Polynuclear Rhenium and Manganese Selenido-Carbonyl Complexes − Reversible Square to Butterfly Conversion of the Re_4Se_2 Core by CO Loss in $[Re_4(\mu_3\text{-}Se)_2(CO)_{16}(PPh_3)_2]$, and the Crystal Structure of $[Mn_2(\mu_2\text{-}Se_2)(CO)_5(PPh_3)_2]$

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Keywords: Cluster compounds / Manganese / Rhenium / Selenium

The reaction of Ph_3PSe with $[Mn_2(CO)_{10}]$ leads to the formation of $[Mn_4(\mu_3\text{-}Se)_2(\mu\text{-}CO)(CO)_{14}(PPh_3)_2]$, which contains a butterfly "Mn_2Se_2 core", along with traces of $[Mn_2(\mu_2\text{-}Se_2)(CO)_5(PPh_3)_2]$ (**1**), which contains a tetrahedral Mn_2Se_2 core. The reaction of Ph_3PSe with $[Re_2(CO)_8(NCMe)_2]$ affords two new complexes, $[Re_4(\mu_3\text{-}Se)_2(CO)_{16}(PPh_3)_2]$ (**2**) and $[Re_4(\mu_3\text{-}Se)_2(\mu\text{-}CO)(CO)_{14}(PPh_3)_2]$ (**3**). Their molecular structures, determined by X-ray diffraction methods, exhibit a nearly square-planar Re_2Se_2 and a butterfly Re_2Se_2 core, respectively. These air-stable tetrarhenium selenido-carbonyl species display a reversible loss/addition of a CO molecule, which is accompanied by the formation/cleavage of a Re–Re bond and the consequent rearrangement of the Re_2Se_2 core, from square to butterfly and vice versa.

Introduction

The chemistry of polynuclear transition-metal chalcogenide complexes is a continuously expanding research area, as pointed out in recent reviews.[1] Apart from their fundamental significance as a class of complexes with peculiar chemical and structural properties, the growing interest in these species stems from their potential applications as catalysts, electrocatalysts and precursors for semiconductors.[2] The presence of chalcogenide ligands often appears decisive in facilitating cluster-growth reactions,[3] and in this regard sulfur atoms have been shown to be highly effective,[4] as are selenium and tellurium atoms, although these have been much less studied.[2a,5,6]In this context, systematic investigations carried out by our group on the reactivity of tertiary phosphane and diphosphane selenides towards $[M_3(CO)_{12}]$ (M = Fe or Ru) have shown that these reactions provide simple, sometimes selective, synthetic routes to phosphane-substituted, selenido-carbonyl metal clusters.[6]

In recent years Adams and co-workers have described the reaction between thiirane and $[Mn_2(CO)_9(MeCN)]$, which gives the simplest sulfido-carbonyl manganese cluster $[Mn_2S_2(CO)_7]$ whose reactivity towards different metal fragments has been widely investigated.[7a,7c−7g] Moreover, the synthesis of the dimetallic selenido-carbonyl Mo−Mn complex $[CpMoMn(CO)_5(\mu\text{-}S_2)]$ has been achieved by treating $[CpMnMo(CO)_8]$ with elemental selenium.[7b,7h,7i]

Manganese clusters and complexes bearing selenide ligands have been scarcely investigated.[7a,7b] In particular, in the syntheses reported in the literature polyselenide anions,[8] diorganyl diselenides[9] and elemental selenium[10] have been used as starting materials.

Recently,[11] we have reacted different phosphane selenides with three manganese carbonyl complexes, namely $[Cp'Mn(CO)_2(THF)]$, $[CpMn(CO)_2(THF)]$ ($Cp = \eta^5\text{-}C_5H_5$, $Cp' = \eta^5\text{-}C_5H_4Me$, THF = tetrahydrofuran) and $[Mn_2(CO)_8(NCMe)_2]$ in order to produce new phosphane-substituted selenido-carbonyl manganese derivatives. In particular, the reactions of tertiary phosphanes R_3PSe with $[Mn_2(CO)_8(NCMe)_2]$ in an equimolar ratio resulted in the formation of the bis-selenido tetramanganese clusters $[Mn_4(\mu_3\text{-}Se)_2(\mu\text{-}CO)(CO)_{14}(PR_3)_2]$, the structures of two of which, $[Mn_4(\mu_3\text{-}Se)_2(\mu\text{-}CO)(CO)_{14}(PPh_3)_2]$[7a] and $[Mn_4(\mu_3\text{-}Se)_2(\mu\text{-}CO)(CO)_{14}(PMePh_2)_2]$,[11] having been determined by X-ray diffraction methods.

