{triphos})M^I$ (M = Rh, Ir) moieties, which provide the same geometrical environment as the $(\text{triphos})M^{II}$ (M = Co, Ni) fragments, but with the metal in a lower oxidation state. Such reactions yielded the compounds $[(\text{triphos})M(P_3X_3)]$ [M = Rh, X = S (**1**), Se (**2**); M = Ir, X = S (**3**), Se (**4**)], which have been

Chart I. Summary of Structure Types Obtained in the Reaction of P_4X_3 with Various Metal Complexes



[†] University of Florence.

[‡] University of Sheffield.

[§] Present address: Istituto ISSECC, CNR, Via J. Nardi 39, 50132 Florence, Italy.

(1) *Rings, Clusters, and Polymers of Main Group Elements*; Cowley, A. H., Ed.; ACS Symposium Series 232; American Chemical Society: Washington, DC, 1983; p 17.
(2) Di Vaira, M., Sacconi, L. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 330.
(3) Di Vaira, M.; Peruzzini, M.; Stoppioni, P. *Polyhedron* **1987**, *6*, 351.
(4) Herrmann, W. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 76.
(5) Draganjac, M.; Rauchfuss, T. B. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 742.
(6) Scherer, O. J. *Comments Inorg. Chem.* **1987**, *6*, 1.
(7) Di Vaira, M.; Peruzzini, M.; Stoppioni, P. *Inorg. Chem.* **1983**, *22*, 2196.
(8) Di Vaira, M.; Peruzzini, M.; Stoppioni, P. *J. Organomet. Chem.* **1983**, *258*, 373.
(9) Cordes, R. W.; Joyner, R. D.; Shores, A. D.; Dill, E. D. *Inorg. Chem.* **1974**, *13*, 132.
(10) Ghilardi, C. R.; Midollini, S.; Orlandini, A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 790.
(11) Di Vaira, M.; Peruzzini, M.; Stoppioni, P. *J. Chem. Soc., Dalton Trans.* **1985**, 291.
(12) Bernal, I.; Brunner, H.; Meier, W.; Pfisterer, H.; Wachter, J.; Ziegler, M. L. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 438.

0020-1669/88/1327-3725$01.50/0

Table I. Crystallographic Data for [(triphos)Rh(P_3S_3)]·C_6H_6 (**1**), [(triphos)Rh(P_3Se_3)]·C_6H_6 (**2**), and [(triphos)Ir(P_3S_3)]·C_6H_6 (**3**)

	1	**2**	**3**
formula	$C_{188}H_{180}P_{24}$-Rh_4S_{12}	$C_{188}H_{180}P_{24}$-Rh_4Se_{12}	$C_{188}H_{180}Ir_4$-$P_{24}S_{12}$
fw	994.82	1135.51	1084.12
space group	$P2_1nb^a$	$P2_1nb^a$	$P2_1nb^a$
a, Å	19.109 (5)	19.277 (7)	19.131 (9)
b, Å	19.445 (5)	19.608 (9)	19.451 (9)
c, Å	12.319 (4)	12.398 (6)	12.293 (6)
V, Å^3	4577.4	4686.2	4574.4
Z	4	4	4
λ(Mo Kα), Å	0.710 69	0.710 69	0.710 69
d(calcd), g cm^{-3}	1.443	1.609	1.574
μ(MoKα), cm^{-1}	7.37	28.98	32.78
T_{max}/T_{min}	0.96/0.93	0.85/0.74	0.61/0.45
R^b	0.052	0.048	0.045
$R_w{}^c$	0.052	0.049	0.054

[a] Alternative setting of $Pna2_1$ (No. 33 of ref 24a). [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

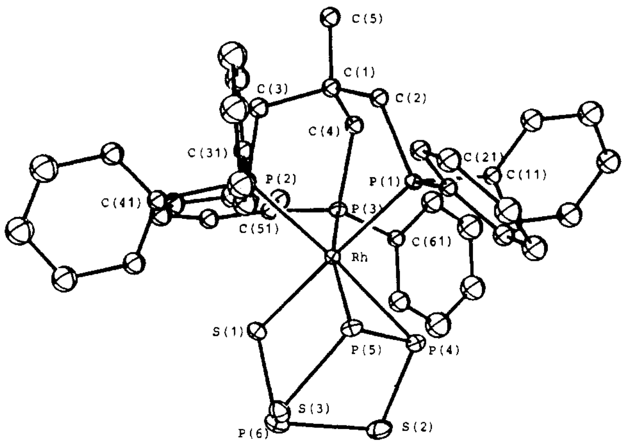
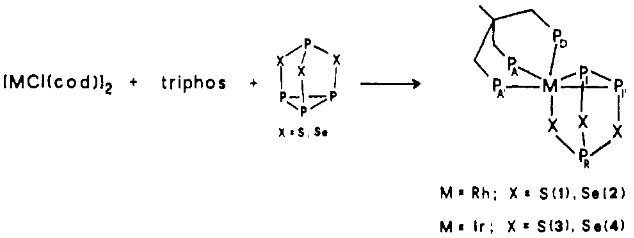


Figure 1. Perspective view of the [(triphos)Rh(P_3S_3)] molecule.

