REACTIVITY OF ARSENIC SELENIDES AND TELLURIDE: COBALT COMPLEXES CONTAINING THE SELENA- OR TELLURA-DIARSIRENE CYCLIC UNITS *TRIHAPTO*-BONDED TO THE METAL ATOM—CRYSTAL AND MOLECULAR STRUCTURES OF [(TRIPHOS)Co(As₂Se)](BF₄)(C₂H₅OH) AND [(TRIPHOS)Co(As₂Te)](BF₄)(C₆H₆)_{0.5}

MASSIMO DI VAIRA, MAURIZIO PERUZZINI and PIERO STOPPIONI*

Dipartimento di Chimica, Università di Firenze and Istituto I.S.S.E.C.C., Via Maragliano, 77, 50144 Firenze, Italy

(Received 8 July 1985; accepted 2 October 1985)

Abstract—The reaction of $Co(BF_4)_2(H_2O)_6$ with arsenic selenides and telluride, As_4Se_3 , As_2Se_3 and As_2Te_3 in the presence of 1,1,1-tris(diphenylphosphinomethyl)ethane (triphos), yielded the complexes

 $[(triphos)Co(As_2Se)](BF_4)(C_2H_5OH)(1)$

and

 $[(triphos)Co(As_2Te)](BF_4)(C_6H_6)_{0.5}$ (2).

The molecular structures of the complexes have been determined by single-crystal X-ray diffraction methods. The isomorphous compounds crystallize in the monoclinic space group $P2_1/n$ with Z = 4 and unit-cell dimensions: (1) a = 17.034(8) Å, b = 20.640(9) Å, c = 13.116(6) Å, $\beta = 105.37(6)^{\circ}$; (2) a = 17.076(7) Å, b = 20.419(9) Å, c = 13.215(7) Å, $\beta = 105.15(7)^{\circ}$. The metal atom in both compounds is in a six-coordinate environment formed by the triphos P atoms and by the atoms of the heterocyclic As₂Se or As₂Te unit.

The E_4X_3 (E = P, X = S or Se; E = As, X = S) cage molecules react with transition-metal-ligand systems to give different products depending on the nature of the metal atom and its oxidation state.¹ In particular, a substantial cleavage of the cage molecules occurs in the reactions with cobalt(II) and nickel(II) tetrafluoroborate in the presence of [triphos = 1, 1, 1-tris(diphenylphosphinotriphos methyl)ethane], affording stable complexes which contain the heterocyclic E_2X (E = P, X = S or Se;² E = As, $X = S^3$) or the homocyclic E_3 ($E = P^4$ or As⁵) units η^3 -bonded to the metal atom. Other small molecules formed by atoms of groups V and VI react with transition-metal complexes, affording compounds which contain either "bare" pnicogen⁶ or chalcogen⁷ atoms, or small groups of such atoms, like S_{2} , ${}^{8}P_{2}$, ${}^{9}P_{3}$, ${}^{10}As_{3}{}^{11}$ or $S_{5}{}^{12}$ bound to the metal atom. Among such compounds, those

containing S or P are much more numerous than the Se, Te or As derivatives. This is probably due to the markedly different chemical behaviour of the latter elements with respect to that of the lighter ones of the same groups.

Here we report the synthesis and characterization of the compounds

 $[(triphos)Co(As_2Se)](BF_4)(C_2H_5OH)(1)$

and

$$[(triphos)Co(As_2Te)](BF_4)(C_6H_6)_{0.5}$$
 (2)

which contain the new As₂Se and As₂Te cyclic units η^3 -bonded to the metal. The comparison between the structures of the present compounds and those of the isomorphous [(triphos)Co(E₂X)](BF₄)(C₆H₆) (E = P, X = S or Se;² E = As, X = S³) complexes reveals the effects due to the presence of the heavier and larger atoms of groups V and VI in the As₂Se and As₂Te rings.

^{*} Author to whom correspondence should be addressed.