In this paper, the synthesis and crystal-structure characterization of the first tetrahedral Mn_2Se_2 carbonyl complex, $[Mn_2(\mu_2\text{-}Se_2)(CO)_5(PPh_3)_2]$, obtained by reacting two equivalents of phosphane selenide with $[Mn_2(CO)_{10}]$ in the presence of Me_3NO is described. Moreover, the reaction of Ph_3PSe with the analogous Re carbonyl derivative $[Re_2(CO)_8(NCMe)_2]$ yielded two new tetrarhenium selenido-carbonyl compounds, namely $[Re_4(\mu_3\text{-}Se)_2(CO)_{16}(PPh_3)_2]$ and $[Re_4(\mu_3\text{-}Se)_2(\mu\text{-}CO)(CO)_{14}(PPh_3)_2]$, whose crystal structures were determined by X-ray diffraction methods. These com-

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DOI: 10.1002/ejic.200400090

pounds show interesting reversible loss/addition of a CO molecule together with the formation/cleavage of a Re−Re bond and the consequent rearrangement of the Re_4Se_2 core.

Results and Discussion

Reaction of $Mn_2(CO)_{10}$ with Ph_3PSe; Crystal Structure of $[Mn_2(\mu_2\text{-}Se_2)(CO)_5(PPh_3)_2]$ (1)

The availability of sulfur-containing starting compounds such as thiirane allows for the efficient synthesis of the simplest tetrahedral Mn_2S_2 complex $[Mn_2(\mu_2\text{-}S_2)(CO)_7]$.[7c] However, the absence of analogous selenium compounds does not permit the easy synthesis of compounds containing an $Mn_2(\mu_2\text{-}Se_2)$ core. As has already been described,[11] the reaction of equimolar amounts of $[Mn_2(CO)_8(CH_3CN)_2]$ and Ph_2MePSe at 50 °C gives $[Mn_4(\mu_3\text{-}Se)_2(\mu\text{-}CO)(CO)_{14}(PMePh_2)_2]$ as the unique product (80% yield). The same compound is also obtained when $Mn_2(CO)_{10}$ is treated with Ph_3PSe in a 1:2 molar ratio and in the presence of Me_3NO. In this case, however, the yield of the $[Mn_4(\mu_3\text{-}Se)_2(\mu\text{-}CO)(CO)_{14}(PMePh_2)_2]$ cluster decreases to 70% while another complex, namely $[Mn_2(\mu_2\text{-}Se_2)(CO)_5(PPh_3)_2]$ (**1**), is also formed. Although only traces of compound **1** were isolated, suitable crystals for X-ray analysis were obtained.

The $^{31}P\{^1H\}$ NMR spectrum of **1** recorded at room temperature shows a broad peak at $\delta = 13.6$ ppm, indicating the equivalence of the two phosphane ligands in solution. In addition, in the carbonyl region of the IR spectrum recorded in the solid state, a band at 1789 cm^{-1} is observed and attributed to a bridging carbonyl group. An ORTEP view of compound **1** is shown in Figure 1, together with the atom numbering scheme; selected bond lengths and angles are listed in Table 1.

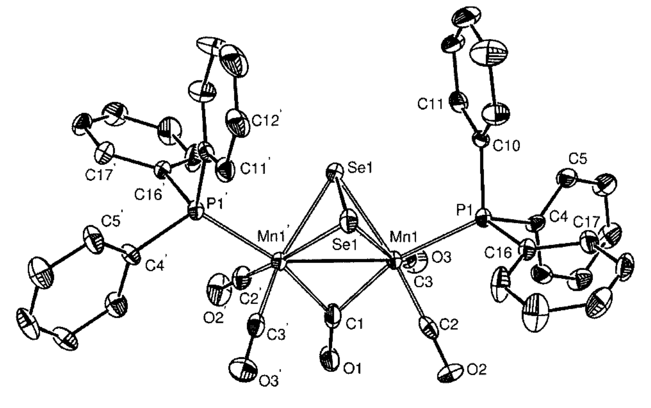


Figure 1. View (ORTEP, 30% probability level) of the molecular structure of **1** with the atom numbering scheme.

