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Stepwise selenium transfer from tertiary phosphine selenides to $[Ru_3(CO)_{12}]$. Structural characterization of the primary product $[Ru_3(\mu_3\text{-Se})(\mu_3\text{-CO})(CO)_7(PPh_3)_2]$

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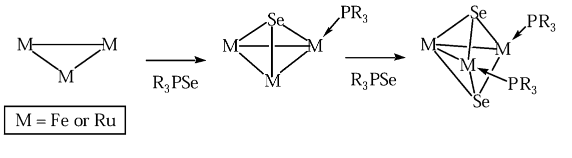
The monoselenido clusters $[Ru_3(\mu_3\text{-Se})(\mu_3\text{-CO})(CO)_7(PR'R_2)_2]$ (R = Ph, R′ = Ph or CH_2Ph; R = R′ = $p\text{-}C_6H_4OMe$) obtained by the reaction of phosphine selenides $R_2R'PSe$ with $[Ru_3(CO)_{12}]$, undergo the second attack by $R_2R'PSe$ affording, under appropriate conditions, the corresponding diselenido derivative $[Ru_3(\mu_3\text{-Se})_2(CO)_7(PR'R_2)_2]$. The crystal structure of $[Ru_3(\mu_3\text{-Se})(\mu_3\text{-CO})(CO)_7(PPh_3)_2]$ **4** showing the first triruthenium triangle bicapped by a selenium atom and a carbonyl ligand, is also reported.

Introduction

The reactions of tertiary phosphine chalcogenides with transition metal carbonyl species lead to the formation of chalcogenido-carbonyl clusters, whose significance in important pure and applied fields has been recently pointed out.[1] This synthetic procedure, which was proposed in the early nineties,[2] has been intensively used by our group in the last five years, obtaining a variety of clusters of different nuclearity starting from $[M_3(CO)_{12}]$ (M = Fe or Ru).[3]

More recently, we have found that the use of heterocyclic phosphine selenides in these processes affords selenido clusters containing coordinated heterocyclic fragments derived from P–C bond cleavages on the metal triangle.[4] Under pyrolytic conditions (*e.g.* refluxing toluene) the main reaction products are generally open-triangular, diselenido clusters of the type $[M_3(\mu_3\text{-Se})_2(CO)_7(PR_3)_2]$; however, also minor amounts of monoselenido species such as $[Fe_3(\mu_3\text{-Se})(\mu\text{-CO})(CO)_7(PPh_3)_2]$ have been recovered.[5]

On the basis of these results we have suggested that these reactions could proceed through two consecutive steps depicted in Scheme 1 (carbonyls omitted). Both mono- (triangular, 48 electrons) and diselenido (open triangular, 50 electrons) species can be isolated with one or two substitution phosphines.



Scheme 1

Very recently, this synthetic approach has been applied by Leong *et al.* to osmium derivatives by reacting $[Os_3(CO)_{12-x}(MeCN)_x]$ (x = 1 or 2) with Ph_3PSe.[6] Two selenido derivatives have been obtained, namely $[Os_3(\mu_3\text{-Se})(CO)_9(PPh_3)]$ and $[Os_3(\mu_3\text{-Se})_2(CO)_9]$, their yields being dependent on the starting molar ratio. As the monoselenido species does not react further with Ph_3PSe at 45 °C in toluene, it has been suggested that in the case of osmium the formation of the two selenido species could follow different pathways.

The aim of this paper is to point out that in the case of ruthenium the monoselenido clusters Ru_3Se are the possible intermediate in the reactions leading to Ru_3Se_2 species, as clusters of the type $[Ru_3(\mu_3\text{-Se})(\mu_3\text{-CO})(CO)_8(PR_3)_2]$ react further with R_3PSe to give the corresponding $[Ru_3(\mu_3\text{-Se})_2(CO)_7(PR_3)_2]$ derivatives. The crystal structure of $[Ru_3(\mu_3\text{-Se})(\mu_3\text{-CO})(CO)_7(PPh_3)_2]$ **4**, showing the first triruthenium triangle bicapped by a selenium atom and a carbonyl ligand, is also reported.