Scheme I



characterized by X-ray diffraction studies and ^{31}P NMR data. A preliminary account of part of this work has already appeared.[17]

Experimental Section

General Data. All solvents were reagent grade and were appropriately dried and freed of molecular oxygen prior to use.[18] All reactions were performed under a nitrogen atmosphere. Conductivity measurements were obtained as previously described.[19] ^{31}P NMR spectra were collected (at 121.48 MHz) on a Bruker CXP spectrometer. Phosphorus-31 positive chemical shifts are to high frequency relative to 85% H_3PO_4, external standard, at 0.0 ppm. The ligand 1,1,1-tris((diphenylphosphino)methyl)ethane (triphos),[20] the complexes [MCl(cod)]$_2$ (M = Rh,[21] Ir;[22] cod = cycloocta-1,5-diene), and P_4Se_3[23] were prepared according to published procedures. P_4S_3 was purchased from Fluka AG and used after recrystallization from benzene. 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 recrystallilzed from methylene chloride and benzene.

Preparation of [(triphos)M(P_3X_3)]·C_6H_6 [M = Rh, X = S (1), Se (2); M = Ir, X = S (3), Se (4)]. P_4X_3 (X = S, Se; 2 mmol) dissolved in benzene (50 mL) was added to a warm solution obtained by mixing triphos (2 mmol) in tetrahydrofuran (20 mL) and [MCl(cod)]$_2$ (M = Rh, Ir; 1 mmol) in tetrahydrofuran (50 mL). The resulting mixture was gently refluxed for 1 h during which time it turned deep red. Warm 1-butanol (40 mL) was added, and the resulting suspension was filtered. Light yellow crystals of the complexes were obtained by refluxing the solutions overnight. Analytical data for the complexes, which crystallize with one molecule of benzene, are in good agreement with the proposed formulas. Anal. Calcd (found) for $C_{47}H_{45}P_6RhS_3$ (**1**): C, 56.75 (56.61); H, 4.56 (4.59); P, 18.68 (18.30); S, 9.67 (9.46). Calcd (found) for $C_{47}H_{45}P_6RhSe_3$ (**2**): C, 49.71 (49.44); H, 3.99 (4.10); P, 16.36 (15.98). Calcd (found) for $C_{47}H_{45}IrP_6S_3$ (**3**): C, 52.07 (51.85); H, 4.18 (4.21); P, 17.14 (16.90); S, 8.87 (8.56). calcd (found) for $C_{47}H_{45}IrP_6Se_3$ (**4**): C, 46.09 (45.93); H, 3.70 (3.79); P, 15.17 (15.05).

X-ray Structural Determinations. The main results of the structural investigation of the compound [(triphos)Rh(P_3S_3)] (**1**) have already been reported as a part of a preliminary communication.[17] The structures of [(triphos)Rh(P_3Se_3)] (**2**) and [(triphos)Ir(P_3S_3)] (**3**) have subsequently been determined in order to achieve a fuller characterization of the compounds of this series. The structure of [(triphos)Ir(P_3Se_3)] could not be investigated because of the bad quality of the crystals. Crystal data for the three compounds are given in Table I. A Philips PW 1100 automated diffractometer and graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å) were used for all operations. Unit-cell parameters were determined by least-squares refinement of the setting angles of 24 reflections having 24° < 2θ < 26° (**1**), 22° < 2θ < 26° (**2**), or 28° < 2θ < 32° (**3**). Intensity data were collected at room temperature by the θ–2θ scan technique, stationary background counts being taken at each end of the scan for a time equal to half the scan time. The intensities of three standard reflections monitored periodically throughout data collections showed only random fluctuations. Corrections for Lorentz, polarization, and X-ray absorption effects were applied. The principal computer programs used in the crystallographic calculations are given in ref 25. The structure of **1** was determined by heavy-atom procedures, and those of compounds **2** and **3** were refined by using as initial atomic positions those from the structure of **1**. In the full-matrix least-squares refinements the function $\sum w(|F_o| - F_c|)^2$ was minimized. In the final cycles the metal, chalcogen, and P atoms were refined anisotropically whereas lighter atoms were assigned isotropic temperature factors (overall *U* for atoms in the benzene solvate molecule). Phenyl groups were refined as rigid bodies with idealized geometry. Hydrogen atoms were introduced in calculated positions (C–H = 1.00 Å, the triphos CH_3 group being refined as a rigid body) with $U_H = 1.2U_C$. Due to the polar nature of the space group, refinements were performed on models of both enantiomorphs for each compound. On the basis of Hamilton's test[26] the correct enantiomorph could be assigned in each case, since the ratios of *R* factors from the refinements on the alternative models were 1.02 (**1**), 1.04 (**2**), and 1.06 (**3**). Scattering factors for the neutral atoms and the anomalous dispersion corrections for Rh, Ir, and Se were taken from ref 24b.

