Inorg. Chem. **2002**, *41*, 1372–1382

Inorganic Chemistry
Article

Reactivity of the Heterometallic Clusters [$HMCo_3(CO)_{12}$] and [Et_4N][$MCo_3(CO)_{12}$] (M = Fe, Ru) toward Phosphine Selenides, Including Selenium Transfer. Crystal Structures of [$HRuCo_3(CO)_7(\mu\text{-}CO)_3(\mu\text{-dppy})$], [$MCo_2(\mu_3\text{-}Se)(CO)_7(\mu\text{-dppy})$], and [$RuCo_2(\mu_3\text{-}Se)(CO)_7(\mu\text{-dppm})$] [dppy = $Ph_2(2\text{-}C_5H_4N)P$, dppm = $Ph_2PCH_2PPh_2$]

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Received August 2, 2001

The reactivity of [$HMCo_3(CO)_{12}$] and [Et_4N][$MCo_3(CO)_{12}$] (M = Fe, Ru) toward phosphine selenides such as Ph_3PSe, $Ph_2P(Se)CH_2PPh_2$, $Ph_2(2\text{-}C_5H_4N)PSe$, $Ph_2(2\text{-}C_4H_3S)PSe$, and $Ph_2\{(2\text{-}C_5H_4N)(2\text{-}C_4H_2S)\}PSe$ has been studied with the aim to obtain new selenido-carbonyl bimetallic clusters. The reactions of the hydrido clusters give two main classes of products: (i) triangular clusters with a μ_3-Se capping ligand of the type [$MCo_2(\mu_3\text{-}Se)(CO)_{9-x}L_y$] resulting from the selenium transfer ($x = y = 1, 2$, with L = monodentate ligand; $x = 2, 4$, and $y = 1, 2$, with L = bidentate ligand) (M = Fe, Ru) and (ii) tetranuclear clusters of the type [$HMCo_3(CO)_{12-x}L_y$] obtained by simple substitution of axial, Co-bound carbonyl groups by the deselenized phosphine ligand. The crystal structures of [$HRuCo_3(CO)_7(\mu\text{-}CO)_3(\mu\text{-dppy})$] (**1**), [$MCo_2(\mu_3\text{-}Se)(CO)_7(\mu\text{-dppy})$] (M = Fe (**16**) or Ru (**2**)), and [$RuCo_2(\mu_3\text{-}Se)(CO)_7(\mu\text{-dppm})$] (**12**) are reported [dppy = $Ph_2(2\text{-}C_5H_4N)P$, dppm = $Ph_2PCH_2PPh_2$]. Clusters **2, 12**, and **16** are the first examples of trinuclear bimetallic selenido clusters substituted by phosphines. Their *core* consists of metal triangles capped by a μ_3-selenium atom with the bidentate ligand bridging two metals in equatorial positions. The *core* of cluster **1** consists of a $RuCo_3$ tetrahedron, each Co–Co bond being bridged by a carbonyl group and one further bridged by a dppy ligand. The coordination of dppy in a pseudoaxial position causes the migration of the hydride ligand to the Ru(μ-H)Co edge. In contrast to the reactions of the hydrido clusters, those with the anionic clusters [$MCo_3(CO)_{12}$]$^-$ do not lead to Se transfer from phosphorus to the cluster but only to CO substitution by the deselenized phosphine.

Introduction

In the last years, chalcogenido carbonyl species have been attracting growing interest both in fundamental research and in technological fields.[1] The presence of chalcogenido ligands appears often decisive in cluster growing reactions and in generating new coordination modes and geometries.[2] We have recently focused our attention on the reactivity of homometallic iron and ruthenium carbonyl clusters toward different phosphine selenides, achieving simple, one-step synthetic routes to phosphine-substituted chalcogenido clusters. Species with different nuclearities can be obtained depending on which combination of metal and phosphine is

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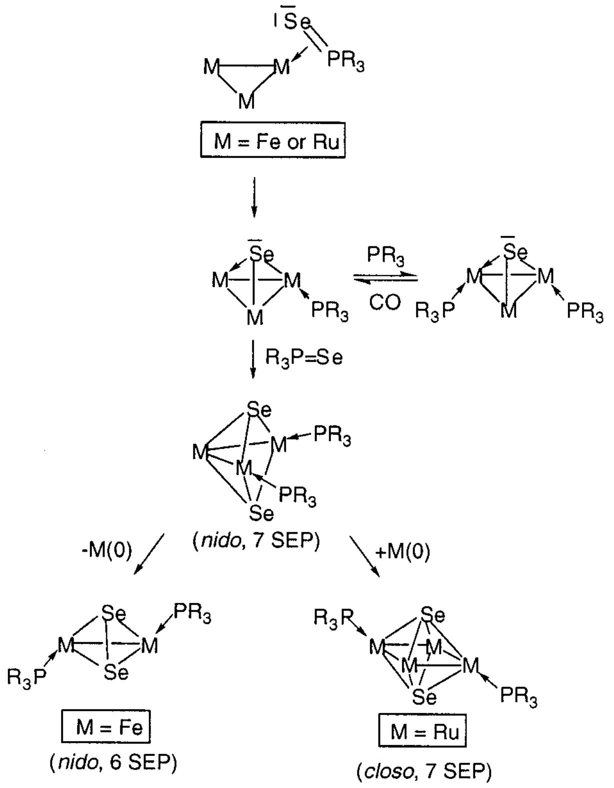
10.1021/ic010824x CCC: $22.00

Scheme 1



used (see Scheme 1). This method takes advantage of the reactivity of the P═Se bond which leads to its formal oxidative addition to the cluster, resulting in the transfer of the selenium atom to low-valent metal centers, followed by release or addition of metal fragments.[3] This terminology is employed here by analogy with the conventional meaning of oxidative addition of an A−B molecule to a metal center; here, a cluster is being oxidized, resulting in the formal retention of the oxidation state of one fragment (here the Se atom) and the reduction of the other (here the phosphorus center is reduced from P(V) to P(III) by the metal cluster).

In some cases, these reactions lead to species not easily accessible by other routes, such as the cubane-like cage complex $[Ru_4(\mu_3\text{-Se})_4(CO)_{10}(\mu\text{-dppm})]$.[4] Furthermore, some compounds of this family exhibit specific activity in cluster growth reactions. For instance, the cluster $[Ru_3(\mu_3\text{-Se})_2(CO)_7(PPh_3)_2]$ reacts with the zero-SEP (SEP = skeletal electron pair) $M(CO)_3$ fragments (M = Mo or W) to give the *closo*-octahedral bimetallic species $[M_2Ru_2(\mu_4\text{-Se})_2(\mu\text{-CO})_4(CO)_6(PPh_3)_2]$.[5]

We have now reacted different phosphine selenides with the tetrahedral clusters $[HMCo_3(CO)_{12}]$ (M = Fe or Ru) in order to obtain new chalcogenido-carbonyl bimetallic clusters. Mixed-metal clusters have been intensively studied in the last two decades, largely because of their often unique reactivity and catalytic properties and their role as molecular precursors to metal particles and novel heterogeneous catalysts.[6] Thus, the presence of different metals, which provides a larger diversity of possible coordination sites, can influence the selectivity of certain processes[7] and lead to the formation of compounds presenting new and not always easily predictable geometries. The reactivity of tetrahedral clusters of the type $[HMCo_3(CO)_{12}]$ (M = Ru and Fe) with nucleophiles (especially tertiary phosphines, phosphites, amines) generally leads to a metallosite-selective substitution of one or more carbonyl ligands (on the basal plane).[8−18] The first substitution by donor ligands generally occurs by replacement of a terminal axial carbonyl of a cobalt atom. A recent exception was observed in the reaction of $[HMCo_3(CO)_{12}]$ with $PCyH_2$ which led to CO substitution at the apical Ru center.[19] On the contrary, the introduction of a second ligand can take place either on a basal or on the apical metal.[10−12,15−18,20] The effects of phosphine substitution on the other ligands are usually restricted to minor distortions, for example, asymmetry in the carbonyl coordination; rarely is the position of the hydride ligand also affected.[13−14,21−23]

This paper deals with the reactions between $[HMCo_3(CO)_{12}]$ and phosphine selenides such as Ph_3PSe (tppSe), $Ph_2P(Se)CH_2PPh_2$ (dppmSe), $Ph_2(2\text{-}C_5H_4N)PSe$ (dppySe), $Ph_2(2\text{-}C_4H_3S)PSe$ (dpthSe), and $Ph_2\{(2\text{-}C_5H_4N)(2\text{-}C_4H_2S)\}PSe$ (dppythSe) (Scheme 2).

Typically, when transfer of the Se atom from phosphorus to the cluster occurs, the metal nuclearity decreases from 4 to 3. In contrast, when simple substitution of a CO ligand

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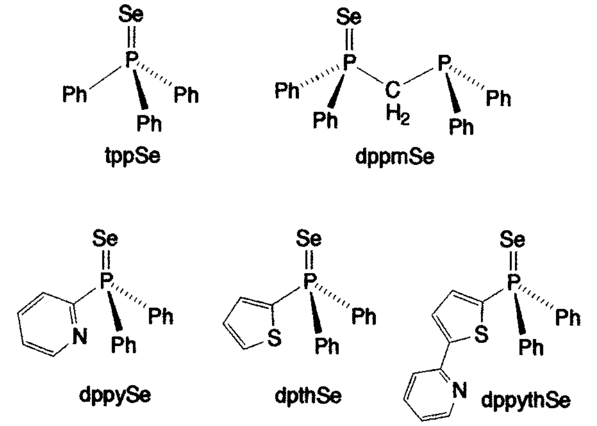
Scheme 2



by the deselenized phosphine takes place, the cluster retains its nuclearity.

For comparison, the reactivity of the anionic bimetallic clusters $[NEt_4][MCo_3(CO)_{12}]$ (M = Fe, Ru) toward phosphine selenides has also been investigated. In these cases, no selenium transfer *to the cluster* has been observed, but rather, substitution of one or two terminal carbonyl groups by the corresponding deselenized phosphine occurred.

Experimental Section

General Procedures. The starting reagents (salts, phosphines, selenium) were pure commercial products (Aldrich, Fluka) except the carbonyl clusters[17] and dpth and dppyth which were prepared as reported in the literature.[24,25] Phosphine selenuration reactions have been carried out by selenide transfer using elemental selenium or KSeCN.[26,27] The solvents (C. Erba) were dried and distilled by standard techniques before use. All manipulations (prior to the TLC separations) were carried out under dry nitrogen by means of standard Schlenk-tube techniques. Elemental (C, H, N, S) analyses were performed with a Carlo Erba EA 1108 automated analyzer. IR spectra (KBr disks or CH_2Cl_2 solutions) were recorded on Nicolet 5PC FT and IR Bruker IFS66 FT spectrometers, respectively. ^1H (300 MHz) and ^{31}P (81.0 MHz, 85% H_3PO_4 as external reference) NMR spectra ($CDCl_3$ solutions) were recorded on Bruker instruments, AC 300 (^1H), CXP 200 (^{31}P), and AMX 400 (^1H). Mass spectra were obtained using a Finnigan MAT SSQ710 spectrometer equipped with an EI/CI source, a direct inlet system, and a quadrupole mass analyzer. The CI source was utilized with methane as the reagent gas (*T* source, 220 °C; methane ionization energy, 70 eV). The quadrupole temperature was maintained at 140 °C; the system was scanned from 400 to 1600 amu, and negative ion (NICI) spectra were recorded.