Experimental

General procedures

The starting reagents $[Ru_3(CO)_{12}]$, KNCSe, elemental selenium, tertiary phosphines and Me_3NO were pure commercial products (Aldrich and Fluka) and were used as received. $[Ru_3(CO)_{10}(MeCN)_2]$ was prepared according to literature.[7] The new tertiary phosphine selenides have been obtained in quantitative yield by selenium transfer from elemental Se or KNCSe to the parent phosphine.[3] 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. TLC were carried out on silica (20 × 20 cm glass plates). After the chromatographic rules, products were extracted with dichlorometane and recrystallized with methanol–dichloromethane mixtures. New compounds were identified by comparison of their spectroscopic data with those of known compounds. Purity was checked by elemental analysis and/or by ^1H and ^{31}P NMR spectroscopy. Elemental (C, H, N) analyses were performed with a Carlo Erba EA 1108 automated analyzer. IR spectra (KBr discs or CH_2Cl_2 solutions) were recorded on Nicolet 5PC and Nexus FT spectrometers. ^1H (300 MHz), ^{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) and CXP 200 (^{31}P). Mass spectra were obtained using a Finnigan MAT SSQ710 spectrometer equipped with an EI/CI source, a direct inlet system and a quadrupole mass analyser. The CI source was utilized with methane as the reagent gas (T source, 220 °C; methane ionization energy, 70 eV). The quadrupole temperature was mantained at 140 °C; the system was scanned from 400 to 1600 u and negative ion (NICI) spectra were recorded.

Reaction of $Ru_3(CO)_{10}(CH_3CN)_2$ with Ph_3PSe

Treatment of an acetonitrile (10 cm^3) solution of $[Ru_3(CO)_{10}(MeCN)_2]$ (0.19 g, 0.3 mmol) with 0.10 g of Ph_3PSe (0.3 mmol)

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for 1 h in toluene, at room temperature, gave a deep orange solution, which was evaporated to dryness and the residue was redissolved in a small amount of dichloromethane. TLC separation on silica, using a CH_2Cl_2/petroleum ether (1 : 2) mixture as eluent yielded a dark yellow, an orange, a yellow and a pale yellow band. The four bands contained respectively the *nido* clusters $[Ru_3(\mu_3\text{-}Se)_2(CO)_8(PPh_3)]$ **1** (yield 22%), $[Ru_3(\mu_3\text{-}Se)_2(CO)_7(PPh_3)_2]$ **2** (yield 33%), $[Ru_3(\mu_3\text{-}Se)(CO)_9(PPh_3)]$ **3** (yield 10%), $[Ru_3(\mu_3\text{-}Se)(\mu_3\text{-}CO)(CO)_7(PPh_3)_2]$ **4** (yield 15%). The structure of compound **4** was solved by X-ray diffraction methods; compound **3** has been identified by spectroscopic methods; the other two complexes have been identified by comparison of their spectroscopic data with those present in the literature.[5] Purification by crystallization (from CH_2Cl_2/MeOH mixture at 5 °C for some days) gave well-formed crystals of **4** suitable for X-ray analysis.

Cluster **3**: FTIR (CH_2Cl_2, ν(CO), cm^{-1}): 2086m, 2079m, 2059vs, 2043s, 2028vs, 2018s, 2004s, 1983sh. Anal. Found: C, 36.5; H, 1.6%. Calc. for $C_{27}H_{15}O_9PRu_3Se$: C, 36.2; H, 1.7%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 40.6 s. MS-NICI, *m*/*z* (%): 868 (100) $[Ru_3(\mu_3\text{-}Se)(CO)_8(PPh_3)]^-$, 840 (73) $[Ru_3(\mu_3\text{-}Se)(CO)_7(PPh_3)]^-$, 808 (67) $[Ru_3(\mu_3\text{-}Se)(CO)_6(PPh_3)]^-$, 780 (3) $[Ru_3(\mu_3\text{-}Se)(CO)_5(PPh_3)]^-$, 752 (1) $[Ru_3(\mu_3\text{-}Se)(CO)_4(PPh_3)]^-$, 724 (1) $[Ru_3(\mu_3\text{-}Se)(CO)_3(PPh_3)]^-$, 696 (1) $[Ru_3(\mu_3\text{-}Se)(CO)_2(PPh_3)]^-$, 668 (1) $[Ru_3(\mu_3\text{-}Se)(CO)(PPh_3)]^-$, 640 (1) $[Ru_3(\mu_3\text{-}Se)(PPh_3)]^-$, 634 (25) $[Ru_3(\mu_3\text{-}Se)(CO)_8]^-$, 606 (16) $[Ru_3(\mu_3\text{-}Se)(CO)_7]^-$, 578 (2) $[Ru_3(\mu_3\text{-}Se)(CO)_6]^-$.