Table 1. Selected bond lengths (Å) and angles (°) for **1**[a]

Mn(1)−Se(1′)[a]	2.4461(13)	Mn(1)−Se(1)	2.4478(13)
Mn(1)−Mn(1′)	2.702(2)	Se(1)−Se(1′)	2.3105(16)
Mn(1)−P(1)	2.308(2)		
P(1)−Mn(1)−Se(1′)	98.46(7)	P(1)−Mn(1)−Se(1)	92.99(7)
Se(1′)−Mn(1)−Se(1)	56.34(4)	P(1)−Mn(1)−Mn(1′)	147.28(6)
Se(1′)−Mn(1)−Mn(1)	56.52(3)	Se(1)−Mn(1)−Mn(1′)	56.46(3)
Se(1′)−Se(1)−Mn(1)	61.87(3)	Se(1′)−Se(1)−Mn(1)	61.79(4)
Mn(1′)−Se(1)−Mn(1)	67.02(5)		

[a] Symmetry transformations used to generate equivalent atoms: $-x, y, -z + 1/2$.

Complex **1** has a crystallographically imposed C_2 symmetry, with the twofold axis passing through the C1 and O1 atoms and the midpoints of the Mn1−Mn1′ and Se1−Se1′ bonds. The structure of this compound is very similar to that of the phosphane-unsubstituted and -monosubstituted sulfur derivatives $[Mn_2(\mu_2\text{-}S_2)(CO)_{7-n}(PPh_3)_n]$ ($n = 0, 1$)[7c,7d,7f] and the iron diselenide compounds $[Fe_2(\mu_2\text{-}Se_2)(CO)_{6-n}(PPh_3)_n]$ ($n = 1, 2$).[12] The complex possesses a tetrahedral Mn_2Se_2 core in which the Mn−Mn bond length is 2.702(2) Å, slightly longer than that observed in the sulfur derivatives [2.6745(5) and 2.6747(5) Å for $n = 0$ and $n = 1$, respectively]. The Se−Se bond length [2.311(2) Å] is in good agreement with those observed in $[Fe_2(\mu_2\text{-}Se_2)(CO)_{6-n}(PPh_3)_n]$ [2.297(2) and 2.296(1) Å for $n = 1$ and $n = 2$, respectively]. Moreover, each manganese atom is coordinated by two terminal carbonyls and by a posphane molecule [P1−Mn1 = 2.308(2) Å], while a CO group symmetrically bridges the Mn−Mn edge, with an Mn−C1 bond length of 2.01(1) Å.

Reaction of $[Re_2(CO)_8(CH_3CN)_2]$ with Ph_3PSe; Crystal Structures of $[Re_4(\mu_3\text{-}Se)_2(CO)_{16}(PPh_3)_2]$ (2) and $[Re_4(\mu_3\text{-}Se)_2(\mu\text{-}CO)(CO)_{14}(PPh_3)_2]$ (3)

The reaction of $[Re_2(CO)_8(CH_3CN)_2]$ with Ph_3PSe, carried out under the same experimental conditions used for the synthesis of $[Mn_4(\mu_3\text{-}Se)_2(\mu\text{-}CO)(CO)_{14}(PMePh_2)_2]$,[11] led to the formation of two new tetrarhenium diselenide phosphane-substituted carbonyl compounds, namely $[Re_4(\mu_3\text{-}Se)_2(CO)_{16}(PPh_3)_2]$ (**2**) and $[Re_4(\mu_3\text{-}Se)_2(\mu\text{-}CO)(CO)_{14}(PPh_3)_2]$ (**3**), whose structures were determined by X-ray diffraction methods.

ORTEP views of compounds **2** and **3** are shown in Figures 2 and 3, respectively, together with the atom numbering scheme; selected bond lengths and angles are listed in Tables 2 and 3.

Complex **2** displays a nearly planar Re_4Se_2 core [the dihedral angle between the Re1Re2Se1 and Re1Re2Se planes is 21.7° and the non-bonding Re1···Re2 and Se1···Se2 separ-

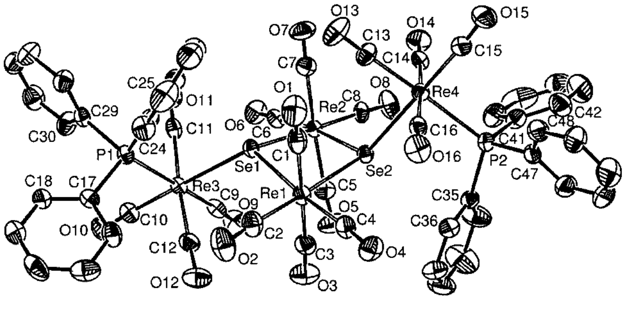


Figure 2. View (ORTEP, 30% probability level) of the molecular structure of **2** with the atom numbering scheme