Table II contains a list of atomic positional parameters and isotropic or equivalent isotropic thermal parameters for **1**. Values of selected bond distances and angles for the three compounds are given in Table III. Available as supplementary material are lists of atomic positional pa-

---

(13) Brunner, H.; Ulrich, K.; Meier, W.; Wachter, J.; Serhadle, O.; Ziegler, M. L. *J. Organomet. Chem.* **1987**, *335*, 339.

(14) Di Vaira, M.; Sacconi, L.; Stoppioni, P. *J. Organomet. Chem.* **1983**, *250*, 183.

(15) Di Vaira, M.; Peruzzini, M.; Stoppioni, P. *J. Chem. Soc., Dalton Trans.* **1984**, 359.

(16) Di Vaira, M.; Peruzzini, M.; Stoppioni, P. *Polyhedron* **1986**, *5*, 945.

(17) Di Vaira, M.; Peruzzini, M.; Stoppioni, P. *J. Chem. Soc., Chem. Commun.* **1983**, 903.

(18) Perrin, O. O.; Armarego, W. L. F.; Perrin, D. R. In *Purification of Laboratory Chemicals*; Pergamon: Oxford, England, 1966.

(19) Sacconi, L.; Morassi, R. *J. Chem. Soc. A* **1968**, 2997.

(20) Hewertson, W.; Watson, H. R. *J. Chem. Soc.* **1962**, 1490.

(21) Herde, J. L.; Lambert, J. C.; Senoff, C. V. *Inorg. Synth.* **1974**, *15*, 18.

(22) Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1979**, *19*, 218.

(23) Irgolic, K.; Zingaro, R. A.; Kudchadker, M. *Inorg. Chem.* **1965**, *4*, 1421.

(24) (a) *International Tables for Crystallography*; Reidel: Dordrecht, Holland, 1983; Vol. A, p 224. (b) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, pp 71, 148.

(25) Sheldrick, G. M. "SHELX, a Program for Crystal Structure Determination"; University of Cambridge: Cambridge, England, 1977. Johnson, C. K. *Oak Ridge Natl. Lab.* [Rep.] *ORNL (U.S.)* **1965**, *ORNL 3794*. These programs have been adapted to a SEL computer by Dr. C. Mealli.

(26) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.

Table II. Positional Parameters and Isotropic Thermal Factors for $[(\text{triphos})\text{Rh}(P_3S_3)]\cdot C_6H_6$[a–c]