Cluster **4**: FTIR (KBr, ν(CO), cm^{-1}): 2064m, 2024s, 2008vs, 1969m, 1953m, 1662m. Anal. Found: C, 46.5; H, 2.6%. Calc. for $C_{44}H_{30}O_8P_2Ru_3Se$: C, 46.7; H, 2.7%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 41.7 s.

Reaction of cluster 4 with Ph_3PSe

Cluster **4** (10 mg, 8.9 10^{-3} mmol) and equimolar amounts of Ph_3PSe and Me_3NO were stirred in dry toluene at 70 °C. The colour turned gradually to orange. The reaction, monitored by IR spectroscopy (Fig. 1), led to the quantitative formation of the *nido* cluster $[Ru_3(\mu_3\text{-}Se)_2(CO)_7(PPh_3)_2]$ **2**.

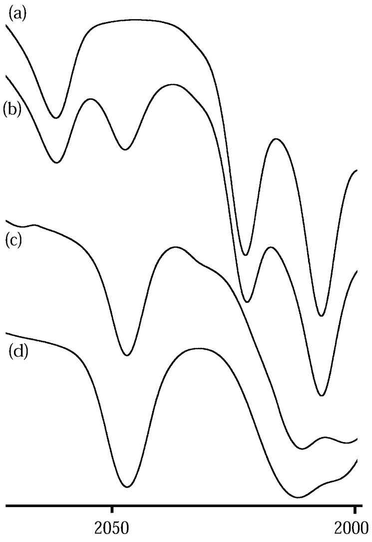

Fig. 1 Progressive transformation of the monoselenido cluster $[Ru_3(\mu_3\text{-}Se)(\mu\text{-}CO)(CO)_7(PPh_3)_2]$ **4** (toluene, 70 °C, presence of Ph_3PSe and Me_3NO, 1 : 1 : 1) into the corresponding diselenido cluster $[Ru_3(\mu_3\text{-}Se)_2(CO)_7(PPh_3)_2]$ **2**, monitored by FT-IR spectroscopy in the carbonyl region (values in cm^{-1}): (a) 0 min, pure **4**; (b) after 15 min; (c) after 30 min; (d) pure $[Ru_3(\mu_3\text{-}Se)_2(CO)_7(PPh_3)_2]$ as reference.

Reaction of $Ru_3(CO)_{12}$ with $(p\text{-}MeOC_6H_4)_3PSe$

Treatment of $Ru_3(CO)_{12}$ (300 mg, 0.468 mmol) with 404 mg of $(p\text{-}MeOC_6H_4)_3PSe$ (0.937 mmol) and 35 mg of Me_3NO (0.468 mmol), for 1.5 h in dry toluene (40 ml) at 70 °C, gave a deep brown solution, which was evaporated to dryness and the residue was redissolved in a small amount of dichloromethane. TLC separation on silica, using a CH_2Cl_2/hexane (2 : 1) mixture as eluent, yielded a orange, a red and a yellow band. The three bands contained respectively the *nido* clusters $[Ru_3(\mu_3\text{-}Se)_2(CO)_8\{P(p\text{-}C_6H_4OMe)_3\}]$ **5** (yield 35%), $[Ru_3(\mu_3\text{-}Se)_2(CO)_7\{P(p\text{-}C_6H_4OMe)_3\}_2]$ **6** (40%) and $[Ru_3(\mu_3\text{-}Se)(\mu_3\text{-}CO)(CO)_7\{P(p\text{-}C_6H_4OMe)_3\}_2]$ **7** (25%). The three compounds were identified by comparison of their spectroscopic data with those of the corresponding clusters **1**, **2** and **4**.