EXPERIMENTAL

All solvents were reagent grade and were dried by distillation from suitable agents.¹³ All reactions and manipulations were carried out under dry nitrogen. Electronic spectra, conductivity and magnetic susceptibilities were measured by procedures already described.¹⁴ ³¹P NMR spectra were collected (at 32.19 MHz) on a Varian CFT20 spectrometer. ³¹P positive chemical shifts are downfield relative to H₃PO₄ at 0.0 ppm.

The compound As_2Te_3 was purchased from Ventron GMBH and used without any purification; the ligand triphos¹⁵ and As_4Se_3 ¹⁶ were prepared according to published procedures. As_2Se_3 was synthesized by reacting in a sealed tube under nitrogen gray As and black Se in a 2:3 ratio for 3 days at 410°C. The solid obtained was finely powdered and stored in an inert atmosphere.

Synthetic procedures

Preparation of 1. Procedure A. Finely powdered As₄Se₃ (3 mmol) was added to a solution of $Co(BF_4)_2(H_2O)_6$ (1 mmol) in ethanol (10 cm³) and triphos (1 mmol) in tetrahydrofuran-benzene (1:1) (50 cm^3) . The resulting mixture was refluxed for 5 days with magnetic stirring and then filtered. The solid was washed with warm dichloromethane (20 cm³). The combined filtrate and washing solutions were concentrated to dryness in vacuo. The solid was extracted with hot dichloromethane (40 cm³) and ethanol-benzene (2:1) (40 cm³) was added. Red crystals of the compound were obtained by concentrating the solution. The complex was collected on a sintered-glass frit, in a closed system, and washed with ethanol and then light petroleum (b.p. 40-70°C) before being dried (yield 50-55%). The compound, which crystallizes with one molecule of ethanol, was recrystallized from dichloromethane and ethanol-benzene (1:1).

Procedure B. As_2Se_3 (2 mmol) was added to a solution of $Co(BF_4)_2(H_2O)_6$ (1 mmol) in ethanol (10 cm³) and triphos (1 mmol) in tetrahydrofuranbenzene (1:1) (50 cm³). The resulting mixture was refluxed for 4 days with magnetic stirring and then filtered. The compound [(triphos)Co(As_2Se)](BF_4) was isolated as described for procedure A.

Preparation of 2. As_2Te_3 (2 mmol) was added to a solution of $Co(BF_4)_2(H_2O)_6$ (1 mmol) in ethanol (10 cm³) and triphos (1 mmol) in tetrahydrofuranbenzene (1:1) (40 cm³). The mixture was refluxed for 8 days, then filtered while hot and ethanol-benzene (1:1) (30 cm³) was added. Dark-red crystals of the compound were obtained by concentrating the solution. The complex was collected by the procedure described above for the As_2Se derivative (yield 15-20%). The compound could not be recrystallized due to its tendency to decompose in solution, releasing tellurium.

X-ray crystal structures

Diffraction data for compounds 1 and 2. These were collected at room temperature from crystals of dimensions $0.20 \times 0.20 \times 0.25$ mm (1) and $0.15 \times 0.10 \times 0.20$ mm (2) using a Philips PW 1100 four-circle diffractometer and graphite-monochromated Mo- K_{α} radiation ($\lambda = 0.71069$ Å). Lattice constants were determined by least-squares refinement of the angular settings of 24 reflections with $22 < 2\theta < 40^{\circ}$ (1) and $18 < 2\theta < 22^{\circ}$ (2).

Crystal data. (1) $C_{43}H_{45}As_2BCoF_4OP_3Se$, $M_r = 1045.3$, monoclinic, a = 17.034(8) Å, b = 20.640(9) Å, c = 13.116(6) Å, $\beta = 105.37(6)^\circ$, U = 4446.4 Å³, Z = 4, $D_c = 1.56$ g cm⁻³, F(000) = 2096, μ (Mo- K_a) = 28.2 cm⁻¹, space group $P2_1/n$.

(2) $C_{44}H_{42}As_2BCoF_4P_3Te$, $M_r = 1086.9$, monoclinic, a = 17.076(7) Å, b = 20.419(9) Å, c = 13.215(7)Å, $\beta = 105.15(7)^\circ$, U = 4447.6 Å³, Z = 4, $D_f = 1.66$ g cm⁻³, $D_c = 1.62$ g cm⁻³, F(000) = 2148, $\mu(Mo-K_a) = 26.5$ cm⁻¹, space group $P2_1/n$.

