

TRANSFORMATIONS OF THE HETERONUCLEAR CLUSTERS $E_n[Co(CO)_3]_{4-n}$ ($E = P, As; n = 1-3$) WHEN TREATED WITH SOFT LEWIS ACIDS AND BASES

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Summary

The tetrahedral pnigogenic clusters $E_n[Co(CO)_3]_{4-n}$ ($E = P, As; n = 1-3$) react with soft Lewis acids and bases to give products of substitution and transformation of the cluster. Lewis acids promote transformations to clusters containing more cobalt atoms and Lewis bases to clusters containing fewer such atoms.

Introduction

Transition metal cluster chemistry is receiving increasing interest, but efforts are mostly focused on preparation of new clusters or their use in homogeneous catalysis. Surprisingly few papers deal with interconversions of the cluster compounds [e.g. 1,2,3]. We describe below reactions in which transformations of the cluster moiety of $E_n[Co(CO)_3]_{4-n}$ ($E = P, As; n = 1-3$) (I) pnigogenic derivatives occur.

Results and discussion

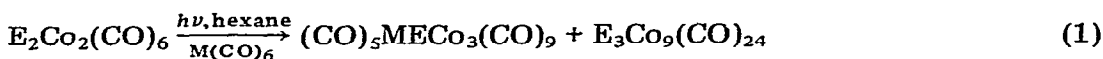
Reactions with metal carbonyls

$PCo_3(CO)_9$ reacts with $(CO)_4Fe(THF)$ [4] and $AsCo_3(CO)_9$ with $(CO)_4Fe(THF)$ or $(CO)_5M(THF)$ ($M = Cr, Mo, W$) [5] to give the corresponding $(CO)_y-MECo_3(CO)_9$ ($M = Fe, y = 4, E = P, As; M = Cr, Mo, W, y = 5, E = As$) adducts. Similar derivatives of an antimony-iron cluster $(SbFe_3(CO)_6(\eta^5-C_5H_5)_3)$ have been prepared previously [6].

In an attempt to use complexes I with $n = 2$ or 3 as Lewis bases we treated their solutions with metal carbonyls with and without UV irradiation.

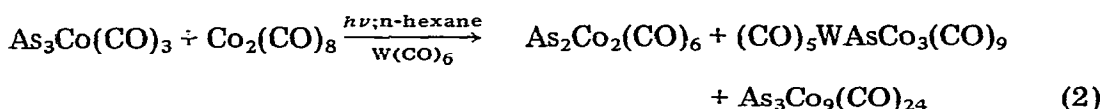
$E_2Co_2(CO)_6$ ($E = P, As$) compounds did not react with $(CO)_5W(THF)$ in THF

at room temperature and the starting compounds were recovered. The bis-pnicogenic complexes, however, did react in hexane under UV irradiation with Group VI hexacarbonyls according to equation 1:



(E = P, M = Cr, Mo, W; E = As, M = W)

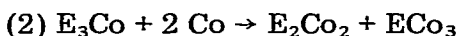
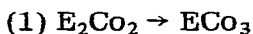
$\text{As}_3\text{Co}(\text{CO})_3$ did not yield stable reaction products either with $(\text{CO})_5\text{W}(\text{THF})$ in THF solution without irradiation or with $\text{W}(\text{CO})_6$ in *n*-hexane solution with UV irradiation, but the starting $\text{As}_3\text{Co}(\text{CO})_3$ could not be recovered. However, when $\text{As}_3\text{Co}(\text{CO})_3$ was treated with $\text{W}(\text{CO})_6$ in *n*-hexane with irradiation in the presence of $\text{Co}_2(\text{CO})_8$ reaction 2 took place:



Some generalizations can be made:

(i) of the $\text{E}_n[\text{Co}(\text{CO})_3]_{4-n}$ (E = P, As) series only the species with $n = 1$ act as ligands for metal carbonyls. This could be interpreted in terms of the separation of the "fourth" (lone pair) hybrid orbital of the pnicogen atom E. In case of complexes I with $n = 2$ or 3, the cluster orbitals are not filled by electrons of the two or three main-group atoms and thus the lone pairs are drawn into the cluster, or in other words, there is not a high enough electron density in the lone-pair orbitals for donor activity to be exhibited. Consequently the compounds I with $n = 2$ or 3 are so weak as Lewis bases as to be unable to compete even with a mobile ligand such as THF.

(ii) The essential core of reactions 1 and 2 can be represented as follows:



Reactions 1 and 2 are therefore cluster transformations.