Synthesis. Reaction of $[HRuCo_3(CO)_{12}]$ with dppySe. Synthesis of $[HRuCo_3(CO)_7(\mu\text{-}CO)_3(\mu\text{-}dppy)]$ (1) and $[RuCo_2(\mu_3\text{-}Se)(CO)_7(\mu\text{-}dppy)]$ (2). Treatment of $[HRuCo_3(CO)_{12}]$ (0.27 g, 0.44 mmol) with 0.15 g of dppySe (0.44 mmol) in toluene at 70 °C for 1 h, or at 35 °C for the same period of time, under N_2, gave a brown solution, which was evaporated to dryness, and the residue was redissolved in a small amount of CH_2Cl_2. TLC separation on silica, using a dichloromethane–hexane (1:2) mixture as eluent, yielded a bordeaux and a green band, some minor ones, and some decomposition. The two main bands contained, respectively, the tetranuclear clusters $[HRuCo_3(CO)_7(\mu\text{-}CO)_3(\mu\text{-}dppy)]$ (**1**, yield 19%) and $[RuCo_2(\mu_3\text{-}Se)(CO)_7(\mu\text{-}dppy)]$ (**2**, yield 23%). Purification by crystallization (from a CH_2Cl_2–MeOH mixture at 5 °C for some days) of the product gave well-formed crystals of **1** and **2** suitable for X-ray analysis.

Cluster **1**. FTIR (CH_2Cl_2, ν(CO), cm^{-1}): 2075m, 2055w, 2007s, 1973w, 1834w, 1812w. Anal. Found: C, 39.5; H, 1.6; N, 2.0%. For $C_{27}H_{15}Co_3NO_{10}PRu$: C, 39.5; H, 1.8; N, 1.7%. ^1H NMR ($CDCl_3$): δ 9.25 (s, broad, 1H, Py), 6.73–7.54 (m, broad, 3H Py, 10H 2Ph), −20.40 (d, ^2J(H,P) 15 Hz, μ_3-H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 34.9 (s, broad, PCo).

Cluster **2**. FTIR (CH_2Cl_2, ν(CO), cm^{-1}): 2060m, 2005s, 1983m. MS-NICI, *m/z* (%): 757 (30), $[RuCo_2(\mu_3\text{-}Se)(CO)_7(\mu\text{-}dppy)]^-$; 729 (100), $[RuCo_2(\mu_3\text{-}Se)(CO)_6(\mu\text{-}dppy)]^-$; 701 (28), $[RuCo_2(\mu_3\text{-}Se)(CO)_5(\mu\text{-}dppy)]^-$; 673 (6), $[RuCo_2(\mu_3\text{-}Se)(CO)_4(\mu\text{-}dppy)]^-$. Anal. Found: C, 38.2; H, 2.1; N, 1.7%. Calcd for $C_{24}H_{14}Co_2NO_7PRuSe$: C, 38.1; H, 1.9; N, 1.9%. ^1H NMR ($CDCl_3$): δ 9.0 (s, broad, 1H Py), 6.7–7.55 (m, 3H Py, 10H 2Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 40.3 (s, broad, PCo).

Reaction of $[HRuCo_3(CO)_{12}]$ with tppSe. Synthesis of $[HRuCo_3(CO)_8(\mu\text{-}CO)_3(PPh_3)]$ (3), $[HRuCo_3(CO)_7(\mu\text{-}CO)_3(PPh_3)_2]$ (4), $[RuCo_2(\mu_3\text{-}Se)(CO)_8(PPh_3)]$ (5), and $[RuCo_2(\mu_3\text{-}Se)(CO)_7(PPh_3)_2]$ (6). Treatment of $[HRuCo_3(CO)_{12}]$ (0.25 g, 0.40 mmol) with 0.14 g of tppSe (0.40 mmol) in THF at 60 °C for 2 h, under N_2, gave a brown solution, which was evaporated to dryness, and the residue was redissolved in a small amount of CH_2Cl_2. TLC separation on silica, using a dichloromethane–hexane (1:1) mixture as eluent, yielded a bordeaux, a violet, a brown, and a green band, some minor ones, and some decomposition. The four main bands contained, respectively, the tetranuclear clusters $[HRuCo_3(CO)_8(\mu\text{-}CO)_3(PPh_3)]$ (**3**, yield 30%) and $[HRuCo_3(CO)_7(\mu\text{-}CO)_3(PPh_3)_2]$ (**4**, yield 5%) and the trinuclear clusters $[RuCo_2(\mu_3\text{-}Se)(CO)_8(PPh_3)]$ (**5**, yield 25%) and $[RuCo_2(\mu_3\text{-}Se)(CO)_7(PPh_3)_2]$ (**6**, yield 14%), identified by comparison of spectroscopic data.

Cluster **3**. FTIR (CH_2Cl_2, ν(CO), cm^{-1}): 2082m, 2045s, 2009s, 1861m, 1846m. Anal. Found: C, 41.2; H, 1.7%. Calcd for $C_{29}H_{16}Co_3O_{11}PRu$: C, 41.0; H, 1.9%. ^1H NMR ($CDCl_3$): δ 7.09–7.54 (m, 15H 3Ph), −19.7 (s, μ_3-H).

Cluster **4**. FTIR (CH_2Cl_2, ν(CO), cm^{-1}): 2065m, 2056m, 2017s, 1980m, 1960sh, 1845w. Anal. Found: C, 49.8; H, 2.7%. Calcd for $C_{46}H_{31}Co_3O_{10}P_2Ru$: C, 51.0; H, 2.9%. ^1H NMR ($CDCl_3$): δ 7.40–6.98 (m, 30H 6Ph), −17.8 (s, μ_3-H).

Cluster **5**. FTIR (CH_2Cl_2, ν(CO), cm^{-1}): 2084m, 2048s, 2019m, 1970sh. MS-NICI, *m/z* (%): 755 (50), $[RuCo_2(\mu_3\text{-}Se)(CO)_7(PPh_3)]^-$; 727 (4), $[RuCo_2(\mu_3\text{-}Se)(CO)_6(PPh_3)]^-$; 700 (2), $[RuCo_2(\mu_3\text{-}Se)(CO)_5(PPh_3)]^-$; 521 (100), $[RuCo_2(\mu_3\text{-}Se)(CO)_8]^-$; 493 (18), $[RuCo_2(\mu_3\text{-}Se)(CO)_7]^-$. Anal. Found: C, 39.7; H, 2.1%. Calcd for $C_{26}H_{15}Co_2O_8PRuSe$: C, 39.8; H, 1.9%. ^1H NMR ($CDCl_3$): δ 7.25–7.44 (m, 15H 3Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 56.8 (s, broad, PCo).

Cluster **6**. FTIR (CH_2Cl_2, ν(CO), cm^{-1}): 2062m, 2009vs, 1989s, 1961sh, 1857w. MS-NICI, *m/z* (%): 755 (100), $[RuCo_2(\mu_3\text{-}Se)(CO)_7(PPh_3)]^-$; 727 (12), $[RuCo_2(\mu_3\text{-}Se)(CO)_6(PPh_3)]^-$; 700 (10), $[RuCo_2(\mu_3\text{-}Se)(CO)_5(PPh_3)]^-$; 521 (10), $[RuCo_2(\mu_3\text{-}Se)(CO)_8]^-$. Anal. Found: C, 50.8; H, 2.8%. Calcd for $C_{43}H_{30}Co_2O_7P_2RuSe$: C, 50.7; H, 3.0%. ^1H NMR ($CDCl_3$): δ 7.20–7.50 (m, 30H 6Ph).

Reaction of $[HRuCo_3(CO)_{12}]$ with dpthSe. Synthesis of $[HRuCo_3(CO)_8(\mu\text{-}CO)_3(dpth)]$ (7), $[RuCo_2(\mu_3\text{-}Se)(CO)_8(dpth)]$ (8), and $[RuCo_2(\mu_3\text{-}Se)(CO)_7(dpth)_2]$ (9). Treatment of $[HRuCo_3(CO)_{12}]$ (0.16 g, 0.3 mmol) with 0.09 g of dpthSe (0.30 mmol) in toluene at 70 °C for 2 h, under N_2, gave a brown solution, which

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was evaporated to dryness, and the residue was redissolved in a small amount of CH_2Cl_2. TLC separation on silica, using a dichloromethane−hexane (1:1) mixture as eluent, yielded a bordeaux, a brown and a green band, some minor ones, and some decomposition. The three main bands contained, respectively, the tetranuclear clusters $[HRuCo_3(CO)_8(\mu\text{-}CO)_3(dpth)]$ (**7**, yield 30%), $[RuCo_2(\mu_3\text{-}Se)(CO)_8(dpth)]$ (**8**, yield 25%), and $[RuCo_2(\mu_3\text{-}Se)(CO)_7(dpth)_2]$ (**9**, yield 18%) that were identified by comparison of spectroscopic data.

Cluster **7**. FTIR (CH_2Cl_2, ν(CO), cm^{-1}): 2083m, 2046s, 2010s, 1862m, 1846m. MS-NICI, *m*/*z* (%): 827 (23), $[HRuCo_3(CO)_{10}(dpth)]^-$; 715 (4), $[HRuCo_3(CO)_6(dpth)]^-$; 687 (2), $[HRuCo_3(CO)_5(dpth)]^-$; 587 (100), $[HRuCo_3(CO)_{11}]^-$; 559 (25), $[HRuCo_3(CO)_{10}]^-$; 531 (4), $[HRuCo_3(CO)_9]^-$. Anal. Found: C, 37.8; H, 1.7; S, 3.5%. Calcd for $C_{27}H_{14}Co_3O_{11}PRuS$: C, 37.9; H, 1.6; S, 3.7%. ^1H NMR ($CDCl_3$): δ 7.16−7.70 (m, 3H th, 10H 2Ph), −19.7 (s, μ_3-H).

Cluster **8**. FTIR (CH_2Cl_2, ν(CO), cm^{-1}): 2085m, 2048s, 2015m. MS-NICI, *m*/*z* (%): 762 (100), $[RuCo_2(\mu_3\text{-}Se)(CO)_7(dpth)]^-$; 735 (22), $[RuCo_2(\mu_3\text{-}Se)(CO)_6(dpth)]^-$; 706 (12), $[RuCo_2(\mu_3\text{-}Se)(CO)_5(dpth)]^-$; 521 (10), $[RuCo_2(\mu_3\text{-}Se)(CO)_8]^-$; 493 (18), $[RuCo_2(\mu_3\text{-}Se)(CO)_7]^-$. Anal. Found: C, 36.7; H, 1.7, S, 4.0%. Calcd for $C_{24}H_{13}Co_2O_8PRuSSe$: C, 36.5; H, 1.7; S, 4.1%. ^1H NMR ($CDCl_3$): δ 7.17−7.44 (m, 3H th, 10H 2Ph).

Cluster **9**. FTIR (CH_2Cl_2, ν(CO), cm^{-1}): 2056m, 2006s, 1966m. MS-NICI, *m*/*z* (%): 1002 (8), $[RuCo_2(\mu_3\text{-}Se)(CO)_6(dpth)_2]^-$; 761 (100), $[RuCo_2(\mu_3\text{-}Se)(CO)_7(dpth)]^-$; 733 (22), $[RuCo_2(\mu_3\text{-}Se)(CO)_6(dpth)]^-$; 704 (10), $[RuCo_2(\mu_3\text{-}Se)(CO)_5(dpth)]^-$; 521 (19), $[RuCo_2(\mu_3\text{-}Se)(CO)_8]^-$. Anal. Found: C, 45.8; H, 2.7; S, 6.1%. Calcd for $C_{39}H_{26}Co_2O_7P_2RuS_2Se$: C, 45.5; H, 2.5; S, 6.2%. ^1H NMR ($CDCl_3$): δ 7.12−7.50 (m, 6H th, 20H 4Ph).