Crystals of 2 did not provide good material for X-ray diffraction, probably due to larger effects of disorder (see below) in the structure of 2 than in that of 1. The intensities of all reflections with k > 0 and l > 0 were measured in the ranges $5 < 2\theta < 44^{\circ}$ (1) and $5 < 2\theta < 40^{\circ}$ (2) in the θ -2 θ scan mode with a scan width of $(1.10+0.30 \tan \theta)^{\circ}$ and scan speed of 6° min⁻¹. No crystal decay was observed. Of the total 5912(1) and 4529 (2) reflections recorded 2432(1) and 1450 (2) having $I > 3\sigma(I)$ were used for structure determination after correction for Lorentz, polarization and X-ray absorption effects. Crystallographic calculations were carried out using SHELX 76.¹⁷

The structures of the two compounds, which are isomorphous to each other as well as to the $[(triphos)Co(E_2X)](BF_4)(C_6H_6)$ (E = P, X = S or Se;² E = As, X = S³) complexes previously investigated, were refined assuming as initial values for the atomic coordinates those from the latter structures. All atoms heavier than carbon were assigned anisotropic thermal parameters, whereas the other atoms were refined isotropically. The solvent molecule in each structure was assigned an overall temperature factor. Phenyl groups of the triphos ligand were refined as rigid bodies with idealized geometry. Hydrogen atoms of the triphos ligand were introduced in calculated positions (C-H = 1.00 Å) with an overall temperature factor. The BF_4^- anion was imposed a tetrahedral geometry, the value of the B-F distance being refined. The scattering factors for the neutral atoms and the anomalous dispersion corrections for Co, Se, As and Te were taken from Ref. 18. It was impossible to identify the As and Se atoms in the triatomic ring of 1. Therefore, in analogy with the model used for the P_2S derivative,² each site of the ring was assigned 0.67 As and 0.33 Se occupancy factors. This led to comparable U_{iso} values for the three sites. The ratio of the C-C and C-O bond lengths in the solvate ethanol molecule of 1 was constrained to an idealized value:¹⁹ the O atom, identified on the basis of peak heights and contact distances, was found from ΔF maps to be distributed with essentially an equal probability between two positions. For 1 no peaks >0.7 e Å⁻³ were observed in the final electrondensity difference map, and refinement with the weighting scheme $w = [\sigma^2(F_o) + 0.0001|F_o|^2]^{-1}$ led to R = 0.056 (R' = 0.062). For 2 it was evident from the peak heights in ΔF Fourier maps that the Te atom was distributed over at least two sites of the As₂Te ring with different occupancy factors. Refinement of the population parameters of the three sites was performed by the procedure already described for the P_2Se^2 and As_2S^3 isomorphs, i.e. imposing that the U_{iso} values for the three sites should be close to each other. The occupancy factors so obtained [essentially 1.00 As for the site labelled As(1), whereas sites As(2) and Te had 0.80 and, respectively, 0.20 As occupancy factors with complementary Te population parameters] were in reasonable agreement with those previously determined for the P_2 Se isomorph,² allowing for replacement of As for P and of Te for Se. The solvate benzene molecule was highly disordered, with peak heights $<1 e Å^{-3}$ in ΔF Fourier maps. The compromise 0.5 value of its population parameter, lower than indicated by the D_f value, was assigned on the basis of the R criterion and in order to avoid an exceedingly high value of the overall temperature factor. Such a benzene ring, without H atoms, was imposed an idealized geometry: the C-C distance was refined to 1.38 Å and the overall U value to 0.195(2) Å². For 2 no peaks >0.8 e Å⁻³ were observed in the final electron-density difference map and refinement with the weighting scheme $w = [\sigma^2(F_o) + 0.0005|F_o|^2]^{-1}$ led to R = 0.068(R' = 0.076). Final atomic positional and thermal parameters, bond lengths and angles and F_o/F_c values have been deposited as supplementary material with the Editor, from whom copies are available on request. Atomic coordinates have also been submitted to the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