atom	*x*	*y*	*z*	U_{eq}/U_{iso}, Å^2
Rh	6000[d]	759 (1)	111 (1)	22
S(1)	6066 (3)	1967 (2)	−268 (3)	37
S(2)	7678 (3)	1716 (3)	396 (4)	52
S(3)	7170 (3)	1393 (2)	−2020 (4)	41
P(1)	5931 (3)	−377 (2)	659 (3)	26
P(2)	4967 (3)	581 (2)	−922 (4)	27
P(3)	5357 (2)	1054 (2)	1661 (3)	29
P(4)	7240 (2)	721 (3)	490 (4)	40
P(5)	6919 (3)	481 (3)	−1152 (4)	33
P(6)	7048 (3)	2165 (2)	−826 (4)	46
C(1)	4467 (8)	−95 (8)	1021 (12)	32 (4)
C(2)	5014 (7)	−633 (8)	701 (13)	32 (4)
C(3)	4272 (8)	355 (8)	13 (12)	39 (4)
C(4)	4736 (8)	353 (8)	1964 (12)	36 (4)
C(5)	3823 (8)	−467 (8)	1402 (13)	39 (4)
C(11)	6243 (6)	−648 (5)	2013 (8)	30 (4)
C(12)	6048 (6)	−1303 (5)	2358 (8)	49 (4)
C(13)	6275 (6)	−1549 (5)	3362 (8)	64 (6)
C(14)	6697 (6)	−1139 (5)	4021 (8)	60 (5)
C(15)	6892 (6)	−483 (5)	3676 (8)	65 (6)
C(16)	6665 (6)	−237 (5)	2672 (8)	42 (4)
C(21)	6389 (4)	−1011 (5)	−166 (7)	26 (3)
C(22)	6077 (4)	−1364 (5)	−1025 (7)	33 (3)
C(23)	6474 (4)	−1811 (5)	−1662 (7)	44 (5)
C(24)	7183 (4)	−1906 (5)	−1440 (7)	54 (5)
C(25)	7495 (4)	−1553 (5)	−581 (7)	51 (5)
C(26)	7099 (4)	−1106 (5)	56 (7)	37 (4)
C(31)	4966 (5)	−104 (6)	−1973 (8)	31 (4)
C(32)	4441 (5)	−598 (6)	−2081 (8)	48 (5)
C(33)	4482 (5)	−1089 (6)	−2904 (8)	66 (6)
C(34)	5049 (5)	−1086 (6)	−3619 (8)	64 (6)
C(35)	5573 (5)	−592 (6)	−3511 (8)	61 (5)
C(36)	5532 (5)	−101 (6)	−2688 (8)	50 (5)
C(41)	4591 (5)	1250 (6)	−1795 (10)	39 (5)
C(42)	5039 (5)	1631 (6)	−2457 (10)	45 (5)
C(43)	4766 (5)	2119 (6)	−3171 (10)	59 (5)
C(44)	4045 (5)	2226 (6)	−3222 (10)	75 (6)
C(45)	3597 (5)	1846 (6)	−2560 (10)	77 (6)
C(46)	3870 (5)	1357 (6)	−1847 (10)	50 (5)
C(51)	4784 (6)	1824 (5)	1648 (7)	30 (4)
C(52)	4554 (6)	2089 (5)	2637 (7)	50 (5)
C(53)	4085 (6)	2639 (5)	2655 (7)	56 (5)
C(54)	3847 (6)	2923 (5)	1684 (7)	59 (5)
C(55)	4077 (6)	2658 (5)	694 (7)	53 (5)
C(56)	4546 (6)	2108 (5)	676 (7)	40 (4)
C(61)	5838 (5)	1220 (5)	2918 (9)	33 (4)
C(62)	5643 (5)	957 (5)	3927 (9)	54 (5)
C(63)	6022 (5)	1133 (5)	4854 (9)	80 (5)
C(64)	6598 (5)	1571 (5)	4772 (9)	74 (6)
C(65)	6794 (5)	1834 (5)	3763 (9)	77 (7)
C(66)	6414 (5)	1658 (5)	2836 (9)	53 (5)
C(71)	2950 (7)	−171 (7)	4017 (12)	91 (3)
C(72)	3481 (7)	−237 (7)	4787 (12)	91 (3)
C(73)	3851 (7)	342 (7)	5129 (12)	91 (3)
C(74)	3690 (7)	987 (7)	4702 (12)	91 (3)
C(75)	3159 (7)	1053 (7)	3932 (12)	91 (3)
C(76)	2789 (7)	474 (7)	3590 (12)	91 (3)

[a] Coordinates are multiplied by 10^4 and temperature factors by 10^3. [b] Standard deviations on the least significant digits are in parentheses. [c] $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j$; $U_{iso} = \exp[-8\pi^2 U(\sin^2\theta)/\lambda^2]$. [d] *x* coordinate of Rh not refined, due to the polar nature of the space group.

rameters for **2** and **3**, lists of anisotropic thermal parameters for the three compounds, extended tables of bond distances and angles, lists of hydrogen atom coordinates, and tables of observed and calculated structure factors. See the paragraph at the end of paper regarding supplementary material.

Results

The transformations observed in this work are summarized in Scheme I.

The isoelectronic $[(\text{triphos})M(P_3X_3)]$ compounds [M = Rh, X = S (**1**), Se (**2**); M = Ir, X = S (**3**), Se (**4**)] have been obtained by reacting the appropriate P_4X_3 cage molecule with $[\text{MCl(cod)}]_2$ in the presence of triphos in a relatively high boiling tetrahydrofuran, benzene, and 1-butanol reaction system.