Reaction of $[HRuCo_3(CO)_{12}]$ with dppythSe. Synthesis of $[HRuCo_3(CO)_8(\mu\text{-}CO)_3(dppyth)]$ (10) and $[RuCo_2(\mu_3\text{-}Se)(CO)_7(dppyth)_2]$ (11). Treatment of $[HRuCo_3(CO)_{12}]$ (0.25 g, 0.4 mmol) with 0.17 g of dppythSe (0.40 mmol) in toluene at 70 °C for 2 h, under N_2, gave a brown solution, which was evaporated to dryness, and the residue was redissolved in a small amount of CH_2Cl_2. TLC separation on silica, using a dichloromethane−hexane (1:1) mixture as eluent, yielded a red and a brown band, some minor ones, and some decomposition. The two main bands contained, respectively, $[HRuCo_3(CO)_8(\mu\text{-}CO)_3(dppyth)]$ (**10**, yield 24%) and $[RuCo_2(\mu_3\text{-}Se)(CO)_7(dppyth)_2]$ (**11**, yield 15%) that were identified by comparison of spectroscopic data.

Cluster **10**. FTIR (CH_2Cl_2, ν(CO), cm^{-1}): 2083m, 2046s, 2010s, 1862m, 1846m. MS-NICI, *m*/*z* (%): 904 (8), $[HRuCo_3(CO)_{10}(dppyth)]^-$; 876 (7), $[HRuCo_3(CO)_9(dppyth)]^-$; 587 (39), $[HRuCo_3(CO)_{11}]^-$; 559 (100), $[HRuCo_3(CO)_{10}]^-$; 531 (8), $[HRuCo_3(CO)_9]^-$. Anal. Found: C, 41.4; H, 1.7; N, 1.3; S, 3.5%. Calcd for $C_{32}H_{17}Co_3NO_{11}PRuS$: C, 41.2; H, 1.8; N, 1.5; S, 3.4%. ^1H NMR ($CDCl_3$): δ 8.51 (d, ^3J(H,H) 4.8 Hz, $1H_\alpha$ Py), 7.31−7.75 (m, 3H Py, 1H th, 10H 2Ph), 7.18 (t, ^3J(P,H) 6 Hz, 1H th), −19.7 (s, μ_3-H).

Cluster **11**. FTIR (CH_2Cl_2, ν(CO), cm^{-1}): 2065sh, 2054m, 2045m, 2015vs, 1991sh. Anal. Found: C, 49.8; H, 2.7; N, 2.3; S, 5.7%. Calcd for $C_{49}H_{32}Co_2N_2O_7P_2RuS_2Se$: C, 49.7; H, 2.7; N, 2.4; S, 5.4%. ^1H NMR ($CDCl_3$): δ 8.5 (s, broad, 2H Py), 7.23−7.90 (m, 6H Py, 4H th, 20H 4Ph).

Reaction of $[HRuCo_3(CO)_{12}]$ with dppmSe. Synthesis of $[RuCo_2(\mu_3\text{-}Se)(CO)_7(\mu\text{-}dppm)]$ (12) and $[RuCo_2(\mu_3\text{-}Se)(CO)_5(\mu\text{-}dppm)_2]$ (13). Treatment of $[HRuCo_3(CO)_{12}]$ (0.15 g, 0.24 mmol) with 0.11 g of dppmSe (0.24 mmol) for 2 h in refluxing toluene, under N_2, gave a brown solution, which was evaporated to dryness, and the residue was redissolved in a small amount of CH_2Cl_2. TLC separation on silica, using a dichloromethane−hexane (1:1) mixture as eluent, yielded one brown and one green band, some minor ones, and some decomposition. The brown band contained $[RuCo_2(\mu_3\text{-}Se)(CO)_7(\mu\text{-}dppm)]$ (**12**, yield 35%), recognized after determination of its crystal structure, while the green band was found to be $[RuCo_2(\mu_3\text{-}Se)(CO)_5(\mu\text{-}dppm)_2]$ (**13**, yield 20%) after comparison of spectroscopic data. Purification by crystallization (from a CH_2Cl_2−MeOH mixture at 5 °C for some days) of the product gave well-formed crystals of **12** suitable for X-ray analysis.

Cluster **12**. FTIR (CH_2Cl_2, ν(CO), cm^{-1}): 2055s, 2007vs, 1973m, 1888w. MS-NICI, *m*/*z* (%): 850 (100), $[RuCo_2(\mu_3\text{-}Se)(CO)_6(\mu\text{-}dppm)]^-$; 822 (2), $[RuCo_2(\mu_3\text{-}Se)(CO)_5(\mu\text{-}dppm)]^-$. Anal. Found: C, 43.6; H, 2.7%. Calcd for $C_{32}H_{22}Co_2O_7P_2RuSe$: C, 43.8; H, 2.5%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 39.6 (d, ^3J(P,P) 46 Hz, PRu), 43.9 (s, broad, PCo).

Cluster **13**. FTIR (CH_2Cl_2, ν(CO), cm^{-1}): 2059s, 2007vs, 1986s, 1850sh. MS-NICI, *m*/*z* (%): 1206 (4), $[RuCo_2(\mu_3\text{-}Se)(CO)_5(\mu\text{-}dppm)_2]^-$; 1178 (12), $[RuCo_2(\mu_3\text{-}Se)(CO)_4(\mu\text{-}dppm)_2]^-$; 850 (100) $[RuCo_2(\mu_3\text{-}Se)(CO)_6(\mu\text{-}dppm)]^-$; 821 (2) $[RuCo_2(\mu_3\text{-}Se)(CO)_5(\mu\text{-}dppm)]^-$; 793 (2) $[RuCo_2(\mu_3\text{-}Se)(CO)_4(\mu\text{-}dppm)]^-$. Anal. Found: C, 54.6; H, 3.5%. Calcd for $C_{55}H_{44}Co_2O_5P_4RuSe$: C, 54.7; H, 3.7%.

Reaction of $[NEt_4][RuCo_3(CO)_{12}]$ with dppySe. Synthesis of $[(Ph_3P)AuRuCo_3(CO)_8(\mu\text{-}CO)_3(dppy)]$ (14). Treatment of $[NEt_4][RuCo_3(CO)_{12}]$ (0.16 g, 0.2 mmol) with 0.07 g of dppySe (0.2 mmol) and 0.015 g of Me_3NO in refluxing acetone for 4 h under N_2 gave a brown solution, which was evaporated to dryness, and the residue was redissolved in a small amount of CH_2Cl_2. An equivalent amount of $[AuCl(PPh_3)]$ (0.2 mmol, 0.1 g) and $TlPF_6$ (0.2 mmol, 0.07 g) was added, which led to the immediate precipitation of TlCl; after filtration to remove the salt, the solution was stirred for ∼2 h, changing color from brown to violet. A TLC separation on silica, using a dichloromethane−hexane (1:2) mixture as eluent, yielded a bordeaux and a brown band, some minor ones, and some decomposition. The bordeaux band contained the pentanuclear cluster $[(Ph_3P)AuRuCo_3(CO)_8(\mu\text{-}CO)_3(dppy)]$ (**14**, yield 37%) which was identified by comparison of spectroscopic data.[9]

Cluster **14**. FTIR (CH_2Cl_2, ν(CO), cm^{-1}): 2083vs, 2047vs, 2011vs, 1973sh, 1891sh, 1862s, 1846m. MS-NICI, *m*/*z* (%): 821 (18), $[RuCo_3(CO)_{10}(dppy)]^-$; 709 (3), $[RuCo_3(CO)_6(dppy)]^-$; 586 (100), $[RuCo_3(CO)_{11}]^-$; 558 (24), $[RuCo_3(CO)_{10}]^-$; 530 (3), $[RuCo_3(CO)_9]^-$. Anal. Found: C, 42.0; H, 2.5; N, 1.2%. Calcd for $C_{46}H_{29}AuCo_3NO_{11}P_2Ru$: C, 42.2; H, 2.2; N, 1.1%. ^1H NMR ($CDCl_3$): δ 7.67 (m, 1H Py), 7.20−7.57 (m, 3H Py, 25H 5Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 37.4 (s, PCo), 52.6 (s, PAu).

Reaction of $[NEt_4][RuCo_3(CO)_{12}]$ with tppSe. Synthesis of $[(Ph_3P)AuRuCo_3(CO)_8(\mu\text{-}CO)_3(PPh_3)]$ (15a and 15b). Treatment of $[NEt_4][RuCo_3(CO)_{12}]$ (0.31 g, 0.4 mmol) with 0.14 g of tppSe (0.4 mmol) and 0.030 g of Me_3NO in refluxing acetone for 4 h under N_2 gave a brown solution, which was evaporated to dryness, and the residue was redissolved in a small amount of CH_2Cl_2. An equivalent amount of $[AuCl(PPh_3)]$ (0.4 mmol, 0.2 g) and $TlPF_6$ (0.4 mmol, 0.14 g) was added, which led to the immediate precipitation of TlCl; after filtration to eliminate the salt, the solution was stirred for ∼2 h and changed color from brown to violet. A TLC separation on silica, using a dichloromethane−hexane (1:2) mixture as eluent, yielded a bordeaux and a violet band, some minor ones, and some decomposition. The two main bands contained the pentanuclear isomeric clusters $[(Ph_3P)AuRuCo_3(CO)_8(\mu\text{-}CO)_3(PPh_3)]$ (**15a** and **15b**, yield 13 and 23% respectively), which were identified by comparison of spectroscopic data.

Cluster **15a**. FTIR (CH_2Cl_2, ν(CO), cm^{-1}): 2083m, 2053w, 2018vs, 1973m, 1956m, 1857m. MS-NICI, *m*/*z* (%): 1045 (24), [AuRuCo$_3$(CO)$_{11}$(PPh$_3$)]$^-$; 1016 (100), [AuRuCo$_3$(CO)$_{10}$(PPh$_3$)]$^-$; 989 (2), [AuRuCo$_3$(CO)$_9$(PPh$_3$)]$^-$. Anal. Found: C, 43.2; H, 2.1.%. Calcd for $C_{47}H_{30}AuCo_3O_{11}P_2Ru$: C, 43.2; H, 2.3.%. ^{1}H NMR (CDCl$_3$): δ 7.20−7.55 (m, 30H 6Ph). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 37.4 (s, broad, PCo), 52.7 (s, PAu).

Cluster **15b**. FTIR (CH$_2$Cl$_2$, ν(CO), cm^{-1}): 2050m, 2012s, 2002s, 1886w, 1847m. MS-NICI, *m/z* (%): 1045 (24), [AuRuCo$_3$(CO)$_{11}$(PPh$_3$)]$^-$; 1016 (100), [AuRuCo$_3$(CO)$_{10}$(PPh$_3$)]$^-$; 989 (2), [AuRuCo$_3$(CO)$_9$(PPh$_3$)]$^-$. Anal. Found: C, 43.0; H, 2.0.%. Calcd for $C_{47}H_{30}AuCo_3O_{11}P_2Ru$: C, 43.2; H, 2.3.%. ^{1}H NMR (CDCl$_3$): δ 7.20−7.55 (m, 30H 6Ph). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 36.4 (s, PRu), 52.9 (s, PAu).

Reaction of [HFeCo$_3$(CO $_{12}$] with dppySe. Synthesis of [FeCo$_2$(μ_3-Se)(CO)$_7$(μ-dppy)] (16). Treatment of [HFeCo$_3$(CO)$_{12}$] (0.12 g, 0.2 mmol) with 0.14 g of dppySe (0.4 mmol) for 2 h in toluene, at 70 °C, under N$_2$, gave a brown solution, which was evaporated to dryness, and the residue was redissolved in a small amount of CH$_2$Cl$_2$. TLC separation on silica, using a dichloromethane−hexane (1:1) mixture as eluent, yielded a green band and some decomposition. The band contained [FeCo$_2$(μ_3-Se)(CO)$_7$(μ-dppy] (**16**, yield 67%), recognized after solution of its crystal structure. Purification by crystallization (from a CH$_2$Cl$_2$−MeOH mixture at 5 °C for some days) of the product gave well-formed crystals of **16** suitable for X-ray analysis.