The reaction of cobalt(II) tetrafluoroborate in the presence of the tripod ligand triphos with As_4Se_3 , As₂Se₃ or As₂Te₃ affords complexes of formula $[(triphos)Co(As_2X)](BF_4)[X = Se(1) \text{ or } Te(2)].$ The analytical data (Table 1) for the complexes, which crystallize with solvent molecules in the lattice, are in good agreement with the proposed formula. The complexes behave as 1:1 electrolytes in nitroethane²⁰ (Table 1). The diamagnetic compounds are moderately air-stable in the solid state. They are slightly soluble in acetone and dichloromethane, whereupon the compound containing the selenadiarsirene unit is stable under nitrogen, whereas the As₂Te derivative decomposes in a short time even in an inert atmosphere by releasing tellurium. A similar behaviour has been found for telluradiphosphirane,²¹ which is the only compound containing a Te atom in a three-membered ring so far reported. The low solubility of both compounds here described prevented us from obtaining ⁷⁷Se and ¹²⁵Te NMR spectra. The ³¹P– $\{^{1}H\}$ NMR spectra of the compounds (Table 2) exhibit a broad resonance at low field (32.56 and 32.39 ppm for compounds 1 and 2, respectively) affected by the cobalt quadrupole moment, that is assigned to the three atoms of the ligand. The triphos $\delta(^{31}P)$ values are practically identical for complexes 1 and 2 and for all the isostructural [(triphos)Co(E_2X)](BF₄) complexes

Table 1. Analytical an	d conductivity data	for the complexes
------------------------	---------------------	-------------------

	A. a.		Analysis (%): found (calc.)					
Compound	$(\Omega^{-1} \operatorname{cm}^2 \mathrm{M}^{-1})$	С	Н	Co	Р	As	Other	
1	[(triphos)Co(As ₂ Se)](BF ₄)(C ₂ H ₅ OH)	84	49.5 (49.4)	4.6 (4.3)	5.5 (5.6)	8.9 (8.9)	14.3 (14.3)	Se: 7.4 (7.5)
2	[(triphos)Co(As ₂ Te)](BF ₄)(C ₆ H ₆) _{0.5}	91	48.5 (48.6)	4.0 (3.9)	5.3 (5.4)	8.4 (8.5)	13.6 (13.8)	Te: 11.9 (11.7)

"Molar conductance of $ca \ 10^{-3}$ M nitroethane solution at 20°C.

	Compound	δ^a (ppm)	ΔP^b	λ_{\max} (nm) [ϵ (dm ³ mol ⁻¹ cm ⁻¹)] ^c
1	[(triphos)Co(As ₂ Se)](BF ₄)(C ₂ H ₅ OH)	32.56 (br)	58.11	470 (sh) (~760), 380 (sh) (~2850)
2	[(triphos)Co(As ₂ Te)](BF ₄)(C ₆ H ₆) _{0.5}	32.39 (br)	57.94	500 (sh) (~700), 390 (2760)

Table 2. ³¹P– $\{^{1}H\}$ NMR and electronic spectral data for the complexes

^a Chemical shifts are relative to 85% H₃PO₄. Positive chemical shifts are downfield : br = broad; sh = shoulder. The complexes were dissolved in (CD₃)₂CO.

 ${}^{b}\Delta P = \delta P \text{ (coord.)} - \delta P \text{ (free ligand).}$

^c Absorption maxima for CH₂Cl₂ solution at 20°C.