Cluster **5** (orange): FTIR (CH_2Cl_2, ν(CO), cm^{-1}): 2075s, 2043vs, 2023m, 2003s, 1973m. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 52.4 (s, br). ^1H NMR ($CDCl_3$): δ 3.84 (s, 9 H, OMe); 6.92 (dd, 6 H, ^3J(H,H) 8 Hz, ^4J(H,P) 2 Hz), 7.41 (dd, 6 H, ^3J(H,P) 12 Hz, ^3J(H,H) 8 Hz). MS-NICI, *m*/*z* (%): 1037 (60) $[Ru_3(\mu_3\text{-}Se)_2(CO)_8(p\text{-}C_6H_4OMe)_3P]^-$, 1009 (100) $[Ru_3(\mu_3\text{-}Se)_2(CO)_7(p\text{-}C_6H_4OMe)_3P]^-$, 981 (10) $[Ru_3(\mu_3\text{-}Se)_2(CO)_6(p\text{-}C_6H_4OMe)_3P]^-$, 953 (30) $[Ru_3(\mu_3\text{-}Se)_2(CO)_5(p\text{-}C_6H_4OMe)_3P]^-$, 925 (35) $[Ru_3(\mu_3\text{-}Se)_2(CO)_4(p\text{-}C_6H_4OMe)_3P]^-$, 897 (10) $[Ru_3(\mu_3\text{-}Se)_2(CO)_3(p\text{-}C_6H_4OMe)_3P]^-$, 869 (40) $[Ru_3(\mu_3\text{-}Se)_2(CO)_2(p\text{-}C_6H_4OMe)_3P]^-$, 841 (15) $[Ru_3(\mu_3\text{-}Se)_2(CO)(p\text{-}C_6H_4OMe)_3P]^-$, 813 (18) $[Ru_3(\mu_3\text{-}Se)_2(p\text{-}C_6H_4OMe)_3P]^-$.

Cluster **6** (red): FTIR (CH_2Cl_2, ν(CO), cm^{-1}): 2043s, 2006vs, 1967m, 1944m. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 51.5 (s), 41.4 (s), 47 (s, br), 39 (s br). ^1H NMR ($CDCl_3$): δ 3.82 (s, 18 H, OMe); 6.90 (dd, 12 H, ^3J(H,H) 9 Hz, ^4J(H,P) 2 Hz), 7.42 (dd, 12 H, ^3J(H,H) 9 Hz, ^3J(H,P) 10 Hz). MS-NICI, *m*/*z* (%): 1361 (10) $[Ru_3(\mu_3\text{-}Se)_2(CO)_7\{(p\text{-}C_6H_4OMe)_3P\}_2]^-$, 1333 (100) $[Ru_3(\mu_3\text{-}Se)_2(CO)_6\{(p\text{-}C_6H_4OMe)_3P\}_2]^-$, 1277 (22) $[Ru_3(\mu_3\text{-}Se)_2(CO)_4\{(p\text{-}C_6H_4OMe)_3P\}_2]^-$, 1249 (35) $[Ru_3(\mu_3\text{-}Se)_2(CO)_3\{(p\text{-}C_6H_4OMe)_3P\}_2]^-$, 1193 (40) $[Ru_3(\mu_3\text{-}Se)_2(CO)\{(p\text{-}C_6H_4OMe\}_2]^-$, 1165 (40) $[Ru_3(\mu_3\text{-}Se)_2\{(p\text{-}C_6H_4OMe)_3P\}_2]^-$.

Cluster **7** (yellow): FTIR (CH_2Cl_2, ν(CO), cm^{-1}): 2060s, 2020vs, 2004vs, 1964m, 1947sh, 1650m. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 37.4 s. ^1H NMR ($CDCl_3$): δ 3.8, s (18 H, OMe); 6.87, dd (12 H, ^3J(H,H) 10 Hz, ^4J(H,P) 2 Hz), 7.46, dd (12 H, ^3J(H,H) 10 Hz, ^3J(H,P) 12 Hz). MS-NICI, *m*/*z* (%): 1282 (5) $[Ru_3(\mu_3\text{-}Se)(\mu_3\text{-}CO)(CO)_6\{(p\text{-}C_6H_4OMe)_3P\}_2]^-$.

Reaction of 7 with R_3PSe (R = Ph or $p\text{-}MeOC_6H_4$)

The monoselenido cluster **7** (20 mg, 0.015 mmol) and equimolar amounts of Me_3NO and R_3PSe (R = Ph or $p\text{-}MeOC_6H_4$) were stirred in dry toluene at 70 °C. The colour turned to bright red. Monitoring by IR spectroscopy revealed the formation of *nido* clusters of the type $[Ru_3(\mu_3\text{-}Se)_2(CO)_7(PR_3)_2]$. In the case of the *p*-methoxyphenyl phosphine traces of the trisubstituted Ru_3Se_2 cluster were also detected.