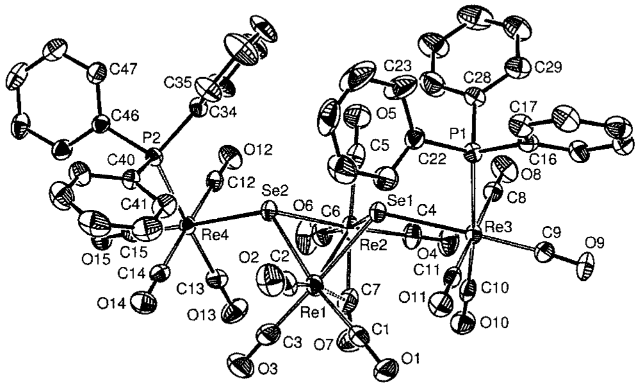


Figure 3. View (ORTEP, 30% probability level) of the molecular structure of **3** with the atom numbering scheme

Table 2. Selected bond lengths (Å) and angles (°) for **2**

Re(1)−Se(1)	2.6610(9)	Re(1)−Se(2)	2.6680(9)
Re(2)−Se(2)	2.6462(9)	Re(2)−Se(1)	2.6675(9)
Re(3)−Se(1)	2.6666(9)	Re(4)−Se(2)	2.6505(9)
Re(4)−P(2)	2.503(2)	Re(3)−P(1)	2.511(2)
Se(1)−Re(1)−Se(2)	79.74(3)	Se(2)−Re(2)−Se(1)	80.02(3)
P(1)−Re(3)−Se(1)	92.27(6)	P(2)−Re(4)−Se(2)	88.00(6)
Re(1)−Se(1)−Re(2)	98.19(3)	Re(1)−Se(1)−Re(3)	119.84(3)
Re(2)−Se(1)−Re(3)	115.35(3)	Re(2)−Se(2)−Re(4)	118.49(3)
Re(2)−Se(2)−Re(1)	98.54(3)	Re(4)−Se(2)−Re(1)	118.32(3)

Table 3. Selected bond lengths (Å) and angles (°) for **3**

Re(1)−Se(1)	2.5701(8)	Re(1)−Se(2)	2.5759(10)
Re(2)−Se(1)	2.6364(9)	Re(1)−Re(2)	2.9978(15)
Re(3)−Se(1)	2.6507(8)	Re(2)−Se(2)	2.6278(8)
Re(4)−Se(2)	2.6445(8)	Re(3)−P(1)	2.5009(17)
Re(1)−C(7)	2.618(8)	Re(4)−P(2)	2.5090(17)
Re(2)−C(7)	2.025(8)	O(7)−C(7)	1.144(10)
Se(1)−Re(1)−Se(2)	75.89(3)	Se(2)−Re(2)−Se(1)	73.90(2)
P(1)−Re(3)−Se(1)	85.31(4)	P(2)−Re(4)−Se(2)	83.44(4)
Re(1)−Se(1)−Re(2)	70.29(3)	Re(1)−Se(1)−Re(3)	117.73(3)
Re(2)−Se(1)−Re(3)	117.73(3)	Re(2)−Se(2)−Re(4)	117.81(3)
Re(1)−Se(2)−Re(2)	70.34(3)	Re(1)−Se(2)−Re(4)	120.09(3)
Se(1)−Re(1)−Re(2)	55.89(2)	Se(1)−Re(2)−Re(1)	53.82(2)
Se(2)−Re(1)−Re(2)	55.64(3)	Se(2)−Re(2)−Re(1)	54.016(16)
Re(2)−C(7)−Re(1)	79.3(3)	Re(2)−C(7)−O(7)	159.5(8)

ations are 4.027(3) and 3.416(1) Å respectively]. Both Re1 and Re2 are bound to four terminal carbonyl groups and to two selenium atoms in a slightly distorted octahedral environment. Each of the two Se atoms is also bound to another Re atom from the $Re(CO)_4(PPh_3)$ group in which the P atom from the phosphane is coordinated to the Re atom [Re3−P1 and Re4−P2 = 2.511(2) and 2.503(2) Å respectively]. The two selenium atoms triply bridge three non-bonded rhenium atoms, with the six Se−Re bond lengths being almost equal [2.646(1)−2.668(1) Å].