 $(E = P, X = S \text{ or } Se^2; E = As, X = S^3)$ having the P_2S , P_2Se or As_2S cyclic unit trihapto bonded to the metal. The scarce sensitivity of the triphos chemical shift to replacement of the chalcogen or pnicogen atoms in the triatomic ring might be due to involvement of the triphos P atoms in lower-energy molecular orbitals than the atoms of the cyclic unit. The absorption spectra of the compounds in dichloromethane solution (Table 2) exhibit a shoulder and a band at ca 470-500 and 380-390 nm, respectively. In the spectrum of the $[(triphos)Co(As_2S)](BF_4)$ derivative the same transitions occur at 450 and 380 nm, their frequencies decreasing slightly with increasing atomic number of the heteroatom in the As₂X ring. The same trend had been noticed for the P_2X (X = S or Se) derivatives² and may be related in part to the accompanying increase, in the mean, of the metal to As_2X or P_2X ring distances, proved by the results of previous ^{2,3} structural analyses combined with those reported here. The crystal structures of the isomorphous compounds 1 and 2 consist of $[(triphos)Co(As_2X)]^+$ cations (X = Se or Te), BF_4^- anions, and interposed ethanol or benzene molecules from the solvent. Figure 1 shows a perspective view of the cation in compound 1, the geometry of the cation in 2 being closely similar. Selected values of bond distances and angles in the two structures are listed in Table 3. The metal atom in each cation is in a six-coordinate environment formed by the triphos P atoms and the atoms of the As₂X unit in a staggered arrangement similar to that previously found for the compounds containing the P₃ homocyclic¹⁰ or the E_2X (E = P, X = S or $Se;^2 E = As$, $X = S^3$) heterocyclic inorganic rings. The distances from the metal atom to the P atoms of the triphos ligand in either compound [2.205(4)-2.227(9) Å] are in the range of values already found for the isomorphous derivatives.^{2,3} A detailed analysis of the dimensions of the CoAs₂X moieties in the two compounds is prevented



Fig. 1. Perspective view of the [(triphos)Co(As₂Se)]⁺ cation with 20% probability ellipsoids. The E(1)– E(3) sites have 0.67 As and 0.33 Se occupancy. Only the first carbon atom of each phenyl group is labelled. The [(triphos)Co(As₂Te)]⁺ cation has substantially the same structure with As₂Te ring site occupancies as specified in Experimental and in footnote ^b to Table 3.

Table 3. Selected bond distances (Å) and angles (°) for the compounds [(triphos)Co(As₂Se)](BF₄)(C₂H₅OH) (1)^a and [(triphos)Co(As₂Te)](BF₄) (C₆H₆)_{0.5} (2)^b

1		2	
CoE(1)	2.393(2)	Co—As(1)	2.413(5)
Co-E(2)	2.413(2)	Co—As(2)	2.476(5)
Co-E(3)	2.410(2)	Co-Te	2.582(4)
CoP(1)	2.218(4)	Co-P(1)	2.227(9)
Co-P(2)	2.205(4)	Co-P(2)	2.206(8)
CoP(3)	2.212(4)	Co-P(3)	2.218(9)
E(1)—E(2)	2.363(2)	As(1)—As(2)	2.408(5)
E(1)—E(3)	2.353(2)	As(1)—Te	2.497(5)
E(2)—E(3)	2.365(2)	As(2)—Te	2.539(4)
E(1)CoE(2)	58.9(1)	As(1)-Co-As(2)	59.0(2)
E(1) - Co - E(3)	58.7(1)	As(1)—Co—Te	59.9(1)
E(1) - Co - P(1)	153.7(1)	As(1)—Co—P(1)	154.9(3)
E(1)—Co—P(2)	101.0(1)	As(1)—Co—P(2)	98.7(3)
E(1)CoP(3)	106.7(1)	As(1)—Co—P(3)	107.1(3)
E(2)—Co—E(3)	58.7(1)	As(2)—Co—Te	60.2(1)
E(2)-Co-P(1)	96.6(1)	As(2)-Co-P(1)	97.1(3)
E(2) - Co - P(2)	106.0(1)	As(2)CoP(2)	105.1(3)
E(2)-Co-P(3)	160.2(1)	As(2)-Co-P(3)	160.9(3)
E(3)—Co—P(1)	101.9(1)	Te-Co-P(1)	103.1(2)
E(3)-Co-P(2)	158.4(1)	Te-Co-P(2)	157.7(3)
E(3) - Co - P(3)	102.8(1)	Te-Co-P(3)	102.1(2)
P(1)—Co— $P(2)$	94.6(2)	P(1)—Co—P(2)	94.9(3)
P(1)—Co—P(3)	94.3(2)	P(1)CoP(3)	94.1(3)
P(2)—Co—P(3)	89.5(1)	P(2)—Co—P(3)	89.3(3)
Co-E(1)-E(2)	61.0(1)	Co-As(1)-As(2)	61.8(2)
Co-E(1)-E(3)	61.0(1)	Co—As(1)—Te	63.4(1)
E(2) - E(1) - E(3)	60.2(1)	As(2)—As(1)—Te	62.3(1)
Co-E(2)-E(1)	60.1(1)	Co-As(2)-As(1)	59.2(2)
Co-E(2)-E(3)	60.6(1)	Co-As(2)-Te	61.9(1)
E(1) - E(2) - E(3)	59.7(1)	As(1)-As(2)-Te	60.5(1)
Co-E(3)-E(1)	60.3(1)	Co-Te-As(1)	56.7(1)
Co-E(3)-E(2)	60.7(1)	Co-Te-As(2)	57.8(1)
E(1) - E(3) - E(2)	60.1(1)	As(1)-Te-As(2)	57.1(1)