Reaction of $Ru_3(CO)_{12}$ with $Ph_2(PhCH_2)PSe$

Treatment of $Ru_3(CO)_{12}$ (300 mg, 0.468 mmol) with $Ph_2(PhCH_2)PSe$ (332 mg, 0.937 mmol) and Me_3NO (35 mg, 0.468 mmol) for 1.5 h in dry toluene (40 ml) at 70 °C, gave a deep brown solution. It was evaporated to dryness and the residue was redissolved in a small amount of dichloromethane. TLC separation on silica, using a CH_2Cl_2/hexane (2 : 1) mixture as eluent, yielded five bands, three of which have been identified as containing the *nido* clusters $[Ru_3(\mu_3\text{-}Se)_2(CO)_8\{P(CH_2Ph)Ph_2\}]$ **8** (yield 20%), $[Ru_3(\mu_3\text{-}Se)(CO)_9\{P(CH_2Ph)Ph_2\}]$ **9** (10%), $[Ru_3(\mu_3\text{-}Se)_2(CO)_7\{P(CH_2Ph)Ph_2\}_2]$ **10** (35%), and $[Ru_3(\mu_3\text{-}Se)(\mu_3\text{-}CO)(CO)_7\{P(CH_2Ph)Ph_2\}_2]$ **11** (10%). The four compounds were identified by comparison of their spectroscopic data with those of the corresponding clusters **1**–**7**.

Cluster **8** (orange): FTIR (CH_2Cl_2, ν(CO), cm^{-1}): 2077s, 2043vs, 2024s, 2006s, 1973sh. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 48.0, s br. ^1H NMR ($CDCl_3$): δ 4.07, (d, 2 H, CH_2, ^2J(H,P) 8 Hz); 6.60–7.59 (m, 15 H).

Cluster **9** (yellow): FTIR (CH_2Cl_2, ν(CO), cm^{-1}): 2085w, 2077w, 2058s, 2042s, 2026vs, 2014s, 1973sh. $^{31}P\{^1H\}$ NMR

Table 1 Crystal data and structure refinement for **4**·CH_2Cl_2

Formula	$Ru_3SeP_2O_8C_{44}H_{30}CH_2Cl_2$
Formula weight	1215.72
Crystal system	Triclinic
Space group	$P\bar{1}$
a/Å	11.614(4)
b/Å	20.341(5)
c/Å	10.685(3)
α/°	86.91(3)
β/°	66.61(2)
γ/°	88.75(3)
V/Å^3	2313(1)
Z	2
D_{calcd}/g cm^{-3}	1.745
F(000)	1192
Crystal size/cm	0.18 × 0.22 × 0.25
μ/cm^{-1}	19.89
Reflections, collected	6240
Reflections, unique	6240
Obs. refl.	4657 [$I > 2\sigma(I)$]
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0281$, $wR2 = 0.0702$
R indices (all data)	$R1 = 0.0463$, $wR2 = 0.0778$

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

($CDCl_3$): δ 43.2 s. ^1H NMR ($CDCl_3$): δ 3.89 (d, 2 H, CH_2, ^2J(H,P) 10 Hz); 6.50–7.71 (m, 15 H).

Cluster **10** (red): FTIR (CH_2Cl_2, ν(CO), cm^{-1}): 2045s, 2007vs, 1972s, 1951m. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 39.6, s; 34.3, s; 43, s br; 39s br. ^1H NMR ($CDCl_3$): δ 3.51–4.21 (m, 4 H, CH_2); 6.47–7.66, m (30 H).

Cluster **11** (yellow): FTIR (CH_2Cl_2, ν(CO), cm^{-1}): 2061s, 2023vs, 2007vs, 1968m, 1947sh, 1653m. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 41.6 s. ^1H NMR ($CDCl_3$): δ 3.77 (d, 4 H, CH_2, ^2J(H,P) 8 Hz); 6.58–7.58 (m, 30 H).

Reaction of 11 with $Ph_2(PhCH_2)PSe$

The monoselenido cluster **11** (30 mg, 0.025 mmol) and equimolar amounts of $Ph_2(PhCH_2)PSe$ and Me_3NO were stirred in dry toluene at 60 °C. The colour turned gradually to reddish orange. IR monitoring showed the progressive and quantitative formation of the *nido* cluster **10** (Fig. 2).