The crystal structure of complex **3** compares well with that of the manganese derivative $[Mn_4(\mu_3\text{-}Se)_2(\mu\text{-}CO)(CO)_{14}(PMePh_2)_2]$.[11] In contrast to compound **2**, in which the Re_4Se_2 group contains a nearly planar Re_2Se_2 array, in complex **3** a butterfly Re_2Se_2 core is observed. Thus, the two Re atoms occupy the hinge [Re1−Re2 bond length of 2.998(1) Å] and the two Se atoms the wing sites [the non-bonding Se1···Se2 separation is 3.164(1) Å and the dihedral angle between the Re1Re2Se1 and Re1Re2Se2 wings is 96.1°]. Both Re1 and Re2 atoms are bound to three terminal carbonyl ligands, while a fourth carbonyl group is involved in an incipient bridging interaction with Re1 [the Re(1)−C(7) and Re(2)−C(7) distances are 2.618(8) and 2.025(8) Å, respectively, and the O(7)−C(7)−Re(2) angle is 159.5(8)°]. The Re1−Re2 distance is in agreement with that expected for a metal−metal bond. Only one example of a carbonyl ligand bridging two Re atoms with a longer M−M distance [3.0391(6) Å] has been reported in the literature.[13] The butterfly Re_2Se_2 array is slightly asymmetrical, with the Re1−Se1 and Re1−Se2 bond lengths [2.5701(8) and 2.5759(10) Å, respectively] being shorter than the Re2−Se1 and Re2−Se2 ones [2.6364(9) and 2.6278(8) Å]. Analogously to compound **2**, each of the two Se atoms is also bound to another Re centre of a $Re(CO)_4(PPh_3)$ group in such a way that the Se atoms triply bridge three Re metal centres. In both complexes the atoms Re3, Se1, Se2, Re4 lie in a nearly planar array [maximum deviation for Se1 in **2** and Se2 in **3** of 0.078(2) and 0.0120(7) Å, respectively]. Regarding the position of the $Re(CO)_4PPh_3$ groups, a *trans* configuration is present in **3** with an Re3−Se1−Se2−Re4 torsion of 175.09° and a *cis* configuration in **2** with the corresponding torsion angle of 6.67°; in both cases the phosphane ligands point in the directions which minimize the steric hindrance. In particular, the disposition of the two phosphane molecules could be described as *cis* in compound **2** and *trans* in compound **3**.

Thermal Treatment of 2; Reversible Conversion to 3 by CO Loss

Stirring a solution of **2** in THF at room temperature leads slowly to the formation of **3**, in quantitative yield, by loss of a carbonyl molecule. This process is found to be faster in polar solvents and under moderate heating. This conversion can be monitored by IR spectroscopy. As shown in Figure 4, the IR absorption bands of the terminal CO group display distinct changes in the regions 1980−2040 (typical of a $Re(CO)_4L$ type of structure), and 2050−2100 cm^{-1}. Finally, the formation of an incipient bridging CO group is observed at 1896 cm^{-1}.

The loss of the carbonyl ligand induces a structural modification. A Re−Re bond is formed and the Re_2Se_2 conformation changes from nearly planar to butterfly. It is not possible to determine which carbonyl leaves the Re_2Se_2 core, although the longer C−Re distances involving the axial carbonyls [spanning from 1.98(1) to 2.01(1) Å] than the equatorial ones [spanning from 1.90(1) to 1.93(1) Å] suggest a higher lability. The subsequent rearrangement of the core carbonyls allows the rotation of the $Re(CO)_4P$ moiety around the Re−Se bond and the inversion of the selenium atom.