^a Each of the E(1)–E(3) sites has been assigned 0.67 As and 0.33 Se occupancy factors (see Experimental).

^b The As(2) and Te sites have the following fractional As/Te occupancies: As(2) (0.80 As, 0.20 Te), Te (0.20 As, 0.80 Te).

by the disorder affecting the triatomic rings. It should however be noted that the overall geometry of the $CoAs_2Se$ fragment in 1 is approximately tetrahedral (Table 3), with metal to ring-site and intraring distances definitely longer [by *ca* 0.14 and 0.24 Å, respectively] than the corresponding distances in the CoP_2S part of the thiadiphosphirene derivative.² The geometry of the $CoAs_2Te$ moiety in 2 is less regular, due to the presence of the large Te atom. The site with the highest Te population is indeed involved in rather long bond distances; in particular, its distance from the metal site, of 2.582(4) Å, is definitely longer than any of the corresponding bond lengths found for compounds of this series. Although the assignment of the oxidation number of the metal atom in these compounds is not unambiguous, the compounds may be considered to contain cobalt(I), assuming that the As₂X moiety behaves as a neutral four-electron donor, consistently with the electron-counting procedure already used for triphosphirene complexes.¹⁰ Therefore, reduction of the metal atom should occur in the formation of the present or previous^{2,3} compounds with the [(triphos)Co(E₂X)](BF₄) stoichiometry as it has been considered¹⁰ to occur in the formation of the [(triphos)M(P₃)]ⁿ⁺ complexes [M = Co,²² Rh²³ or Ir²³; n = 0: M = Ni,⁴ Pd²⁴ or Pt²⁴; n = 1) or of the triple-decker com-

pounds with P₃ or As₃ internal slices.¹⁰ In such processes, at variance with those where no reduction of the metal atom occurs, 1(a), 1(c), 1(d) substantial cleavage of the reacting cage molecule (P4, As4, or a molecule of the E_4X_3 class) is invariably involved. An unprecedented feature of the present results is however due to the fact that compounds with the $[(triphos)Co(As_2X)](BF_4)$ stoichiometry have now been obtained not only by reaction of a cobalt(II) salt with the molecular As₄Se₃ compound, but also with polymeric species, such as As₂Se₃²⁵ or As₂Te₃.²⁶ While these results are compatible with the view that the disruptive attack of the chalcogenide by the metal-ligand system involves a redox process, they point to the efficiency of the (triphos)Co system in directing the course of the reaction toward the formation of compounds with suitable electron counts, irrespective of the structure of the chalcogenide used as a reactant.

Acknowledgements—Thanks are expressed to Mr F. Nuzzi for microanalyses. Financial support for this work from Italian C.N.R. under the "Progetto Finalizzato Chimica Fine e Secondaria" is gratefully acknowledged.