Crystal structure determination of 4·CH_2Cl_2

The intensity data of the dichloromethane solvate of **4** were collected at room temperature on a Siemens AED single-crystal diffractometer using a graphite monochromated MoKα radiation and the θ/2θ scan technique. Crystallographic and experimental details for the structure are summarized in Table 1. A correction for absorption was made [maximum and minimum value for the transmission coefficient was 1.000 and 0.8492].[8] The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures (based on F_o^2) (SHELX-97)[9a,b] first with isotropic thermal parameters and then 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 $w = 1/[\sigma^2 F_o^2 + (0.0470\,P)^2 + 0.3901\,P]$, where $P = (F_o^2 + 2\,F_c^2)/3$, was used.

CCDC reference number 169377.

See http://www.rsc.org/suppdata/dt/b2/b203004g/ for crystallographic data in CIF or other electronic format.

Results and discussion

The reactions of $[Ru_3(CO)_{12}]$ with different tertiary phosphine selenides R_3PSe lead to the formation of disubstituted triruthenium diselenido carbonyl clusters $[Ru_3(\mu_3\text{-}Se)_2(CO)_7(PR_3)_2]$ as major products. Under certain conditions ($[Ru_3(CO)_{12}]/R_3PSe$ 1 : 2, refluxing toluene, R = Ph), we found that the process is quite selective affording high yields (*ca.* 90%) of the diselenido species.[5] As pointed out in the Introduction, we suggested monoselenido clusters of core Ru_3Se as the possible intermediates in these reactions. However, these species cannot be recovered when the reaction is carried out under the above mentioned conditions, as the reactions go to completeness, with the formation of the thermal stable diselenido triruthenium species. Probably monoselenido species were present to a certain extent in the reaction mixtures obtained in deficiency of phosphine selenide (1 : 1 molar ratio). Nevertheless, the large number of product did not allow to isolate and identify them.[5]

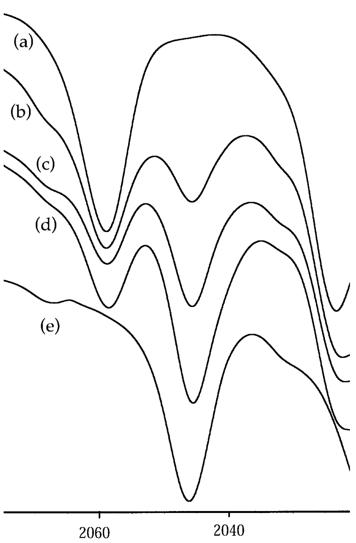

Fig. 2 Progressive transformation of the monoselenido cluster $[Ru_3(\mu_3\text{-}Se)(\mu\text{-}CO)(CO)_7\{P(CH_2Ph)Ph_2\}_2]$ **11** (toluene, 60 °C, presence of $Ph_2(PhCH_2)PSe$ and Me_3NO, 1 : 1 : 1) into the corresponding diselenido cluster $[Ru_3(\mu_3\text{-}Se)_2(CO)_7\{P(CH_2Ph)Ph_2\}_2]$ **10**, monitored by FT-IR spectroscopy in the carbonyl region (values in cm^{-1}): (a) 0 min, pure **11**; (b) after 30 min; (c) after 60 min; (d) after 120 min; (e) pure **10** as reference.

On the other hand, triruthenium monoselenido clusters substituted with different phosphines can be obtained by reacting the desired phosphine selenide with the labile intermediate $[Ru_3(CO)_{10}(CH_3CN)_2]$ at room temperature. In particular the reaction between $[Ru_3(CO)_{10}(CH_3CN)_2]$ and an equimolar amount of Ph_3PSe leads to the formation of workable amounts of the monoselenide mono and disubstituted ruthenium carbonyl clusters of formula $[Ru_3(\mu_3\text{-}Se)(CO)_{10-n}(PR_3)_n]$ (n = 1 or 2) (compounds **3** and **4**; yields 10, 15%). In the case of $Ph_2(PhCH_2)P$ and $(p\text{-}MeOC_6H_4)_3P$ monoselenido species can be obtained also by reaction of the corresponding selenide with $[Ru_3(CO)_{12}]$ at 70 °C (compounds **7**, **9** and **11**; yield 25, 15, 10%).