Cluster **16**. FTIR (CH$_2$Cl$_2$, ν(CO), cm^{-1}): 2051s, 2009s, 1996s, 1980sh, 1942w. MS-NICI, *m/z* (%): 712 (28), [FeCo$_2$(μ_3-Se)(CO)$_7$(μ-dppy)]$^-$; 684 (100), [FeCo$_2$(μ_3-Se)(CO)$_6$(μ-dppy)]$^-$; 656 (29), [FeCo$_2$(μ_3-Se)(CO)$_5$(μ-dppy)]$^-$; 628 (6), [FeCo$_2$(μ_3-Se)(CO)$_4$(μ-dppy)]$^-$; 449 (8), [FeCo$_2$(μ_3-Se)(CO)$_7$]$^-$. Anal. Found: C, 40.8; H, 1.3; N, 2.2%. Calcd for $C_{24}H_{14}Co_2FeNO_7PSe$: C, 40.5; H, 1.9; N, 2.0%. ^{1}H NMR (CDCl$_3$): δ 8.94 (m, 1H Py), 7.07−7.70 (m, 2H Py, 10H 2Ph), 6.79 (m, 1H Py). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 45.3 (s, broad, PCo).

Reaction of [HFeCo$_3$(CO)$_{12}$] with tppSe. Synthesis of [HFeCo$_3$(CO)$_8$(μ-CO)$_3$(PPh$_3$)] (17), [FeCo$_2$(μ_3-Se)(CO)$_8$(PPh$_3$)] (18), and [FeCo$_2$(μ_3-Se)(CO)$_7$(PPh$_3$)$_2$] (19a and 19b). Treatment of [HFeCo$_3$(CO)$_{12}$] (0.25 g, 0.44 mmol) with 0.15 g of tppSe (0.44 mmol) in toluene at 70 °C for 1 h, under N$_2$, gave a green solution, which was evaporated to dryness, and the residue was redissolved in a small amount of CH$_2$Cl$_2$. TLC separation on silica, using a dichloromethane−hexane (1:2) mixture as eluent, yielded a violet, a brown, and two green bands, some minor ones, and some decomposition. The four main bands contained, respectively, the tetranuclear cluster [HFeCo$_3$(CO)$_8$(μ-CO)$_3$(PPh$_3$)] (**17**, yield 13%), [FeCo$_2$(μ_3-Se)(CO)$_8$(PPh$_3$)] (**18**, yield 36%), and the two isomers [FeCo$_2$(μ_3-Se)(CO)$_7$(PPh$_3$)$_2$] (**19a** and **19b**, yield 19 and 24% respectively) identified by comparison of their spectroscopic data.

Cluster **17**. FTIR (CH$_2$Cl$_2$, ν(CO), cm^{-1}): 2078m, 2035s, 2009m, 1968w, 1863m, 1847m. Anal. Found: C, 43.2; H, 1.7%. Calcd for $C_{29}H_{16}Co_3FeO_{11}P$: C, 43.3; H, 2.0%. ^{1}H NMR (CDCl$_3$): δ 6.91−7.32 (m, 15H 3Ph), −21.0 (s, μ_3-H).

Cluster **18**. FTIR (CH$_2$Cl$_2$, ν(CO), cm^{-1}): 2077s, 2035vs, 2012s, 1977m. MS-NICI, *m/z* (%): 711 (100), [FeCo$_2$(μ_3-Se)(CO)$_7$(PPh$_3$)]$^-$; 683 (4), [FeCo$_2$(μ_3-Se)(CO)$_6$(PPh$_3$)]$^-$; 627 (4), [FeCo$_2$(μ_3-Se)(CO)$_4$(PPh$_3$)]$^-$; 477 (21), [FeCo$_2$(μ_3-Se)(CO)$_8$]$^-$; 449 (6), [FeCo$_2$(μ_3-Se)(CO)$_7$]$^-$. Anal. Found: C, 42.5; H, 2.1%. Calcd for $C_{26}H_{15}Co_2FeO_8PSe$: C, 42.3; H, 2.0%. ^{1}H NMR (CDCl$_3$): δ 7.25−7.50 (m, 15H 3Ph). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 52.3 (s, broad, PCo).

Cluster **19a**. FTIR (CH$_2$Cl$_2$, ν(CO), cm^{-1}): 2054sh, 2042s, 2008vs, 1977s. MS-NICI, *m/z* (%): 711 (50), [FeCo$_2$(μ_3-Se)(CO)$_7$(PPh$_3$)]$^-$; 477 (100), [FeCo$_2$(μ_3-Se)(CO)$_8$]$^-$; 449 (12), [FeCo$_2$(μ_3-Se)(CO)$_7$]$^-$. Anal. Found: C, 52.9; H, 3.2%. Calcd for $C_{43}H_{30}Co_2FeO_7P_2Se$: C, 53.1; H, 3.1%. ^{1}H NMR (CDCl$_3$): δ 7.25−7.80 (m, 30H 6Ph). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 49.6 (s, PFe).

Cluster **19b**. FTIR (CH$_2$Cl$_2$, ν(CO), cm^{-1}): 2053w, 2019s, 1991vs. MS-NICI, *m/z* (%): 711 (50), [FeCo$_2$(μ_3-Se)(CO)$_7$(PPh$_3$)]$^-$; 477 (100), [FeCo$_2$(μ_3-Se)(CO)$_8$]$^-$; 449 (12), [FeCo$_2$(μ_3-Se)(CO)$_7$]$^-$. Anal. Found: C, 52.8; H, 3.4%. Calcd for $C_{43}H_{30}Co_2FeO_7P_2Se$: C, 53.1; H, 3.1%. ^{1}H NMR (CDCl$_3$): δ 7.25−7.80 (m, 30H 6Ph).

Reaction of [HFeCo$_3$(CO)$_{12}$] with dppythSe. Synthesis of [HFeCo$_3$(CO)$_7$(μ-CO)$_3$(dppyth)$_2$] (20), [FeCo$_2$(μ_3-Se)(CO)$_8$(dppyth)] (21), and [FeCo$_2$(μ_3-Se)(CO)$_7$(dppyth)$_2$] (22). Treatment of [HFeCo$_3$(CO)$_{12}$] (0.20 g, 0.33 mmol) with 0.28 g of dppythSe (0.66 mmol) in toluene at 70 °C for 2 h, under N$_2$, gave a brown solution, which was evaporated to dryness, and the residue was redissolved in a small amount of CH$_2$Cl$_2$. TLC separation on silica, using a dichloromethane−hexane (1:2) mixture as eluent, yielded a deep green, a light green and a brown band, some minor ones, and some decomposition. The three main bands contained, respectively, the tetranuclear [HFeCo$_3$(CO)$_7$(μ-CO)$_3$(dppyth)$_2$] (**20**, yield 25%), [FeCo$_2$(μ_3-Se)(CO)$_8$(dppyth)] (**21**, yield 30%), and [FeCo$_2$(μ_3-Se)(CO)$_7$(dppyth)$_2$] (**22**, yield 18%), whose structures were identified by comparison of their spectroscopic data.

Cluster **20**. FTIR (CH$_2$Cl$_2$, ν(CO), cm^{-1}): 2054vs, 2022vs, 1992s, 1955sh, 1871w, 1863m, 1840m. MS-NICI, *m/z* (%): 860 (100), [HFeCo$_3$(CO)$_{10}$(dppyth)]$^-$. Anal. Found: C, 51.6; H, 2.8; N, 2.6; S, 5.1%. Calcd for $C_{52}H_{33}Co_3FeN_2O_{10}P_2S_2$: C, 51.8; H, 2.9; N, 2.3; S, 5.3%. ^{1}H NMR (CDCl$_3$): δ 8.48 (m, 2H 2Py), 7.02−7.70 (m, 6H 2Py, 4H 2nd, 20H 4Ph), −21.0 (s, μ_3-H).

Cluster **21**. FTIR (CH$_2$Cl$_2$, ν(CO), cm^{-1}): 2077m, 2035vs, 2011s, 1971m, 1864w, 1847w. Anal. Found: C, 42.5; H, 2.1%. Calcd for $C_{29}H_{16}Co_2FeNO_8PSSe$: C, 42.3; H, 2.0%. ^{1}H NMR (CDCl$_3$): δ 8.51 (s, broad, 1H Py), 7.18−7.65 (m, 3H Py, 2H th, 10H 2Ph).

Cluster **22**. FTIR (CH$_2$Cl$_2$, ν(CO), cm^{-1}): 2077vw, 2044s, 2010vs, 1977s. MS-NICI, *m/z* (%): 794 (100), [FeCo$_2$(μ_3-Se)(CO)$_7$(dppyth)]$^-$. Anal. Found: C, 51.4; H, 2.7; N, 2.5; S, 5.3%. Calcd for $C_{49}H_{32}Co_2FeN_2O_7P_2S_2Se$: C, 51.6; H, 2.8; N, 2.5; S, 5.6%. ^{1}H NMR (CDCl$_3$): δ 8.52 (d, ^3J(H,H) 4.8 Hz, 2H 2Py), 7.35−7.68 (m, 6H 2Py, 4H 2th, 20H 4Ph). ^{31}P{^{1}H} NMR (CDCl$_3$): δ 39.6 (s, PFe).

X-ray Crystallographic Studies. The crystal structures of complexes **1**, **2**, **12**, and **16** were determined by X-ray diffraction methods. Intensity data and cell parameters were recorded at room temperature (25 °C) on a Philips PW 1100 single-crystal diffractometer using graphite monochromated Mo Kα radiation and the $\theta/2\theta$ scan technique. Crystallographic and experimental details are summarized in Table 1. A correction for absorption was made for complex **1** [maximum and minimum values for the transmission coefficient were 1.000 and 0.7318], **2** [1.000 and 0.4916], **12** [1.000 and 0.5891], and **16** [1.000 and 0.7515].[28,29] The structures were solved by Patterson and Fourier methods using SHELXS-97 programs;[30] the refinements were carried out by full-matrix least-squares procedures based on F_o^2 values with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions and refined *riding* on the corresponding parent atoms. In the final cycles of refinement, a weighting scheme $w = 1/[\sigma^2F_o^2 + (0.0129P)^2]$ (**1**), $w = 1/[\sigma^2F_o^2 + (0.0350P)^2]$ (**2**), $w = 1/[\sigma^2F_o^2 + (0.0477P)^2]$ (**12**), $w = 1/[\sigma^2F_o^2 + (0.0393P)^2]$ (**16**), where

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Table 1. Crystallographic Data for Compounds **1, 2, 12, 16**