Table III. Selected Bond Distances (Å) and Angles (deg) for the Compounds $[(\text{triphos})\text{Rh}(P_3S_3)]\cdot C_6H_6$ (**1**), $[(\text{triphos})\text{Rh}(P_3Se_3)]\cdot C_6H_6$ (**2**), and $[(\text{triphos})\text{Ir}(P_3S_3)]\cdot C_6H_6$ (**3**)[a]

	1	**2**	**3**
M–P(1)	2.313 (4)	2.322 (6)	2.304 (3)
M–P(2)	2.374 (5)	2.377 (7)	2.289 (6)
M–P(3)	2.342 (4)	2.338 (7)	2.285 (4)
M–P(4)	2.416 (4)	2.440 (7)	2.527 (4)
M–P(5)	2.408 (5)	2.404 (8)	2.477 (6)
M–X	2.400 (4)	2.524 (3)	2.418 (4)
P(4)–P(5)	2.165 (6)	2.152 (10)	2.164 (7)
P(1)–M–P(2)	88.3 (2)	88.2 (3)	89.8 (2)
P(1)–M–P(3)	88.1 (1)	87.8 (2)	89.2 (2)
P(2)–M–P(3)	92.1 (2)	92.2 (3)	95.6 (2)
P(4)–M–P(5)	53.3 (2)	52.7 (2)	51.2 (2)
P(4)–M–X	90.9 (2)	92.6 (2)	88.9 (2)
P(5)–M–X	93.2 (2)	95.1 (2)	91.2 (2)

[a] Legend: M = Rh (**1**, **2**), Ir (**3**); X = X (**1**, **3**), Se (**2**).

The compounds are air-stable both in the solid state and in solution. They are sparingly soluble in dichloromethane and in nitroethane, where they behave as nonelectrolytes. The compounds are obtained in different yields: 35–40% for **1** and **3** and 15–20% for **2** and **4**, lower yields pertaining to reactions with P_4Se_3, which is more reactive than P_4S_3.

Structures have been determined for complexes **1**–**3**, which are isomorphous and isostructural. The structures consist of neutral $[\text{triphos})M(P_3X_3)]$ molecules (M = Rh, X = S, Se; M = Ir, X = S) and of solvate benzene molecules. The metal atom of the (triphos)M system in each compound replaces one P atom of the triatomic P_3 side of the original P_4X_3 cage (Figure 1). The resulting P_3X_3 fragment is bound to the metal through the two undisplaced P atoms of the original P_3 side and through the chalcogen atom that was linked to the atom removed from the cage molecule. The metal atom is coordinated in addition by the three P atoms of the triphos ligand. The iridium derivative with the P_3Se_3 group may be safely assigned the same structure on the basis of the ^{31}P NMR spectral data (see below) and on the overall similarity of properties with those of the other compounds.

There are no notable differences between the structures of the two rhodium compounds, except for the obvious dissimilarities in bond lengths involving the S or Se atoms. On the other hand, the following trend is observed on going from the rhodium compounds to the iridium one: an overall shortening of the M–P(triphos) bonds occurs whereas lengthening of the M–P bonds formed by the P_3X_3 fragment takes place. A similar trend was observed[14] for the $[(\text{triphos})M(P_3)]$ (M = Rh, Ir)[27] compounds and the $[(\text{triphos})M(P_3)]^+$ (M = Pd, Pt)[28] complexes, where shortening of the M–P(triphos) distances and lengthening of the M–P(P_3) ones occurs on going from the 4d to the 5d compounds. Such similarities support our view that these trends are due to electronic factors originating at the metal atoms.[14]

The geometry of each coordinated P_3X_3 fragment does not deviate considerably from that of the parent P_4X_3 molecule. The most significant change is due to shortening of the P–P bond: 2.165 (6) Å (**1**), 2.152 (10) Å (**2**), and 2.164 (7) Å (**3**) vs the 2.235 (11)[29] and 2.228 (9) Å[8] mean values respectively found for the P_4S_3 and P_4Se_3 molecules. The present P–P values are in line with those found for the P_3 derivatives of Rh or Ir.[27]

Discussion

In their reactions with various transition-metal fragments the tetraphosphorus trichalcogenide cage molecules may undergo both disruptive and nondisruptive processes, depending on the initial

---

[27] Bianchini, C.; Mealli, C.; Meli, A.; Sacconi, L. *Inorg. Chim. Acta* **1979**, *37*, L543.

[28] Dapporto, P.; Sacconi, L.; Stoppioni, P.; Zanobini, F. *Inorg. Chem.* **1981**, *20*, 3834.