REFERENCES

- (a) M. Di Vaira, M. Peruzzini and P. Stoppioni, *Inorg.* Chem. 1983, 22, 2196; (b) M. Di Vaira, M. Peruzzini and P. Stoppioni, J. Chem. Soc., Chem. Commun. 1983, 903; (c) M. Di Vaira, M. Peruzzini and P. Stoppioni, J. Chem. Soc., Dalton Trans. 1985, 291; (d) C. A. Ghilardi, S. Midollini and A. Orlandini, Angew. Chem., Int. Ed. Engl. 1983, 22, 790.
- 2. M. Di Vaira, M. Peruzzini and P. Stoppioni, J. Chem. Soc., Dalton Trans. 1984, 359.
- 3. M. Di Vaira, P. Innocenti, S. Moneti, M. Peruzzini and P. Stoppioni, *Inorg. Chim. Acta* 1984, **83**, 161.
- 4. M. Di Vaira, L. Sacconi and P. Stoppioni, J. Organomet. Chem. 1983, 250, 183.
- 5. P. Stoppioni and M. Peruzzini, J. Organomet. Chem. 1983, 262, C5.
- 6. A. Vizi-Orosz, V. Galamb, G. Pàlyi, L. Markò, G. Bor and G. Natile, J. Organomet. Chem. 1976, 107,

235; D. Seyferth, J. S. Merola and R. S. Henderson, Organometallics 1982, 1, 859.

- L. Y. Goh, T. W. Hambley and G. B. Robertson, J. Chem. Soc., Chem. Commun. 1983, 1458; L. Y. Goh, C. Wei and E. Sinn, J. Chem. Soc., Chem. Commun. 1985, 462; W. A. Herrmann, C. Hecht, M. L. Ziegler and B. Balbach, J. Chem. Soc., Chem. Commun. 1984, 686.
- H. Brunner, J. Wachter, E. Guggolz and M. L. Ziegler, J. Am. Chem. Soc. 1982, 104, 1765.
- 9. O. J. Scherer, H. Sitzmann and G. Wolmershäuser, J. Organomet. Chem. 1984, 268, C9.
- M. Di Vaira and L. Sacconi, Angew. Chem., Int. Ed. Engl. 1982, 21, 330 (and references listed therein).
- I. Bernal, H. Brunner, W. Meier, H. Pfisterer, J. Wachter and M. L. Ziegler, Angew. Chem., Int. Ed. Engl. 1984, 23, 438.
- D. Coucouvannis, P. R. Patil, N. G. Kanatzidis, B. Detering and N. C. Baenziger, *Inorg. Chem.* 1985, 24, 24.
- O. O. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*. Pergamon Press, Oxford (1966).
- L. Sacconi and R. Morassi, J. Chem. Soc. A 1968, 2997;
 L. Sacconi, I. Bertini and F. Mani, Inorg. Chem. 1968, 7, 1417.
- W. Hewertson and H. R. Watson, J. Chem. Soc. 1962, 1490.
- B. H. Christian, R. J. Gillespie and J. F. Sawyer, *Inorg. Chem.* 1981, 20, 3410.
- 17. G. M. Sheldrick, "SHELX 76" System of Computing Programs, University of Cambridge (1976).
- International Tables for X-ray Crystallography, Vol. 4. Kynoch Press, Birmingham (1974).
- 19. "Interatomic Distances", Chemical Society, Special Publication No. 18 (1965).
- 20. W. J. Geary, Coord. Chem. Rev. 1971, 7, 81.
- 21. W.-W. du Mont, T. Severengiz and B. Meyer, Angew. Chem., Int. Ed. Engl. 1983, 22, 983.
- C. A. Ghilardi, S. Midollini, A. Orlandini and L. Sacconi, *Inorg. Chem.* 1980, 19, 301.
- C. Bianchini, C. Mealli, A. Meli and L. Sacconi, *Inorg. Chim. Acta* 1979, 37, L543.
- 24. P. Dapporto, L. Sacconi, P. Stoppioni and F. Zanobini, *Inorg. Chem.* 1981, 20, 3834.
- 25. N. Morimoto, Mineral. J. 1954, 1, 160.
- 26. G. J. Carron, Acta Cryst. 1963, 16, 338.