	1	**2**	**12**	**16**
formula	$C_{27}H_{15}Co_3NO_{10}PRu$	$C_{24}H_{14}Co_2NO_7PRuSe$	$C_{32}H_{22}Co_2O_7P_2RuSe$	$C_{24}H_{14}Co_2FeNO_7PSe$
fw	822.23	757.22	878.33	712.00
cryst syst	monoclinic	monoclinic	orthorhombic	monoclinic
space group	*P*21/*c*	*P*21/*c*	*Pbca*	*P*21/*c*
a, Å	12.459(4)	12.148(4)	20.798(4)	12.206(4)
b, Å	11.083(5)	21.466(5)	27.858(5)	21.226(5)
c, Å	22.472(5)	11.400(4	11.272(3)	11.276(4)
β, deg	103.47(6)	116.27(6)	90	115.96(6)
V, *Å*^{3}	3018(2)	2666(1)	6531(2)	2627(1)
Z	4	4	4	4
ρ_{calcd}, g cm^{-3}	1.810	1.887	1.787	1.8
μ, cm^{-1}	22.20	32.58	27.19	32.84
F(000)	1616	1472	3456	1400
cryst size, mm^3	0.27 × 0.22 × 0.19	0.19 × 0.20 × 0.33	0.21 × 0.18 × 0.26	0.27 × 0.21 × 0.35
reflns collected	7449	6045	9490	7981
independent reflns	7281 (R_{int} = 0.0617)	5786 (R_{int} = 0.0568)	9490 (R_{int} = 0.000)	7668 (R_{int} = 0.0235)
obs reflns [$I > 2\sigma(I)$]	2629	2440	3955	4500
data/restr/params	7281/0/395	5786/0/337	9490/0/411	7688/0/337
GOF on F^2	0.644	0.808	0.831	0.890
final R indices [$I > 2\sigma(I)$]^a	R1 = 0.0356, wR2 = 0.0538	R1 = 0.0444, wR2 = 0.0809	R1 = 0.0397, wR2 = 0.0851	R1 = 0.0348, wR2 = 0.0700
R indices (all data)	R1 = 0.1540, wR2 = 0.0796	R1 = 0.1425, wR2 = 0.1044	R1 = 0.1479, wR2 = 0.1168	R1 = 0.0885, wR2 = 0.0824

^{a} $R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR2 = [\Sigma[w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

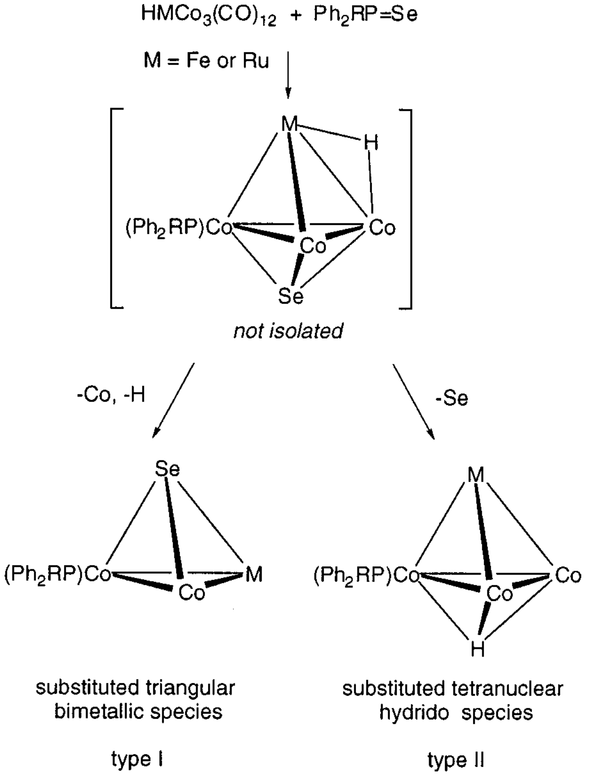
$P = (F_o^2+2F_c^2)/3$, was used. All calculations were carried out on the DIGITAL AlphaStation 255 computers of the "Centro di Studio per la Strutturistica Diffrattometrica" of CNR, Parma.

Results and Discussion

The reactions between [$HMCo_3(CO)_{12}$] and phosphine selenides gave two main classes of products: (i) trinuclear selenido clusters of the type [$MCo_2(\mu_3$-Se)$(CO)_{9-x}L_y$] ($x = y = 1$, 2 with L = monodentate ligand; $x = 2$, 4, and $y = 1$, 2, with L = bidentate ligand) (M = Fe, Ru) (type I) resulting from the selenium transfer and (ii) tetranuclear clusters of the type [$HMCo_3(CO)_{12-x}L_y$] obtained by substitution of carbonyl groups by the deselenized phosphine ligand (type II) (see Scheme 3, carbonyls are omitted for clarity).

Both series belong to the *nido*-type derived from a trigonal bipyramid. While compounds of type II have been already reported in the literature, this is the first time that closed triangular bimetallic clusters capped by a μ_3-selenide unit and substituted by a phosphine ligand (type I) have been obtained and fully characterized. Another μ_3-Se bridged Fe_2Co complex substituted by phosphines has been reported,[31a] but it contains only one metal−metal bond between the two iron atoms. One possible hypothesis for the formation of clusters of type I is that the reactions proceed first with an oxidative addition of the phosphine selenide, resulting in selenium transfer to the cluster giving an intermediate species in which both the resulting phosphine ligand and the selenium are coordinated. This intermediate would then lose a metal fragment (which is always a cobalt fragment) and a hydride ligand or a selenium atom to give I or II, respectively (see Scheme 3).

Scheme 3. Possible Pathways Leading to Clusters of Types I and II (Carbonyl Ligands Not Shown for Clarity).



1. Formation of Selenide Clusters. In clusters of type I, the main group element Se may be considered part of the skeleton, which leads to a total electron count (TEC) of 50 and 6 skeletal electron pairs (SEPs), consistent with a *nido* structure. These clusters could alternatively be viewed as trinuclear, *arachno* clusters with TEC = 48 and SEP = 6 with the μ_3-Se ligand being a 4-electron donor.

Compounds [$RuCo_2(\mu_3$-Se)$(CO)_8(PPh_3)$] (**5**), [$RuCo_2(\mu_3$-Se)$(CO)_8$(dpth)] (**8**), [$FeCo_2(\mu_3$-Se)$(CO)_8(PPh_3)$] (**18**), and [$FeCo_2(\mu_3$-Se)$(CO)_8$ (dppyth)] (**21**) belong to type I with the

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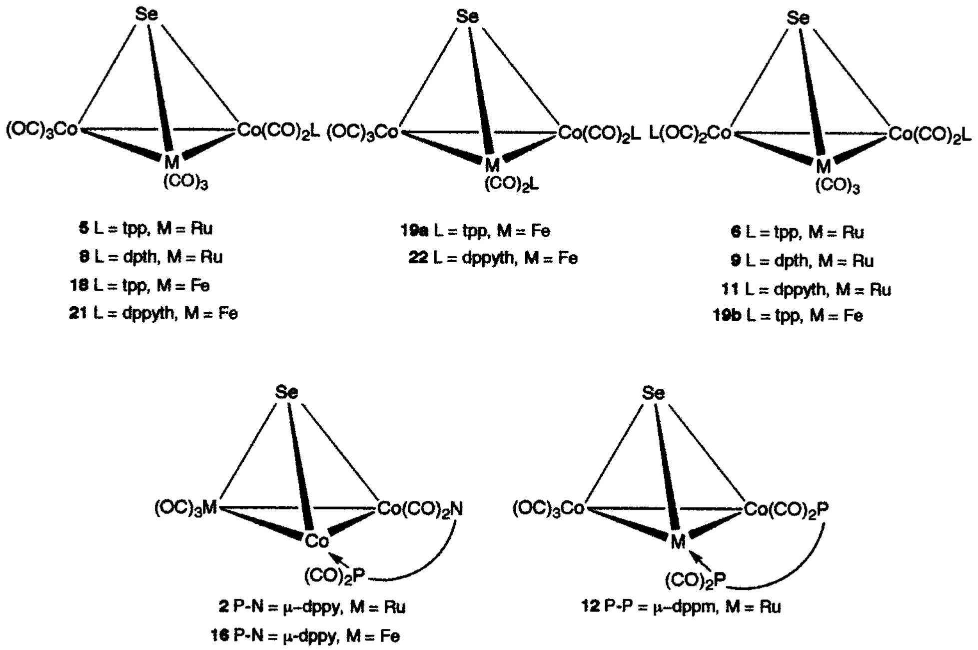
(31) (a) Mathur, P.; Sekar, P. *J. Organomet. Chem.* **1997**, *527*, 29. (b) Mathur, P.; Hossain, M. M.; Rheingold, A. L. *Organometallics* **1994**, *13*, 3909. (c) Mathur, P.; Ghose, S.; Hossain, M. M.; Satyanarayana, C. V. V.; Mahon, M. F. *J. Organomet. Chem.* **1997**, *543*, 189. (d) Mathur, P.; Ghose, S.; Hossain, M. M.; Satyanarayana, C. V. V.; Chadha, R. K.; Banerjee, S.; Kumar, G. R. *J. Organomet. Chem.* **1998**, *568*, 197.

Scheme 4



MCo_2 metal triangle capped by a μ_3-Se ligand; one phosphine ligand is coordinated to the cobalt atom (Scheme 4). The order of elution during the TLC separation, the IR pattern in the carbonyl region, the ^1H and $^{31}P\{^1H\}$ NMR signals, and the NICI mass spectra are consistent with the suggested structure. The $^{31}P\{^1H\}$ NMR spectrum of **5** and **18** presents a broad signal at δ 56.8 and 52.3, respectively, while in **21** and **8** the signal has not been detected, which is consistent with a coordination of the phosphine on the quadrupolar ^{59}Co nucleus, ($I = {}^7/_2$). The NICI mass spectrum of **18** shows peaks derived from M^- by loss of one phosphine molecule and carbonyl groups: $[FeCo_2(\mu_3\text{-Se})(CO)_7(PPh_3)]^-$, $[FeCo_2(\mu_3\text{-Se})(CO)_6(PPh_3)]^-$, $[FeCo_2(\mu_3\text{-Se})(CO)_4(PPh_3)]^-$, $[FeCo_2(\mu_3\text{-Se})(CO)_8]^-$, and $[FeCo_2(\mu_3\text{-Se})(CO)_7]^-$. For compounds **5** and **8**, the $[RuCo_2(\mu_3\text{-Se})(CO)_7(PPh_3)]^-$ and $[RuCo_2(\mu_3\text{-Se})(CO)_7(dpth)]^-$ signals have been observed, which correspond to the molecular peak after loss of a carbonyl group, along with other signals resulting from further fragmentation.

Clusters $[RuCo_2(\mu_3\text{-Se})(CO)_7(PPh_3)_2]$ (**6**), $[RuCo_2(\mu_3\text{-Se})(CO)_7(dpth)_2]$ (**9**), $[RuCo_2(\mu_3\text{-Se})(CO)_7(dppyth)_2]$ (**11**), the two isomers $[FeCo_2(\mu_3\text{-Se})(CO)_7(PPh_3)_2]$ (**19a** and **19b**), and $[FeCo_2(\mu_3\text{-Se})(CO)_7(dppyth)_2]$ (**22**) present the same *core* MCo_2Se; two phosphine ligands coordinate two metal atoms, giving the possibility of Co−M and/or Co−Co isomers. The two isomers **19a** and **19b** present the same color, similar IR spectra in the carbonyl region, similar ^1H NMR spectra and NICI mass spectra; all the spectroscopic data are in good agreement with those found for compounds **6**, **9**, **11**, and **22**. Their isomerism probably derives from a different coordination position of the phosphine on the metal triangle; in **6** and in **19b**, the absence of ^{31}P signal indicates coordination on two cobalt atoms, while in **19a**, the signal at δ 49.6 suggests coordination of one phosphine ligand on the iron atom. In the ^{31}P spectrum of **22**, a signal at δ 39.6 has been observed, indicative of the coordination of one of the two dppyth ligands on the iron atom. The IR pattern in the ν(CO) region and the ^1H NMR are consistent with the formulations and structures drawn for all the compounds. The order of elution during the TLC separation is also informative: the disubstituted clusters are usually more polar than the corresponding monosubstituted ones, and, therefore, interact more strongly with the silica support. Finally, in the NICI mass spectra for cluster **9**, the peak $[RuCo_2(\mu_3\text{-Se})(CO)_6(dpth)_2]^-$ is present, while in the case of the other compounds only the fragments derived by loss of one phosphine ligand and carbonyl groups are present.