[29] Lenng, Y. C.; Waser, I.; van Houten, S.; Vos, A.; Wiegers, G. A.; Wiebenga, E. *Acta Crystallogr.* **1957**, *10*, 574.

electron count at the metal atom and the geometry-determined bonding mode of the specific metal–ligand system provided by the reactant. In particular, the d^{10}-ML_3 $(np_3)M$ (M = Ni, Pd; L stands for a monodentate ligand)[7,8] and d^6-ML_5 $Mo(CO)_5$[9] electron-rich metal moieties may be assumed to preserve the intact cage molecules because they favor processes in which the 18-electron configuration of the metal atom is also preserved.[7]

The insertion of the isolobal d^{10}-ML_2 $Pt(PPh_3)_2$[11] or d^8-ML_4 $IrCl(CO)(PPh_3)_2$[10] fragments into a P–P bond of the cage may involve changes in formal oxidation numbers but not in the overall electron count on going from the interacting species to the final products.

On the other hand, the interactions with $(triphos)Co^{II}$, $(triphos)Ni^{II}$, or other systems,[12-15] leading to the extrusion of triatomic groups (homocyclic, P_3, or heterocyclic, P_2S or P_2Se) from the cage molecules definitely involve redox processes.[16]

Intermediate cleavage has been obtained through the present reactions of the P_4S_3 or P_4Se_3 molecules with the $(triphos)M^I$ (M = Rh, Ir) fragments, which provide metal atoms in an oxidation state lower than that of the similar $(triphos)M^{II}$ (M = Co, Ni) fragments. However, the rather low yields for formation of the present compounds, and the different yields when P_4S_3 or P_4Se_3 are employed, are suggestive of the existence of alternative reaction paths, so that detailed assumptions about the reaction mechanism are prevented. Nevertheless, the following general considerations should be appropriate.

The fact that a basal P atom of the cage is displaced in the course of these reactions suggests that suitable directions for attack of the cage molecule by the triphos–metal systems are those pointing toward its triangular P_3 side. This is also in line with (i) the propensity of conical ML_3 fragments of suitable electron count to form a set of bonds with approximate 3-fold symmetry,[30] (ii) the well-documented ability of some d^9-ML_3 units to symmetrically link to cyclic P_3 or As_3 groups[31] or the preference of formally d^8-ML_3 units for the P_2S or isoelectronic heterocyclic groups,[15] and (iii) the geometry of overlap, as suggested by the MO picture for cage compounds of geometry similar to that of the present ones.[32] However, the interaction of a d^8 $(triphos)M^I$ (M = Rh, Ir) system with the intact P_4X_3 molecule does not seem to provide a stable electronic configuration at the metal atom, so that further disruptive steps may be anticipated. Actually, the metal atom of the formally d^9 (triphos)M fragment in each of the present compounds reaches the 18e configuration by borrowing 3e from the P_3X_3 framework, as the displaced P atom would be considered to do in the original cage molecule.

All of the compounds exhibit, in their ^{31}P NMR spectra, four groups of signals that are well separated, the components being symmetrically distributed about the center of each multiplet. The spectrum of $[(triphos)Rh(P_3Se_3)]$ is reported in Figure 2. The magnetic nuclei occurring in the molecules are labeled as shown in Scheme I. The iridium derivatives yield an overall AA′DII′R spin system, and the rhodium compounds, which contain the magnetically active metal ^{103}Rh $(I = {}^1/_2)$, form an AA′DII′RZ (Z = Rh) spin system. Since $^1J(P_I–P_{I'}) \gg$ all ^2J(P–M–P), the P_A and P_I atoms give rise to two pseudotriplets, which are split in addition by P_D, P_R, and Z. This feature, which has already been found for other compounds containing unsubstituted P atoms bound inter se, does not allow the calculation of the coupling constants between P_A and P_I.[33]

The chemical shifts of the four groups of phosphorus atoms are reported in Table IV. The two resonances at lower frequency have an intensity ratio of 1:2 for all compounds and are assigned to P_D and P_A, respectively, as the corresponding chemical shifts are in the expected range for rhodium and iridium complexes with