Diselenido species mono and disubstituted are always present even if the starting Ru_3/PSe molar ratio is 1 : 1. This suggests that once coordinatively unsaturated Ru_3Se species are formed, they rapidly undergo the second selenium transfer (till ligand unsaturation persists in the reaction medium), competing with Ru_3 derivatives in reacting with phosphine selenides. Regarding the presence of mono- and disubstituted phosphine derivatives, this is not surprising considering that CO/PR_3 exchanges between selenido clusters has been already observed, even at room temperature in the case of iron.[5]

In order to demonstrate the stepwise selenium transfer, we have treated the monoselenido clusters with another equivalent of phosphine selenide, obtaining quantitatively the corresponding diselenido species. The process (at 60–70 °C, in the presence of Me_3NO) can be monitored by IR spectroscopy, as shown in Fig. 1 in the case of Ph_3PSe and in Fig. 2 in the case of $Ph_2(PhCH_2)PSe$. These results clearly indicate that monoselenido species can rapidly turn to the corresponding diselenido ones in the presence of R_3PSe, provided that coordinative unsaturation is present.

It is interesting to note that selenium transfer occurs without introducing a further phosphine ligand in the triruthenium ensemble, as transfer reactions start from and lead to disubstituted species. This is probably because the third phosphine should substitute a carbonyl ligand on the apical ruthenium atom, which is known to be not so prone for substitution process. Actually, trisubstituted derivatives are attainable to a certain extent, especially under excess of phosphines,[5] and there is spectral evidence that trace amount of a trisubstituted species has been formed in the transfer reaction with the monoselenido cluster substituted with *p*-methoxyphenyl phosphine.

The two spectral sequences shown in Fig. 1 and 2 emphasize the temperature dependence of the rate of these processes. At 70 °C the reactions with Ph_3PSe (Fig. 1) and $Ph_2(PhCH_2)P$ are complete after 30 min, whereas at 60 °C the same reaction with $Ph_2(PhCH_2)P$ takes 2 h to reach about 70% of yield.

Finally, the availability of suitable crystals of **4** prompted us to solve its crystal structure, in order to confirm its identity and considering the scantiness of clusters of formula $[M_3(\mu_3\text{-}E)(L)_{10}]$ (M = Fe, Ru or Os; E = S, Se or Te; L = two-electron ligand) characterized by single-crystal X-ray studies. In fact, to our knowledge, this family of clusters counts only other five members structurally characterized, namely $[M_3(\mu_3\text{-}S)(\mu_3\text{-}CO)(CO)_9]$ (M = Fe,[10] Ru[11] or Os[12]), $[Fe_3(\mu_3\text{-}Se)(\mu\text{-}CO)(CO)_7(PPh_3)_2]$[5] and $[Os_3(\mu_3\text{-}Se)(CO)_9(PPh_3)]$.[6]

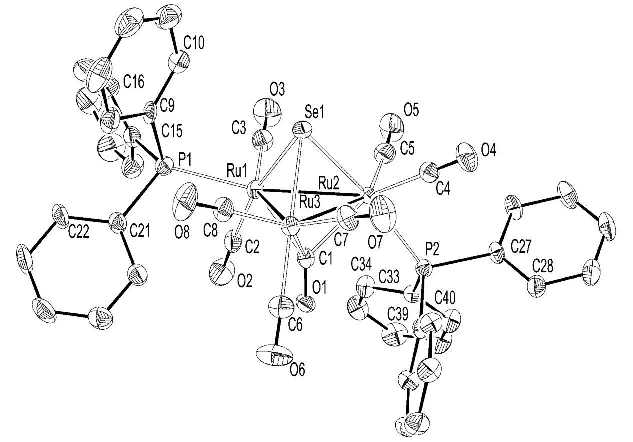

Fig. 3 View (ORTEP, 30% probability level) of the molecular structure of **4** with the atom numbering scheme.