Compounds $[RuCo_2(\mu_3\text{-Se})(CO)_7(\mu\text{-dppy})]$ (**2**) and $[FeCo_2(\mu_3\text{-Se})(CO)_7(\mu\text{-dppy})]$ (**16**), whose structure has been solved by X-ray diffraction methods, are Ru(Fe)−Co clusters of type I, in which a MCo_2 triangle is capped by a μ_3-Se ligand. The bidentate phosphine ligand bridges the Co−Co edge through the phosphorus and the nitrogen atoms; the coordination around the metals is completed by the presence of seven terminal carbonyl groups. To our knowledge**,** no selenido carbonyl clusters with a mixed-metal triangular *core* substituted by phosphines have been reported in the literature. However, Mathur et al.,[31] Konchenko et al.,[32] as well as other research groups,[33] have studied a series of triangular μ_3-selenido unsubstituted clusters, along with other systems of different nuclearity.[34] On the other hand, similar compounds containing a μ_3-S unit and substituted by phosphines have been reported.[35,36] The NICI mass spectra for **2** and **16** show the molecular peaks along with other signals corresponding to the loss of one, two, and three carbonyl groups, respectively; the presence of ruthenium and selenium (**2**) and iron

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(32) (a) Konchenko, S. N.; Virovets, A. V.; Tkachev, S. V.; Alekseev, V. I.; Podberezskaya, N. V. *Polyhedron* **1996**, *15*, 1221. (b) Konchenko, S. N.; Virovets, A. V.; Tkachev, S. V.; Podberezskaya, N. V. *Polyhedron* **1997**, *16*, 707. (c) Konchenko, S. N.; Virovets, A. V.; Podberezskaya, N. V. *Polyhedron* **1997**, *16*, 1689.

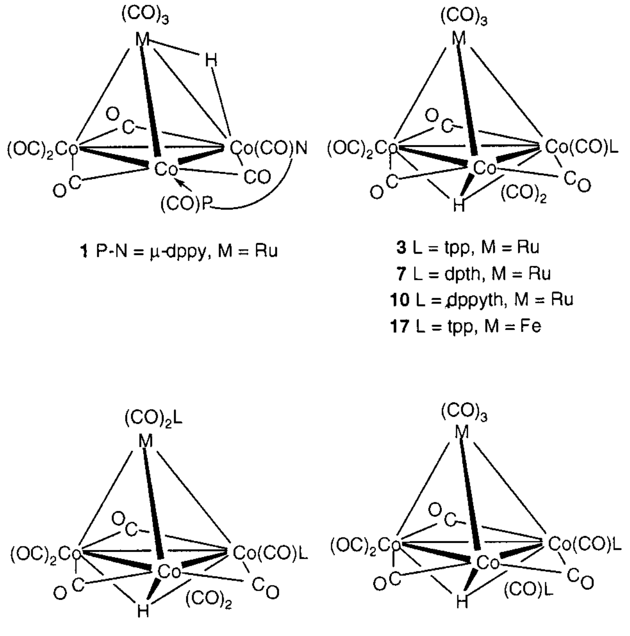
(33) (a) Ding, E.-R.; Yin, Y.-Q.; Sun, J. *J. Organomet. Chem.* **1998**, *559*, 157. (b) Zhang, Y.-H.; Wu, S.-L.; Li, Q.-S.; Yin, I.-Q.; Huang, X.-Y. *J. Chem. Res.* **1999**, *9*, 550.

and selenium (**16**) is also indicated by the characteristic isotopic pattern. The ^{1}H NMR spectrum shows a broad signal at δ 9.0 (**2**) and 8.94 (**16**) relative to the H_α of the N-coordinated pyridyl group, while the other protons of the heterocycle and of the phenyl groups give two series of unresolved multiplets in the δ 6.7−7.55 region. The $^{31}P\{^{1}H\}$ NMR spectrum presents a broad signal at δ 40.3 (**2**) and at δ 45.3 (**16**), typical for the phosphorus atom interacting with the cobalt atom.

The reaction between $[HRuCo_3(CO)_{12}]$ and the bidentate dppmSe gave two main products, $[RuCo_2(\mu_3\text{-}Se)(CO)_7(\mu\text{-}dppm)]$ (**12**), identified by its crystal structure, and $[RuCo_2(\mu_3\text{-}Se)(CO)_5(\mu\text{-}dppm)_2]$ (**13**). In **12**, three bridging ligands are present: a μ_3-Se atom capping the $RuCo_2$ triangle and, on the two Ru−Co edges, a μ_2-CO group and a μ_2-dppm ligand. Together with **2** and **16**, **12** is one of the first examples of trinuclear bimetallic selenido clusters substituted by a phosphine ligand. The two phosphorus atoms of the ligand in **12** are not chemically equivalent, as evidenced by the $^{31}P\{^{1}H\}$ NMR spectroscopy. The phosphorus atom bound to the ruthenium atom presents a doublet at δ 39.6 with a coupling constant ^{3}J(P,P) of 46 Hz; the other one, bound to the quadrupolar ^{59}Co atom, shows a broad signal at δ 43.9 (coupling constant not resolved). Compound **13** probably derives from **12** by further substitution of two carbonyl groups with another dppm ligand. Evidence comes both from the TLC behavior and from the mass spectral data; compound **13** migrates slowly on the TLC plate, remaining far behind compound **12**, which is consistent with the presence of a second phosphine group. The NICI mass spectrum shows two peaks with *m*/*z* ratios of 1206 and 1178 which correspond to the species $[RuCo_2(\mu_3\text{-}Se)(CO)_5(\mu\text{-}dppm)_2]^-$ and $[RuCo_2(\mu_3\text{-}Se)(CO)_4(\mu\text{-}dppm)_2]^-$, respectively; the main peak (*m*/*z* 850) is relative to the fragment $[RuCo_2(\mu_3\text{-}Se)(CO)_6(\mu\text{-}dppm)]^-$, while the other signals derive from this species for loss of carbonyl groups.

2. Formation of Hydrido, Phosphine-Substituted Clusters. Compounds $[HRuCo_3(CO)_8(\mu\text{-}CO)_3(PPh_3)]$ (**3**), $[HRuCo_3(CO)_8(\mu\text{-}CO)_3(dpth)]$ (**7**), $[HRuCo_3(CO)_8(\mu\text{-}CO)_3(dppyth)]$ (**10**), and $[HFeCo_3(CO)_8(\mu\text{-}CO)_3(PPh_3)]$ (**17**) (Scheme 5) derive from the starting reagent via substitution of one carbonyl group by a phosphine ligand and are thus of type II (see Scheme 3).

Scheme 5



1 P-N = μ-dppy, M = Ru

3 L = tpp, M = Ru
7 L = dpth, M = Ru
10 L = dppyth, M = Ru
17 L = tpp, M = Fe

4 L = tpp, M = Ru

20 L = dppyth, M = Fe

The solid-state structures for **17** and **3** have already been reported in the literature by Hidai et al.[15] and Pakkanen et al.[11] along with their spectroscopic data in solution. For all compounds, the colors, IR ν(CO) band patterns in the carbonyl region, and the NMR hydride chemical shifts are all in good agreement with those found in the literature.[9] Also, the elution order during chromatographic separation is in agreement with monosubstitution by the phosphines. The absence of the ^{31}P NMR signal in solution and the color of the compounds suggest coordination of the phosphines to cobalt atoms. The NICI mass spectrum of **7** shows the peak $[HRuCo_3(CO)_{10}(dpth)]^-$; also in **10** it is possible to detect the peak corresponding to the loss of one carbonyl group $[HRuCo_3(CO)_{10}(dppyth)]^-$; in both cases, other signals derived by further fragmentation are present.

In compounds $[HRuCo_3(CO)_7(\mu\text{-}CO)_3(PPh_3)_2]$ (**4**) and $[HFeCo_3(CO)_7(\mu\text{-}CO)_3\ (dppyth)_2]$ (**20**), two carbonyl groups have been substituted by two monodentate phosphines (Schemes 3, 5); they have been identified by comparison of their spectroscopic data (IR, ^{1}H NMR, color, elution order on TLC) with those found in the literature.[11,15] In particular, compound **4** is supposed to be the Ru, Co isomer on the basis of the sharp hydride signal in the ^{1}H NMR spectrum at $\delta = -17.8$.

Compound **1**, whose structure has been determined by X-ray diffraction methods, is a tetranuclear $RuCo_3$ carbonyl cluster of type II in which two carbonyl groups have been substituted by the dppy ligand which bridges two cobalt metals via P and N atoms. Perhaps because of the steric hindrance resulting from this coordination, the hydride has migrated from its original μ_3-capping position to the Ru−Co edge. The ^{1}H NMR spectrum shows a broad signal at δ 9.25 which corresponds to the H_α of the pyridine group;

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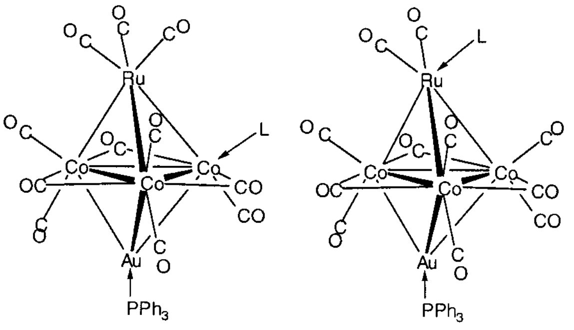
(34) (a) Mathur, P.; Sekar, P.; Satyanarayana, C. V. V.; Mahon, M. F. *Organometallics* **1995**, *14*, 2115. (b) Mathur, P.; Sekar, P. *Chem. Commun.* **1996**, 727. (c) Mathur, P.; Sekar, P.; Satyanarayana, C. V. V.; Mahon, M. F *J. Chem. Soc., Dalton Trans.* **1996**, 2173. (d) Mathur, P.; Sekar, P.; Satyanarayana, C. V. V.; Mahon, M. F. *J. Organomet. Chem.* **1996**, *522*, 291. (e) Mathur, P.; Sekar, P.; Rheingold, A. L.; Liable-Sands, L. M. *J. Chem. Soc., Dalton Trans.* **1997**, 2949. (f) Harvey, P. D.; Eichhöfr, A.; Fenske, D. *J. Chem. Soc., Dalton Trans.* **1998**, 3901. (g) Mathur, P.; Ghosh, S.; Sarkar, A.; Rheingold, A. L.; Guzei, I. A. *Tetrahedron*, **2000**, *56*, 4995. (h) Mathur, P.; Payra, P.; Ghose, S.; Hossain, M. M.; Satyanarayana, C. V. V.; Chicote, F. O.; Chadha, R. K. *J. Organomet. Chem.* **2000**, *606*, 176. (i) Mathur, P.; Ahmed, M. O.; Dash, A. K.; Kaldis, J. H. *Organometallics* **2000**, *19*, 941. (l) Mathur, P.; Mukhopadhyay, S.; Ahmed, M. O.; Lahiri, G. K.; Chakraborty, S.; Walawalkar, M. G. *Organometallics* **2000**, *19*, 5787.

(35) (a) Richter, F.; Vahrenkamp, H. *Chem. Ber.* **1982**, *115*, 3224. (b) Richter, F.; Vahrenkamp, H. *Chem. Ber.* **1982**, *115*, 3243. (c) Bantell, H.; Bernhardt, W.; Powell, A. K.; Vahrenkamp, H. *Chem. Ber.* **1988**, *121*, 1247. (d) Wang, X.-L.; Suo, Q.-L.; Wang, Y.-B.; Lu, Q.-W.; Sun, J. *Jiegou Huaxue* **1998**, 17, 97.

(36) Edwards, A. J.; Mack, S. R.; Mays, M. J.; Mo, C.-Y.; Raithby, P. R.; Rennie, M.-A. *J. Organomet. Chem.* **1996**, *519*, 243.