Table IV. $^{31}P\{^1H\}$ NMR Spectral Data for the $[(triphos)M(P_3X_3)]$ Compounds[a,b]

compd	δ				^1J			^2J				^3J		$^2J_{av}$-[c]
	$P_{A,A'}$	P_D	$P_{I,I'}$	P_R	P_A–Rh, $P_{A'}$–Rh	P_D–Rh	P_I–Rh, $P_{I'}$–Rh	P_R–Rh	P_I–P_R, $P_{I'}$–P_R	P_A–P_D, $P_{A'}$–P_D	P_I–P_D, $P_{I'}$–P_D	P_D–P_R	P_A–P_R, $P_{A'}$–P_R	$(P_{A/A'}$–P)
$[(triphos)Rh(P_3S_3)]$ (**1**)	−1.48	20.97	107.02	126.39	106.8	104.6	24.3	3.9	48.3	33.5	9.8	13.7	15.4	24.5
$[(triphos)Rh(P_3Se_3)]$ (**2**)	−4.49	19.28	113.48	87.38	106.8	104.3	23.8	3.5	45.0	32.3	9.8	9.6	10.7	22.5
$[(triphos)Ir(P_3S_3)]$ (**3**)	−29.12	−13.94	32.77	76.03					43.6	22.6	17.7	5.1	7.9	26.1
$[(triphos)Ir(P_3Se_3)]$ (**4**)	−31.85	−14.36	41.02	32.54					42.5	22.3	17.6	2.7	5.1	24.3

[a] Obtained at 121.48 MHz in CD_2Cl_2 and reported downfield from external H_3PO_4. Coupling constants (*J*) are in Hz. [b] AA′DII′RZ (Z = Rh) and AA′DII′R spectra; $^1J(P_I–P_{I'}) \gg$ all ^2J(P–M–P) $[^2J(P–M–P) = {}^1/_2[^2J(P_A–P_I)_{cis} + {}^2J(P_A–P_{I'})_{trans}]$. Two pseudotriplets result, which do not allow calculation of all coupling constants. [c] Average value for the two pseudotriplets.

---

(30) Elian, M.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 1058.

(31) Ghilardi, C. A.; Midollini, S.; Sacconi, L. *Inorg. Chem.* **1978**, *19*, 301. Faust, A. S.; Foster, M. S.; Dahl, L. F. *J. Am. Chem. Soc.* **1969**, *91*, 5631.

(32) Gleiter, A.; Koppel, H.; Hofmann, P.; Schmidt, H. R.; Ellermann, J. *Inorg. Chem.* **1985**, *24*, 4020.

(33) Schäfer, H.; Binder, D.; Fenske, D. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 522.

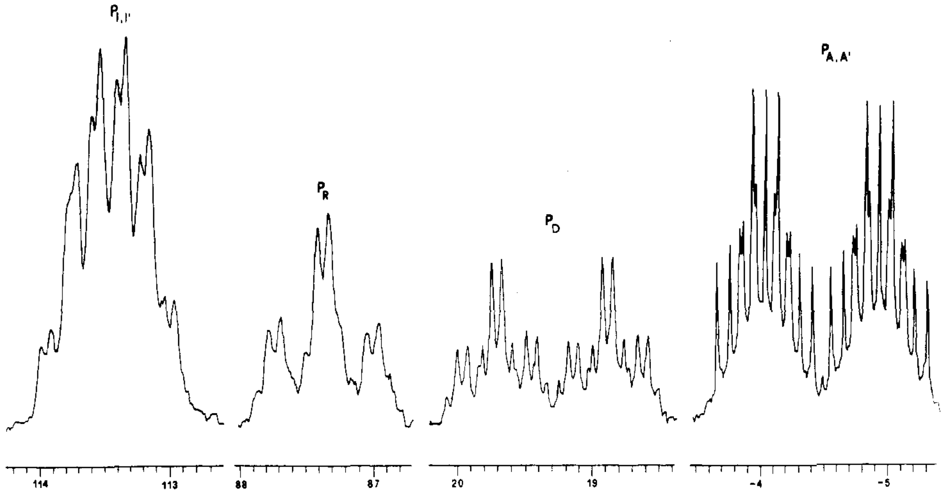


Figure 2. ^{31}P NMR spectrum of the [(triphos)Rh(P_3Se_3)] compound. The assignments of the various multiplets are indicated in the spectrum.