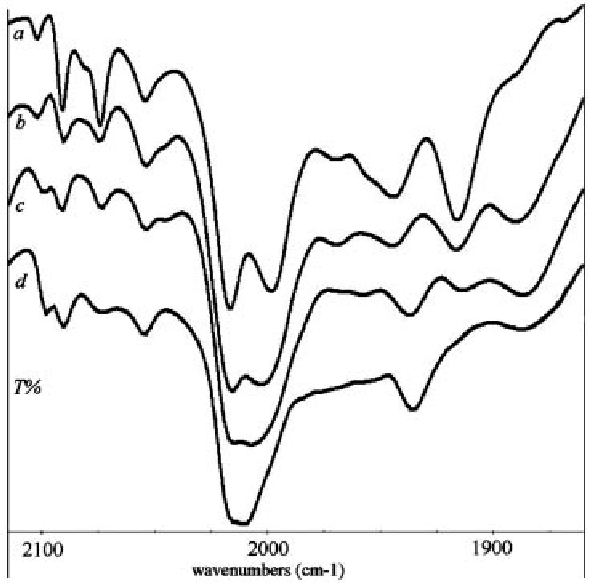
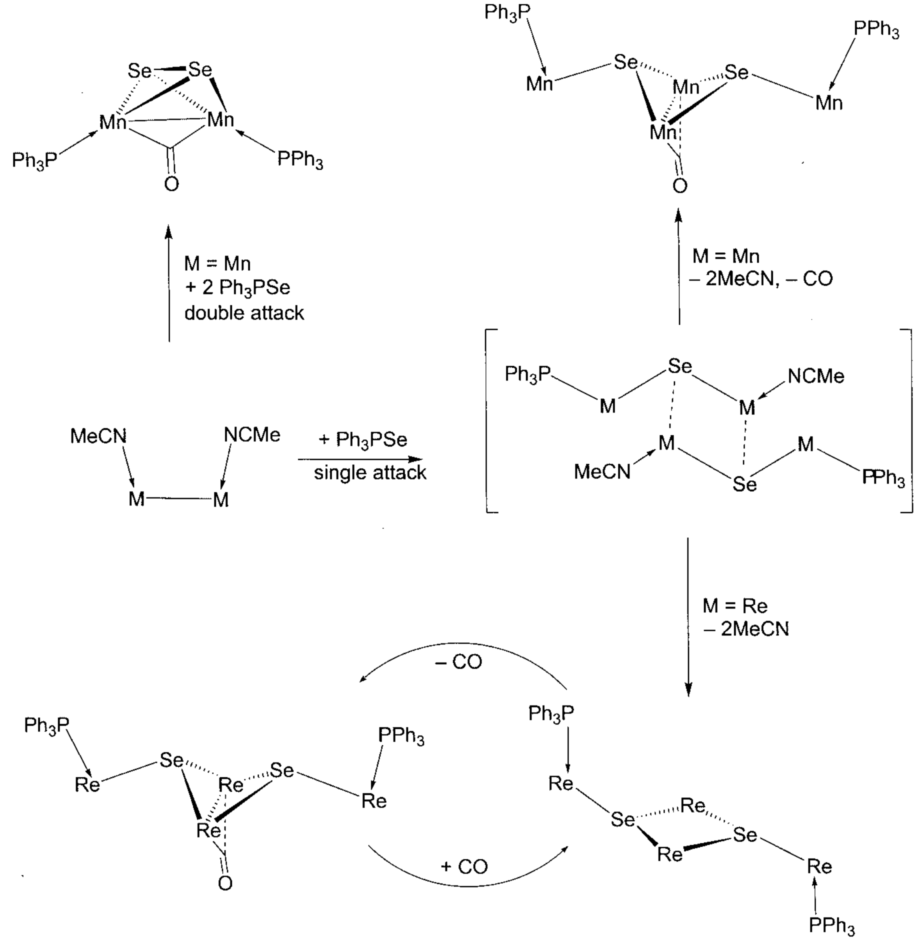


Figure 4. Conversion of **2** into **3** in THF/CH_2Cl_2 (1:1) at 50 °C monitored by FT-IR spectroscopy by sampling the mixture, drying *in vacuo* and redissolving the sample in CH_2Cl_2: (a) pure **2** (t = 0 min); (b) t = 15 min; (c) t = 30 min; (d) pure **3** (t = 45 min)

The process can be reversed by placing **3** under moderate CO pressure, obtaining complex **2** in quantitative yields. There are only a few known examples of reversible CO addition to transition metal compounds, mainly those supported on inorganic matrices or in high-nuclearity clusters.[14a,14b] Some examples of M−M bond cleavage due to reversible CO addition are knwon in the literature,[15] but very few involve two stable species.[16]

As pointed out for the synthesis of $[Mn_4(\mu_3\text{-}Se)_2(\mu\text{-}CO)(CO)_{14}(PMePh_2)_2]$,[11] the reaction mechanism leading to the synthesis of M_4Se_2 core compounds (M = Mn, Re) is believed to proceed via the formation of intermediates of the type $[M_2(\mu\text{-}Se)(CO)_8(PR_3)]$ (PR_3 = tertiary phosphane ligand). This product results from the initial attack of the phosphane selenide on the dinuclear compound and can, in turn, undergo a dimerization, leading to the formation of $[M_4(\mu_3\text{-}Se)_2(CO)_{16}(PR_3)_2]$ complexes. Finally, the loss of a carbonyl ligand from the aforementioned structures can give rise to novel $[M_4(\mu_3\text{-}Se)_2(\mu\text{-}CO)(CO)_{14}(PR_3)_2]$ complexes. In the case of rhenium, both final products were isolated, and seem to have similar thermodynamic stabilities. On the other hand, the manganese compound $[Mn_4(\mu_3\text{-}Se)_2(CO)_{16}(PR_3)_2]$ could not be isolated, probably because



Scheme 1. (terminal carbonyl groups omitted for clarity)

of the greater stability of the related decarbonylated compound (see Scheme 1).