Scheme 6



14 L = dppy, M = Ru

15a L = tpp, M = Ru

15b L = tpp, M = Ru

coordination of the nitrogen atom shifts the signal to higher fields with respect to the free phosphine for which this hydrogen resonates at δ 8.71. The hydride signal gives a doublet at δ -20.40 owing to the coupling with the phosphorus atom (^2J(H,P) = 15 Hz); this chemical shift value is in good agreement with those found in $HRuCo_3(CO)_9$-[$HC(PPh_3)_2$] in which the hydride is bridging the Ru$-$Co edge.[14] The $^{31}P\{^1H\}$ NMR shows a rather broad signal at δ 34.9 for the phosphorus atom coordinated to the metal, the broadening being caused by the ^{59}Co nucleus.

3. Compounds Obtained from the Anionic Cluster [NEt_4][$RuCo_3(CO)_{12}$]. The M$-$CO bonds for these complexes are stronger compared to those in the corresponding neutral derivatives, and thus, the carbonyl substitution by a donor ligand is relatively more difficult.[9] As it is impossible to separate by TLC the products of the reactions between these anionic species and the phosphine selenides, a preliminary general procedure was used consisting of the derivatization with [$AuCl(PPh_3)$] in the presence of $TlPF_6$. The isolobal analogy between H^+ and $Au(PPh_3)^+$ allows the formation of neutral species with a [$Ph_3PAuMCo_3$] pentanuclear core, in which the Au atom is bound to the three cobalt atoms.[37]

3.1. Reaction of [NEt_4][$RuCo_3(CO)_{12}$] with dppySe. To separate the product by TLC, the original reaction mixture was first treated with [$AuCl(PPh_3)$] and $TlPF_6$. This transforms the anionic products into neutral ones by substituting NEt_4^+ with the $Au(PPh_3)^+$ fragment; this fragment (isolobal with H^+) generally coordinates in a μ_3 mode to the cobalt triangle to give a triangular bipyramidal $AuCo_3Ru$ core (Scheme 6).[37,38]

Thus, the reaction between [NEt_4][$RuCo_3(CO)_{12}$] and dppySe followed by the addition of [$AuCl(PPh_3)$] led to one main product, the pentanuclear cluster [$(Ph_3P)AuRuCo_3$-$(CO)_8(\mu$-$CO)_3$(dppy)] (**14**) (Scheme 6). It results from the substitution of one carbonyl group of the ruthenium atom by deselenized phosphine, however without selenium transfer to the cluster. Its IR pattern of the carbonyl region is in good agreement with the data found in the literature for similar compounds.[9] The $^{31}P\{^1H\}$ NMR spectrum presents two singlets at δ 37.4 and δ 52.6, attributable to P on Co and to P on Au, respectively. The NICI mass spectrum shows that the $AuPPh_3$ group is easily lost, the main fragments being [$RuCo_3(CO)_{10}$(dppy)]$^-$, [$RuCo_3(CO)_6$(dppy)]$^-$, [$RuCo_3$-$(CO)_{11}$]$^-$, [$RuCo_3(CO)_{10}$]$^-$, and [$RuCo_3(CO)_9$]$^-$, obtained by loss of carbonyl groups and of the phosphine ligand.

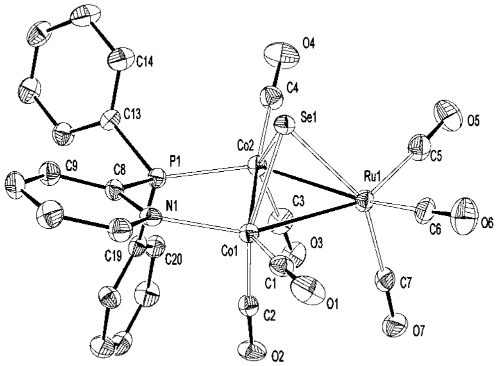


Figure 1. View of the molecular structure of **2** together with the atomic numbering system. Thermal ellipsoids are drawn at 30% probability level.

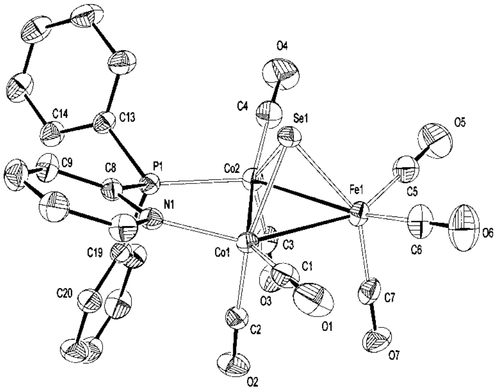


Figure 2. View of the molecular structure of **16** together with the atomic numbering system. Thermal ellipsoids are drawn at 30% probability level.

3.2. Reaction of [NEt_4][$RuCo_3(CO)_{12}$] with tppSe. The reaction between [NEt_4][$RuCo_3(CO)_{12}$] and tppSe followed by treatment with [$AuCl(PPh_3)$] and $TlPF_6$ gave two pentanuclear isomeric clusters [$Ph_3PAuRuCo_3(CO)_8(\mu$-$CO)_3$-(PPh_3)] (**15a** and **15b**) whose structures were identified by their spectroscopic data (Scheme 6). They result from the substitution by the phosphine ligand of one carbonyl group on a cobalt (**15a**) or on a ruthenium (**15b**) atom in the bipyramidal core $AuCo_3Ru$. Their IR patterns in the carbonyl region are different, and both are in good agreement with those found in the literature for similar compounds;[9] in each case, the $^{31}P\{^1H\}$ NMR spectra show two singlets, one due to the phosphorus atom bound to cobalt (δ 37.4, broad) or ruthenium (δ 36.4) and the other due to the phosphorus atom of the $AuPPh_3$ moiety (δ 52.7 **15a**, 52.9 **15b**).

4. Crystal Structures of Selenido Clusters 2, 16, and 12. ORTEP views of the molecular structure of **2** and **16** are given in Figure 1 and Figure 2, respectively; selected bond distances and angles are given in Tables 2 and 3.

The MCo_2Se (M = Fe, Ru) *core* of the two isostructural clusters can be described as a triangular pyramid with the selenium atom at the vertex; the bidentate phosphine asym-

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[37] Braunstein, P.; Rosé, J.; Dusausoy, Y.; Mangeot, J. P. *C. R. Acad. Sci., Ser. II* **1982**, *294*, 967.

[38] Kakkonen, H. J.; Ahlgrèn, M.; Pakkanen, T. A.; Pursiainen, J. *Acta Crystallogr.* **1994**, *C50*, 528.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2**

Ru(1)−Se(1)	2.430(1)	Ru(1)−C(6)	1.888(8)
Ru(1)−Co(1)	2.622(2)	Ru(1)−C(5)	1.92(1)
Ru(1)−Co(2)	2.637(2)	Ru(1)−C(7)	1.93(1)
Co(1)−Co(2)	2.530(2)	Co(1)−N(1)	2.027(6)
Co(1)−Se(1)	2.313(2)	Co(2)−C(4)	1.76(1)
Co(2)−Se(1)	2.306(2)	Co(2)−C(3)	1.76(1)
Co(1)−C(1)	1.739(8)	Co(2)−P(1)	2.192(2)
Co(1)−C(2)	1.780(8)		
Co(1)−Ru(1)−Co(2)	57.52(5)	Se(1)−Co(1)−Ru(1)	58.60(4)
Co(2)−Co(1)−Ru(1)	61.54(5)	Se(1)−Co(2)−Co(1)	56.92(5)
Co(1)−Co(2)−Ru(1)	60.94(4)	Se(1)−Co(2)−Ru(1)	58.44(4)
Co(2)−Se(1)−Co(1)	66.43(6)	N(1)−Co(1)−Se(1)	98.3(2)
Co(2)−Se(1)−Ru(1)	67.61(4)	N(1)−Co(1)−Co(2)	97.8(2)
Co(1)−Se(1)−Ru(1)	67.06(4)	N(1)−Co(1)−Ru(1)	154.5(2)
Se(1)−Co(1)−Co(2)	56.65(4)	P(1)−Co(2)−Se(1)	107.91(8)
Se(1)−Ru(1)−Co(1)	54.34(3)	P(1)−Co(2)−Co(1)	83.81(7)
Se(1)−Ru(1)−Co(2)	53.95(3)	P(1)−Co(2)−Ru(1)	144.37(7)

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **16**

Fe(1)−Se(1)	2.296(7)	Fe(1)−C(6)	1.778(4)
Fe(1)−Co(1)	2.557(1)	Fe(1)−C(5)	1.776(4)
Fe(1)−Co(2)	2.566(1)	Fe(1)−C(7)	1.791(4)
Co(1)−Co(2)	2.516(1)	Co(1)−N(1)	2.024(2)
Co(1)−Se(1)	2.300(1)	Co(2)−C(4)	1.778(4)
Co(2)−Se(1)	2.291(1)	Co(2)−C(3)	1.783(4)
Co(1)−C(1)	1.769(3)	Co(2)−P(1)	2.205(2)
Co(1)−C(2)	1.791(3)		
Co(1)−Fe(1)−Co(2)	58.82(4)	Se(1)−Co(1)−Fe(1)	56.13(3)
Co(2)−Co(1)−Fe(1)	60.77(4)	Se(1)−Co(2)−Fe(1)	56.08(3)
Co(1)−Co(2)−Fe(1)	60.41(3)	Se(1)−Co(2)−Co(1)	56.93(3)
Co(2)−Se(1)−Co(1)	66.46(5)	N(1)−Co(1)−Se(1)	97.71(8)
Co(2)−Se(1)−Fe(1)	68.03(3)	N(1)−Co(1)−Co(2)	98.49(7)
Fe(1)−Se(1)−Co(1)	67.61(3)	N(1)−Co(1)−Fe(1)	152.24(7)
Se(1)−Co(1)−Co(2)	56.61(3)	P(1)−Co(2)−Se(1)	107.10(6)
Se(1)−Fe(1)−Co(1)	56.26(2)	P(1)−Co(2)−Co(1)	83.96(4)
Se(1)−Fe(1)−Co(2)	55.89(2)	P(1)−Co(2)−Fe(1)	144.34(4)

metrically bridges the two cobalt atoms of the base through the phosphorus and the nitrogen atoms. The coordination around the metals is completed by seven terminal carbonyl groups (three in axial and four in equatorial positions). In **2**, the two Se−Co bond distances are nearly equal [2.313(2) and 2.306(2) Å], and the Se(1)−Ru(1) is 2.430(1) Å; in **16**, the Co(1)−Se(1), Co(2)−Se(1), and Fe(1)−Se(1) bond distances are 2.300(1), 2.291(1), and 2.296(1) Å, respectively, in good agreement with those found by Dahl et al.[39] for the unsubstituted complex [$FeCo_2(\mu_3\text{-}Se)(CO)_9$]. The P(1)−Co(2) and N(1)−Co(1) bond distances are 2.192(2) and 2.027(6) Å in compound **2** and 2.205(2) and 2.024(2) Å in **16**. The bidentate bridging phosphine forms a five-membered ring which is fused with the metal triangle on one side and with the pyridyl ring on the other (the dihedral angle between the metal plane and the mean plane passing through the pyridyl moiety and the phosphorus is 24.7(1) (**2**) and 27.3(1)° (**16**)). The chelation ring presents an envelope conformation with the Co(2) atom deviating 0.76(1) (**2**) and 0.77(1) (**16**) Å from the mean plane passing through the other four atoms of the ring. The Co(1)−Co(2) bond distances, 2.516(1) and 2.530(2) Å for **16** and **2**, respectively, are shorter than those of 2.583(1) and 2.580(1) Å found by Dahl et al.[39] for the unsubstituted complex [$FeCo_2(\mu_3\text{-}Se)(CO)_9$].