The $\text{E}_2\text{Co}_2 \rightarrow \text{ECo}_3$ transformation shows a close analogy with the recently observed [7] formation of $[\text{CCo}_3(\text{CO})_9]_2$ from $(\mu_2\text{-IC}_2\text{I})\text{Co}_2(\text{CO})_6$ and $\text{Co}_2(\text{CO})_8$ or $[\text{Co}(\text{CO})_4]^-$. While in the former case the presence of trapping (UV-excited) partners(s) leads to "monomeric" $((\text{CO})_5\text{MECo}_3(\text{CO})_9)$ or "trimeric" $(\text{E}_3\text{Co}_9(\text{CO})_{24})$ products, in the latter the retention of one C—C bond of the starting acetylene leads to almost exclusive formation of the "dimeric" ethane derivative. However in both cases the components of the original triple bond are "turned outward" towards two Co_3 moieties.

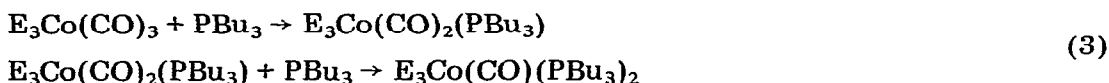
(iii) The possible pathway of these transformations can be deduced from the facts that UV irradiation and the presence of a $\text{Co}(\text{CO})_3$ source [$\text{Co}_2(\text{CO})_8$ or $\text{E}_2\text{Co}_2(\text{CO})_6$] were required to bring about reactions 1 and 2. This indicates that complexes with $n = 2$ or 3 cannot compete as weak Lewis bases with ligand THF, but react with the unsaturated species formed under the influence of irradiation. Because the bonding electron density in the cluster core of the derivatives so formed is reduced beyond that required for stability, further transfor-

mations take place leading to products which contain fewer pnictogenic atoms than the starting compound.

(iv) Reaction 2 permits the synthesis of the previously inaccessible compounds $(\text{CO})_5\text{MPCo}_3(\text{CO})_9$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$).

Reactions with trivalent phosphorus compounds

The complexes $\text{E}_3\text{Co}(\text{CO})_3$ ($\text{E} = \text{P}, \text{As}$) react with tributylphosphine to give the corresponding mono- and disubstituted products (reaction 3).



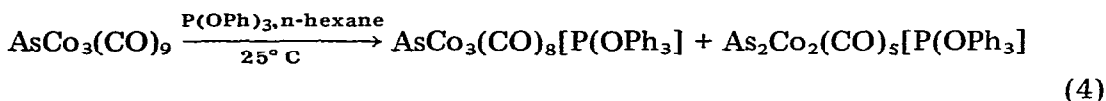
Less basic phosphines do not react with $\text{E}_3\text{Co}(\text{CO})_3$ complexes.

The complexes $\text{E}_2\text{Co}_2(\text{CO})_6$ ($\text{E} = \text{P}, \text{As}$) readily gave monosubstitution products on treatment with various phosphines and even with $\text{P}(\text{OEt})_3$ [8]. The phosphine ligand was found to be in an axial position by X-ray (P [9], As [10]) and spectroscopic [8] studies.

As a representative of the $\text{ECo}_3(\text{CO})_9$ series we used the more stable $\text{AsCo}_3(\text{CO})_9$ compound for our experiments. When $\text{AsCo}_3(\text{CO})_9$ was treated (in n-hexane at room temp.) with tertiary normal and branched alkyl and aryl phosphines the starting compound completely disappeared * but none of its substitution products could be isolated. Minor amounts of monosubstituted phosphine derivatives of $\text{As}_2\text{Co}_2(\text{CO})_6$ [8] were found. The main products of the reaction were oils, insoluble in hexane, showing very complex $\nu(\text{C}-\text{O})$ spectra in CH_2Cl_2 .

In the case of tris(n-alkyl)phosphines light yellow oils were obtained in low ($\sim 1\%$) yields. The analyses of these substances agree with the formula $\text{Co}_2(\text{CO})_2(\text{PR}_3)_4\text{As}_4$, $\nu(\text{C}-\text{O})$ (n-hexane): 1975s, 1910vs cm^{-1} (slightly depending on R). Efforts to establish the structures of these substances are in progress.

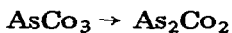
$\text{AsCo}_3(\text{CO})_9$ reacted with $\text{P}(\text{OPh})_3$ according to equation 4.



Conclusions can be drawn as follows:

(i) The greater the number of pnictogen atoms present in clusters I, the lower the tendency for phosphine substitution.

(ii) The cluster transformation observed in reaction 4 can be depicted as



indicating that the effect of phosphines (soft Lewis bases) on the transformations of the cluster core is the inverse of that observed in the reactions with metal carbonyls (Lewis acids).

We conclude that the pattern of stability of the $\text{E}_n\text{Co}_{4-n}$ cluster cores results in the formation of species containing fewer E atoms in reactions with electro-

* Some $\text{As}_3\text{Co}_9(\text{CO})_{24}$ was detected. This might have been formed from unreacted $\text{AsCo}_3(\text{CO})_9$ during chromatography.

philic substrates while nucleophilic reagents induce transformations giving molecules containing more E atoms. The rearrangements are probably governed by the tendency of the cluster core to achieve optimum filling of the cluster orbitals: supplying electrons from "outside" increases the stability of clusters containing more E atoms (and contributing less electrons to cluster orbitals) while withdrawing electrons has the opposite effect. The cluster transformations can be utilized preparatively.