Experimental Section

General Remarks: The starting reagents triphenylphosphane selenide, [$Re_2(CO)_{10}$] and [$Mn_2(CO)_{10}$] were pure commercial products (Aldrich and Fluka) and were used as received. The solvents (C. Erba) were dried and distilled by standard techniques before use. Preparative TLC was carried out on silica (Merck, 60 PF_{254}, 20 × 20 cm glass plates). After the chromatographic workup, the products were extracted with dichloromethane. Purity was checked by elemental analysis and ^{31}P NMR spectroscopy. Elemental (C, H) analyses were performed with a Carlo Erba EA 1108 automated analyzer. IR spectra (CH_2Cl_2 solutions) were recorded on a Nexus FT spectrometer. ^1H (300 MHz) and $^{31}P\{^1H\}$ (161.90 MHz, 85% H_3PO_4 as external reference) NMR spectra ($CDCl_3$ solutions) were recorded on a Bruker AC 300 and a Bruker AMX 400 instrument, respectively.

Synthesis of [$Mn_2(\mu_2\text{-}Se)_2(\mu\text{-}CO)(CO)_4(PPh_3)_2$] (1): Ph_3PSe (350 mg, 1.03 mmol) and Me_3NO (23 mg, 1.03 mmol) were dissolved in toluene (60 mL) and the resulting solution brought to 45 °C. A 15 mL toluene solution of [$Mn_2(CO)_{10}$] (200 mg, 0.52 mmol) was then added dropwise. A progressive colour change from yellow to deep brown was observed. The reaction was stopped after 30 min, the solvents removed in vacuo and the brown solid redissolved in a small amount of dichloromethane. Two products were isolated by preparative TLC (CH_2Cl_2/hexane, 2:1), namely brownish red [$Mn_4(\mu_3\text{-}Se)_2(\mu\text{-}CO)(CO)_{14}(PPh_3)_2$] (yield 70%), identified by comparison of the spectroscopic data with those observed previously,[11] and [$Mn_2(\mu_2\text{-}Se)_2(\mu\text{-}CO)(CO)_4(PPh_3)_2$] (**1**) (yield 5%) as a brown crystalline solid.
1: FTIR (CH_2Cl_2): ν(CO) = 1979 vs, 1944 vs, 1890 vs, 1865 m, 1789 vs. $^{31}P\{^1H\}$ NMR: δ = 13.6 ppm. $C_{41}H_{30}Mn_2O_5P_2Se_2$: calcd. C 52.81, H 3.24; found C 52.84, H 3.25.

Reaction of [$Re_2(CO)_8(MeCN)_2$] with Ph_3PSe: CH_3CN (41 mg, 1 mmol) and Me_3NO (68 mg, 0.61 mmol) were added to a dichloromethane solution of [$Re_2(CO)_{10}$] (200 mg, 0.31 mmol in 40 mL) and the resulting reaction mixture stirred at room temperature for 2 h. Evaporation of the solvent gave [$Re_2(CO)_8(MeCN)_2$] as a yellow solid, which was redissolved in 50 mL of toluene. Ph_3PSe (105 mg, 0.31 mmol) was added and the reaction mixture warmed to 70 °C for 2 h. A colour change from yellow to intense red was observed after 30 mins. Evaporation of the solvent yielded the crude product as an orange solid. Cromatography (preparative TLC; CH_2Cl_2/hexane, 1:1) gave red [$Re_4(\mu_3\text{-}Se)_2(CO)_{16}(PPh_3)_2$] (**2**) and orange-yellow [$Re_4(\mu_3\text{-}Se)_2(\mu\text{-}CO)(CO)_{14}(PPh_3)_2$] (**3**) bands together with some decomposition material and small amounts of unchanged reagents. Compound **2** is more soluble than **3** in all common laboratory solvents.
2: FT-IR (CH_2Cl_2): ν(CO) = 2090 w, 2074 w, 2016 vs, 1998 vs, 1954 sh, 1943 m, 1916 m. $^{31}P\{^1H\}$ NMR: δ = 1.0 (br) ppm. $C_{52}H_{30}O_{16}P_2Re_4Se_2$: calcd. C 33.30, H 1.64; found C 33.29, H 1.62.
3: FT-IR (CH_2Cl_2): ν(CO) = 2098 w, 2091 w, 2016 vs, 2011 vs (sh), 1936 m, 1895 m. $^{31}P\{^1H\}$ NMR: δ = 0.8 (br) ppm. $C_{51}H_{30}O_{15}P_2Re_4Se_2$: calcd. C 33.16, H 1.64; found C 33.14, H 1.61.