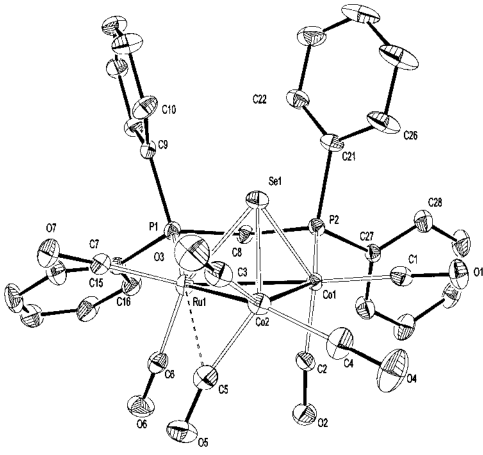

Figure 3. View of the molecular structure of **12** together with the atomic numbering system. Thermal ellipsoids are drawn at 30% probability level.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for 12

Co(1)−Co(2)	2.569(1)	Co(2)−C(4)	1.753(7)
Ru(1)−Co(1)	2.643(1)	Co(2)−C(3)	1.799(7)
Ru(1)−Co(2)	2.643(1)	Co(2)−C(5)	1.816(7)
Se(1)−Co(2)	2.310(1)	Ru(1)−C(7)	1.876(5)
Se(1)−Co(1)	2.309(1)	Ru(1)−C(6)	1.911(6)
Se(1)−Ru(1)	2.465(1)	Ru(1)−P(1)	2.311(1)
Co(1)−P(2)	2.210(2)	Ru(1)−C(5)	2.530(6)
Co(1)−C(1)	1.786(6)	P(1)−C(8)	1.843(5)
Co(1)−C(2)	1.756(6)	P(2)−C(8)	1.831(5)
Co(2)−Se(1)−Co(1)	67.56(3)	Se(1)−Co(2)−Ru(1)	59.24(2)
Co(2)−Se(1)−Ru(1)	67.12(3)	Co(1)−Co(2)−Ru(1)	60.92(3)
Co(1)−Se(1)−Ru(1)	67.12(3)	P(1)−Ru(1)−Co(2)	147.38(4)
Se(1)−Ru(1)−Co(1)	53.62(2)	P(2)−Co(1)−Co(2)	148.91(5)
Se(1)−Ru(1)−Co(2)	53.64(2)	C(8)−P(1)−Ru(1)	109.3(2)
Co(1)−Ru(1)−Co(2)	58.14(3)	C(8)−P(2)−Co(1)	112.1(2)
Se(1)−Co(1)−Co(2)	56.24(3)	O(5)−C(5)−Co(2)	160.0(5)
Se(1)−Co(1)−Ru(1)	59.26(2)	O(5)−C(5)−Ru(1)	127.2(5)
Co(2)−Co(1)−Ru(1)	60.94(2)	P(2)−C(8)−P(1)	114.1(3)
Se(1)−Co(2)−Co(1)	56.21(3)	Se(1)−Co(2)−Ru(1)	59.24(2)

The molecular structure of cluster **12** is shown in Figure 3; selected bond distances and angles are given in Table 4. The *core* of the cluster, as in **2**, consists of a $RuCo_2$ triangle capped by a μ_3-Se unit. The two Ru−Co distances are equal [2.643(1) Å] and longer than those found in compound **2**. While in compound **2** the bidentate phosphine bridges two cobalt atoms, in this case, the dppm ligand prefers the Ru(1)−Co(1) edge, even if the Co(1)−Co(2) distance of 2.569(1) Å would allow an undistorted coordination of the ligand.[40] This is probably due to the different hard−soft properties of the nitrogen and the phosphorus atoms which prefer cobalt and ruthenium, respectively. The bidentate bridging phosphine forms a five-membered ring which presents an envelope conformation with the C(8) deviating 0.592(5) Å from the mean plane passing through the other four atoms of the ring. Of seven carbonyls, six are terminal, and one is semibridging, C(5)−O(5), [C(5)−Co(2) 1.82(1) and C(5)−Ru(1) 2.53(1) Å, Co(2)−C(5)−O(5) 160.0(5)°].

5. Crystal Structure of Hydrido Cluster 1. An ORTEP view of the molecular structure of cluster **1** is given in Figure 4. Selected bond distances and angles are given in Table 5.

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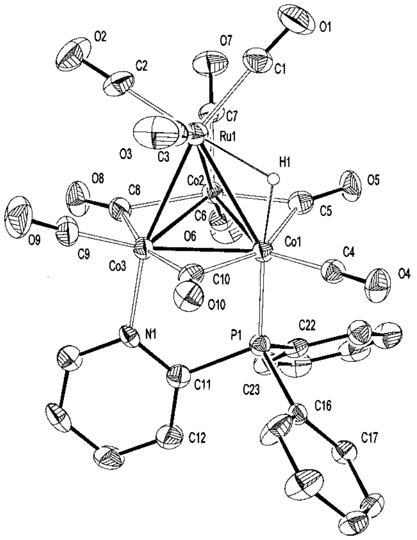

Figure 4. View of the molecular structure of **1** together with the atomic numbering system. Thermal ellipsoids are drawn at 30% probability level.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **1**

Ru(1)−C(3)	1.904(7)	Co(2)−C(7)	1.743(6)
Ru(1)−C(1)	1.933(6)	Co(2)−C(6)	1.769(7)
Ru(1)−C(2)	1.926(7)	Co(2)−C(5)	1.922(6)
Ru(1)−Co(3)	2.628(2)	Co(2)−C(8)	1.986(6)
Ru(1)−Co(2)	2.656(1)	Co(2)−Co(3)	2.520(1)
Ru(1)−Co(1)	2.769(2)	Co(3)−C(9)	1.763(6)
Co(1)−C(4)	1.767(6)	Co(3)−C(10)	1.871(6)
Co(1)−C(5)	1.963(6)	Co(3)−C(8)	1.917(6)
Co(1)−C(10)	1.986(6)	Co(3)−N(1)	2.009(4)
Co(1)−P(1)	2.177(2)	Ru(1)−H(1)	1.86(5)
Co(1)−Co(3)	2.441(1)	Co(1)−H(1)	1.71(4)
Co(1)−Co(2)	2.519(1)		
Co(3)−Ru(1)−Co(2)	56.96(4)	P(1)−Co(1)−Co(3)	88.05(5)
Co(3)−Ru(1)−Co(1)	53.71(5)	N(1)−Co(3)−Co(1)	99.4(1)
Co(2)−Ru(1)−Co(1)	55.29(4)	C(11)−P(1)−Co(1)	114.0(2)
Co(3)−Co(1)−Co(2)	61.04(3)	C(11)−N(1)−Co(3)	122.2(4)
Co(1)−Co(2)−Co(3)	57.96(4)	O(5)−C(5)−Co(2)	139.8(5)
Co(3)−Co(1)−Ru(1)	60.20(4)	O(5)−C(5)−Co(1)	139.2(5)
Co(2)−Co(1)−Ru(1)	60.08(3)	O(8)−C(8)−Co(3)	142.9(5)
Co(1)−Co(2)−Ru(1)	64.63(4)	O(8)−C(8)−Co(2)	136.7(5)
Co(3)−Co(2)−Ru(1)	60.97(4)	O(10)−C(10)−Co(3)	146.2(5)
Co(1)−Co(3)−Co(2)	61.00(4)	O(10)−C(10)−Co(1)	135.2(5)
Co(1)−Co(3)−Ru(1)	66.09(4)	N(1)−C(11)−P(1)	115.7(4)
Co(2)−Co(3)−Ru(1)	62.07(3)	Ru(1)−H(1)−Co(1)	101(2)

It consists of a tetranuclear $RuCo_3$ carbonyl cluster in which two carbonyl groups have been substituted by the bidentate dppy ligand. The phosphine bridges the Co(1)−Co(3) edge through the P(1) and N(1) atoms [P(1)−Co(1) 2.177(2) Å, N(1)−Co(3) 2.009(4) Å]. This metal−metal bond is shorter [2.441(1) Å] than the other two [2.519(1) for Co(1)−Co(2) and 2.520(1) Å for Co(2)−Co(3)]. The bridging dppy forms a five-membered ring which presents an envelope conformation with the Co(1) atom deviating by 0.182(1) Å from the mean plane passing through the other four atoms. The dihedral angle between the planes passing through the cobalt triangle and Co(3)−C(10)−Co(1) is 13.0(2)°. A hydride ligand bridges the Ru(1)−Co(1) edge [Ru(1)−H(1) 1.86(5), Co(1)−H(1) 1.71(4) Å], while in the precursor it was μ_3-bridging the cobalt triangle. This shift is probably due to the steric hindrance with the phosphine ligand bridging the Co(1)−Co(3) edge. The hydride influences the Ru−Co bond distances: in fact, the Ru(1)−Co(1) bond distance is 2.769(2) Å, longer then the other two [2.655(1) Å for Ru(1)−Co(2) and 2.628(2) Å for Ru(1)−Co(3)].[14] Moreover, the Ru(1)−Co(1)−C(4) angle, 118.8(2)°, in good agreement with that found in $[HRuCo_3(CO)_9\{HC(PPh_2)_3\}]$ by Kakkonen et al.,[14] is much larger than the Ru(1)−Co(2)−C(7) and Ru(1)−Co(3)−C(9) ones [73.5(2) and 92.9(2)°, respectively].

Conclusion

With the aim of obtaining new selenido-carbonyl bimetallic clusters, we have found that the reactions of $[HMCo_3(CO)_{12}]$ and $[Et_4N][MCo_3(CO)_{12}]$ (M = Fe, Ru) with phosphine selenides such as Ph_3PSe, $Ph_2P(Se)CH_2PPh_2$, $Ph_2(2\text{-}C_5H_4N)PSe$, $Ph_2(2\text{-}C_4H_3S)PSe$, and $Ph_2\{(2\text{-}C_5H_4N)(2\text{-}C_4H_2S)\}PSe$ follow different patterns. The reactions of the hydrido clusters give either clusters with a $MCo_2(\mu_3\text{-Se})$ core (M = Fe, Ru) or tetranuclear clusters of the type $[HMCo_3(CO)_{12-x}L_y]$ resulting from substitution of axial, Co-bound carbonyl groups by the deselenized phosphine ligand. The crystal structures of $[HRuCo_3(CO)_7(\mu\text{-CO})_3(\mu\text{-dppy})]$ (**1**), $[MCo_2(\mu_3\text{-Se})(CO)_7(\mu\text{-dppy})]$ (M = Fe (**16**) or Ru (**2**)), and $[RuCo_2(\mu_3\text{-Se})(CO)_7(\mu\text{-dppm})]$ (**12**) are reported [dppy = $Ph_2(2\text{-}C_5H_4N)P$, dppm = $Ph_2PCH_2PPh_2$]. Clusters **2**, **12**, and **16** are the first examples of trinuclear bimetallic selenido clusters substituted by phosphines. Their *cores* consist of metal triangles capped by a μ_3-selenium atom with the bidentate ligand bridging two metals in equatorial positions. In contrast to the reactions of the hydrido clusters, those with the anionic clusters $[MCo_3(CO)_{12}]^-$ do not lead to Se transfer from phosphorus to the cluster but only to CO substitution by the deselenized phosphine. It therefore appears that reduction in cluster nuclearity from 4 to 3, which always involves elimination of a cobalt-containing fragment, is favored in the case where a hydrido ligand is present in the precursor. This observation may be related to the easier reductive elimination reactions observed in heterobimetallic hydrido complexes which lead to formation of mononuclear fragments.[41]

Acknowledgment. We are grateful to the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (Cofin 1998 and 2000) and to the CNRS and the Ministère de la Recherche (Paris) for financial support.

Supporting Information Available: Complete listings of atomic positions, bond lengths and angles, anisotropic thermal parameters, hydrogen atom coordinates, data collection, and crystal parameters for all crystallographically characterized complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

IC010824X

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