polyphosphanes,[14,34] even though the P_A resonances are well separated from the P_D ones. Such assignment is confirmed for the rhodium derivatives by values of the $^1J(P_A–Rh)$ and $^1J(P_D–Rh)$ coupling constants (see below), which are in the usual range for rhodium phosphane complexes. The two resonances at lower field have also an intensity ratio of 1:2 and are ascribed to the P_R and P_I atoms, respectively. The chemical shifts of coordinated PPh_2 groups of triphos are substantially unaffected (Table IV) on replacing sulfur for selenium; they are at lower frequencies in the iridium derivatives than in the rhodium ones, in agreement with the trend reported for phosphane complexes formed by metal atoms of different transition rows, having the same coordination number, molecular geometry, phosphane ligand, and oxidation state of the metal atom.[14] The P_D chemical shifts for compounds **1–4** compare with those of the polyphosphane in the [(triphos)M(P_3)] (M = Rh, Ir) derivatives, in which the metal is six-coordinate, being bound to the three P atoms of the ligand and to three "naked" P atoms. The P_A chemical shifts, on the other hand, occur at significantly lower frequencies.[14] This effect may be related to the notable high-frequency shift, with respect to the free cage molecule signals,[35] exhibited by resonances of the P_I nuclei of the P_3X_3 framework (see below), which lie in the same plane as the P_A nuclei. Both effects may be due in turn to a transfer of electron density from the P_I to the P_A atoms. A similar transfer of electron density from a small cluster of "naked" main-group atoms to a trans ligand has been shown to occur in a P_4 complex, on the basis of Xα calculations.[36] Such transfer is accompanied by a high-frequency shift of P resonances with respect to uncoordinated P_4 signals.[36,37] A further indication that an electron density transfer of this sort occurs in the present compounds is provided by the shortening of the P–P bond mentioned in the previous section, which may be switched on by a release of antibonding interactions.

Values of the coupling constants, which have been confirmed by computer simulation (program Laocoon), are reported in Table IV. The coupling constants between the phosphorus atoms of triphos [i.e. $^2J(P_A–P_D)$], as well as those between the same P atoms and the metal in the rhodium derivatives, have typical values for phosphane complexes. On the other hand, the coupling constants of the unsubstituted P atoms to the metal atom [$^1J(P_I–Rh)$] are significantly smaller than the former, in accordance with values reported for the rhodium or platinum to "naked" phosphorus interactions.[13] Low metal–"naked" P coupling constants are also found in η^3-P_3 complexes of Rh and Pt[14] and in η^2-P_4 complexes of rhodium.[36]

The free P_4X_3 cage molecules (X = S, Se) exhibit one low-frequency resonance [−121 ppm (P_4S_3) and −106 ppm (P_4Se_3)][35] for the basal phosphorus atoms and a high-frequency signal for the apical phosphorus [68 ppm (P_4S_3) and 36 ppm (P_4Se_3); $^2J(P_{apical}–P_{basal})$ 71 Hz (P_4S_3) and 72 Hz (P_4Se_3)].[35] The P_I atoms of complexes **1–4** are greatly deshielded (by ca. 220 ppm for rhodium derivatives and ca. 150 ppm for iridium compounds; Table IV) relative to those of the free P_4X_3 molecules. The P_R signals are also deshielded relative to those of the intact cage molecules, although to a smaller extent. The $^2J(P_I–P_R)$ values for compounds **1–4** (Table IV) are significantly smaller than the $^2J(P_{basal}–P_{apical})$ values in the free P_4X_3 molecules.

Registry No. **1**·C_6H_6, 87890-72-0; **2**·C_6H_6, 115890-24-9; **3**·C_6H_6, 115912-34-0; **4**, 115890-25-0; P_4S_3, 1314-85-8; P_4Se_3, 1314-86-9; [RhCl(cod)]$_2$, 12092-47-6; [IrCl(cod)]$_2$, 12112-67-3.

Supplementary Material Available: Full details on the crystal data and crystallographic data collections (Table SI), positional and isotropic thermal parameters for **2** and **3** (Tables SII and SIII), anisotropic thermal parameters for **1–3** (Tables SIV–SVI), bond distances (Tables SVII–SIX) and angles (Tables SX–SXII) for **1–3**, and hydrogen atom coordinates (Tables SXIII–SXV) for **1–3** (24 pages); listings of observed and calculated structure factors (38 pages). Ordering information is given on any current masthead page.

---

(34) Pregosin, P. S.; Kunz, R. W. In *NMR Basic Principles and Progress*; Diehl, P., Fluck, E., Kosfeld, R., Eds.; Springer-Verlag: Berlin, FRG, 1979; Vol. 16.

(35) Blachnik, R.; Wickel, U.; Schmitt, P. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39B*, 1135.

(36) Ginsberg, A. P.; Lindsell, W. E.; McCullogh, K. J.; Sprinkle, C. R.; Welch, A. J. *J. Am. Chem. Soc.* **1986**, *108*, 403.

(37) Mark, V.; Dungan, C. H.; Crutchfield, M. M.; Van Wazer, J. R. In *Topics in Phosphorus Chemistry*; Grayson, M., Griffith, E. J., Eds.; Interscience: New York, 1967; Vol. 5, p 238.