Table 2 Selected bond distances and angles for $\mathbf{4}\cdot CH_2Cl_2$

Bond distances/Å			
Ru(1)–Ru(2)	2.855(1)	P(1)–Ru(1)	2.357(2)
Ru(1)–Ru(3)	2.878(1)	P(2)–Ru(2)	2.363(1)
Ru(2)–Ru(3)	2.815(1)	C(1)–Ru(2)	2.164(5)
Se(1)–Ru(2)	2.480(1)	C(1)–Ru(1)	2.168(4)
Se(1)–Ru(1)	2.482(1)	C(1)–Ru(3)	2.204(5)
Se(1)–Ru(3)	2.486(1)	C(1)–O(1)	1.189(5)
Bond angles/deg			
Ru(2)–Se(1)–Ru(1)	70.24(3)	P(2)–Ru(2)–Ru(3)	113.05(5)
Ru(2)–Se(1)–Ru(3)	69.06(3)	P(1)–Ru(1)–Se(1)	98.47(4)
Ru(1)–Se(1)–Ru(3)	70.79(3)	P(2)–Ru(2)–Se(1)	168.43(4)
Ru(2)–Ru(1)–Ru(3)	58.82(3)	C(1)–Ru(1)–Se(1)	89.7(1)
Ru(3)–Ru(2)–Ru(1)	60.99(3)	C(1)–Ru(2)–Se(1)	89.9(1)
Ru(2)–Ru(3)–Ru(1)	60.19(3)	C(1)–Ru(3)–Se(1)	88.8(1)
Se(1)–Ru(1)–Ru(2)	54.85(3)	C(1)–Ru(1)–P(1)	132.2(2)
Se(1)–Ru(1)–Ru(3)	54.66(3)	C(1)–Ru(2)–P(2)	82.8(1)
Se(1)–Ru(2)–Ru(1)	54.91(3)	O(1)–C(1)–Ru(2)	132.9(4)
Se(1)–Ru(2)–Ru(3)	55.56(3)	O(1)–C(1)–Ru(1)	130.5(3)
Se(1)–Ru(3)–Ru(1)	54.55(3)	O(1)–C(1)–Ru(3)	129.4(4)
Se(1)–Ru(3)–Ru(2)	55.38(3)	Ru(2)–C(1)–Ru(1)	82.5(2)
P(1)–Ru(1)–Ru(2)	151.56(3)	Ru(2)–C(1)–Ru(3)	80.3(1)
P(1)–Ru(1)–Ru(3)	99.21(4)	Ru(1)–C(1)–Ru(3)	82.3(1)
P(2)–Ru(2)–Ru(1)	123.72(4)		

The molecular structure of **4** is shown in Fig. 3, together with the atom labelling scheme; selected bond distances and angles are given in Table 2. The triangle of ruthenium atoms is capped on one side by a selenido ligand and on the other by a carbonyl group. The two PPh_3 ligands coordinate to Ru(1) and Ru(2) respectively in *pseudo*-equatorial and *pseudo*-axial position through the P atoms (the P1–Ru1 and P2–Ru2 bond distances are 2.357(2) and 2.363(2) Å respectively). The coordination on the metal atoms is completed by seven terminal carbonyl groups. The μ_3-Se ligand is practically equidistant from the three Ru atoms, whereas the μ_3-CO group bridges in a slightly asymmetrical way, the two shortest distances involving the ruthenium atoms coordinated by the two phosphines (the Ru1–C1 and Ru2–C1 bond distances are 2.168(4) and 2.164(5) Å respectively, while the Ru3–C1 bond length is slightly longer 2.204(5) Å). This slight asymmetry has been also observed in the case of the unsubstituted cluster $[Ru_3(\mu_3\text{-}S)(\mu_3\text{-}CO)(CO)_9]$.[11] It is interesting to note that, differently from the other two phosphine-substituted homologues with Fe and Os, cluster **4** exhibits a μ_3-carbonyl ligand. In the IR spectrum of compound **4** a medium absorption at 1662 cm^{-1} is present, due to the μ_3-CO group; analogously, compounds **7** and **11** each show a band at 1650 and 1653 cm^{-1}, respectively. On the other hand, no low frequency bands are present in the IR spectrum of the monosubstituted monoselenide species **3** and **9**, suggesting the absence of the μ_3 coordination mode of the carbonyl moiety. The three Ru–Ru distances span from 2.815(1) to 2.878(1) Å and appear significantly longer than those observed in the unsubstituted cluster $[Ru_3(\mu_3\text{-}S)(\mu_3\text{-}CO)(CO)_9]$, where the intermetallic distances lie in the narrower range of 2.786(1)–2.812(1) Å.[11]

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