Thermal Treatment of 2; Conversion into 3: A solution of compound **2** (100 mg, 0.051 mmol) in 10 mL of THF was stirred for 40 minutes at 50 °C. The quantitative formation of **3** was monitored by FT-IR spectroscopy.

Reaction of 3 with CO; Conversion into 2: A suspension of **3** (100 mg, 0.054 mmol) in 5 mL of CH_2Cl_2 was stirred under 5 atm. of CO. After 5 h an orange solution was formed. Cluster **3** was quantitatively converted into **2**, as confirmed by FT-IR spectroscopy in CH_2Cl_2.

X-ray Data Collection, Structure Solution and Refinement for Complexes 1, 2·CH_2Cl_2 and 3: Crystals suitable for X-ray analysis were obtained by layering methanol on dichloromethane solutions (**1** and **2·CH_2Cl_2**) or by slow evaporation of solvent from a THF solution (**3**). The intensity data were collected at room temperature on a Philips PW 1100 (**1**) or on a Bruker area detector AXS Smart 1000 (**2·CH_2Cl_2** and **3**) diffractometer (both using graphite-monochromated Mo-K_α radiation, λ = 0.71073 Å). Crystallographic and experimental details for the structures are summarized in

Table 4. Crystal data and structure refinement for compounds **1**, **2·CH_2Cl_2** and **3**

	1	2·CH_2Cl_2	3
Empirical formula	$C_{41}H_{30}Mn_2O_5P_2Se_2$	$C_{52}H_{30}O_{16}P_2Re_4Se_2$ CH_2Cl_2	$C_{51}H_{30}O_{15}P_2Re_4Se_2$
Mol. mass	932.39	1960.35	1847.41
Cryst system	monoclinic	monoclinic	monoclinic
Space group	*C*2/*c*	*C*2/*c*	*P*2$_1$/*n*
a (Å)	19.387(1)	47.584(2)	9.613(5)
b (Å)	10.328(1)	10.154(2)	21.859(5)
c (Å)	19.723(1)	32.376(2)	25.998(5)
β (°)	101.69(1)	128.25(1)	98.84(1)
V (Å^3)	3867(1)	12285(3)	5398(3)
Z	4	8	4
$D_{calcd.}$ (g·cm^{-3})	1.601	2.120	2.273
F(000)	1856	7280	3416
Crystal size	0.11 × 0.12 × 0.14	0.14 × 0.12 × 0.15	0.10 × 0.13 × 0.50
μ (cm^{-1})	26.62	92.44	104.14
Reflns. coll.	4802	67151	60529
Reflns. unique	4678 (R_{int} = 0.0984)	14263 (R_{int} = 0.0766)	12606 (R_{int} = 0.0432)
Obsd. reflns. [$I > 2\sigma(I)$]	1757	8391	6866
Parameters	236	727	668
R_{int} [$I > 2\sigma(I)$]	$R1$ = 0.0633,[a] $wR2$ = 0.1010[b]	$R1$ = 0.0400, $wR2$ = 0.0846	$R1$ = 0.0344, $wR2$= 0.0387
R_{int} (all data)	$R1$ = 0.2033, $wR2$ = 0.1361	$R1$ = 0.0896, $wR2$ = 0.0970	$R1$ = 0.0908, $wR2$= 0.0442

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

Table 4. An empirical absorption correction was made for **1** (maximum and minimum value for the transmission coefficient 1.000 and 0.625).[17a,17b] For complexes **2**·CH_2Cl_2 and **3** (maximum and minimum effective transmission value 1.000 and 0.405, 1.000 and 0.534. respectively) the raw frame data were processed using SAINT and SADABS to yield the reflection data file and the Bruker software was used for the absorption correction.[17c−17e] The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures (based on F_o^2) (SHELX-97),[18] first with isotropic thermal parameters and then with anisotropic thermal parameters in the last cycles of refinement for all the non-hydrogen atoms. In the crystals of **2**·CH_2Cl_2 dichloromethane molecules of solvation were found. The hydrogen atoms in **1**, **2**·CH_2Cl_2 and **3** were introduced into their geometrically calculated positions and refined as riding on the corresponding parent atoms, except the hydrogen atoms of the solvent molecule.

CCDC-230259 (for **1**), -230260 (for **2**·CH_2Cl_2) and -230261 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

Financial support from Ministero dell'Università e della Ricerca Scientifica e Tecnologica (Cofin 2000) is gratefully acknowledged. The facilities of the Centro Interfacoltà di Misure "G. Casnati" (Università di Parma) were used to record the NMR spectra.

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Received February 3, 2004
Early View Article