Experimental

All experiments were conducted with exclusion of air under Ar, N₂ or CO atmosphere, using carefully dried solvents.

Starting compounds were of commercial origin except for Co₂(CO)₈, which was prepared as described by Szabó et al. [12].

IR spectra were recorded on a SPECORD IR-75 (Carl Zeiss, Jena, GDR) spectrometer with simultaneous DCl calibration [13]. Mass spectra were obtained using the direct sample introduction system of an MAT-111 (Varian, Palo Alto, USA) instrument.

Reaction of P₂Co₂(CO)₆ with M(CO)₆ (M = Cr, Mo, W) complexes. Preparation of (CO)₅MPCo₃(CO)₉ complexes

0.2 mmol of M(CO)₆ was added to a solution of 70 mg (0.2 mmol) of P₂Co₂(CO)₆ [14] in 20 ml of n-hexane. The mixture was irradiated with UV light, stirred, and cooled with running water. The progress of the reaction was monitored by recording the $\nu(\text{C-O})$ spectrum every 30 min. (The most characteristic feature is the gradual disappearance of the strong band of the M(CO)₆ compounds at 2000–1980 cm⁻¹.) After 3 h the conversion was ~80%, and the mixture was then concentrated to half volume at reduced pressure and chromatographed on a silica gel column (80–90 cm × 20 mm) with n-hexane as eluent. Three coloured fractions were collected; the first orange, band was unreacted P₂Co₂(CO)₆, while the third, dark green, band was P₃Co₉(CO)₂₄ (5–10%), identified by its $\nu(\text{C-O})$ spectrum [11]. The second fraction was dark red, and yielded black crystals after concentration (to 10–15 ml) and chilling (–70 to –75°C). These crystals were identified as (CO)₅MPCo₃(CO)₉ (M = Cr, Mo, W) from their analyses and IR spectra (Table 1). Yields were ~5%.

As₂Co₂(CO)₆ [10] reacted similarly with M(CO)₆ compounds to give the known As₃Co₉(CO)₂₄ [11] and (CO)₅MAsCo₃(CO)₉ [5], identified from the $\nu(\text{C-O})$ bands in their IR spectra. Yields were about 5%.

Reaction of As₃Co(CO)₃ with W(CO)₆ in the presence of Co₂(CO)₈

A solution of 35 mg (0.1 mmol) of W(CO)₆ and 34 mg (0.1 mmol) of Co₂(CO)₈ in 10 ml n-hexane was added to the solution of 37 mg (0.1 mmol) of As₃Co(CO)₃ [16] in 20 ml of n-hexane. The mixture was irradiated with UV light, stirred, and cooled with running water. The reaction was monitored by observing the disappearance of the 1983.4 cm⁻¹ band of the W(CO)₆. After 60 min all the W(CO)₆ had disappeared. (The IR $\nu(\text{C-O})$ spectrum of the mixture showed bands characteristic of As₂Co₂(CO)₆, (CO)₅WAsCo₃(CO)₉, and As₃Co₉(CO)₂₄.) The mixture was then concentrated to 10–15 ml and chromatographed on a

TABLE 1
IDENTIFICATION OF THE NEW COMPOUNDS

Compound	Analysis. Found (Calcd.) (%)		IR data. $\nu(\text{C—O})$ (cm^{-1}) ^a
	Co	P	
(CO) ₅ CrPCo ₃ (CO) ₉ ^b (CrPCo ₃ C ₁₄ O ₁₄)	27.8 (27.43)	4.9 (4.74)	2112.9w, 2078.3s, 2069.0vs 2052.8w, 2043.9vw, 1972.3vs(br), 1957.5m, 1935.3vw(br)
(CO) ₅ MoPCo ₃ (CO) ₉ ^c (MoPCo ₃ C ₁₄ O ₁₄)	25.9 (25.70)	4.2 (4.44)	2108.1m, 2073.5vs, 2065.9m, 2052.8s, 2047.7m, 2037.5w, 1969.2vs(br), 1940.2vw(br)
(CO) ₅ WPCo ₃ (CO) ₉ ^d (WPCo ₃ C ₁₄ O ₁₄)	22.9 (22.83)	4.05 (3.94)	2103.4m, 2070.7vs, 2066.8m, 2048.4s, 2042.1m, 2025.1w, 1962.4vs(br), 1933.6vw(br)
P ₃ Co(CO) ₂ (PBu ₃) ^e P ₃ Co(CO)(PBu ₃)			2028.6vs, 1986.5s 1955.8
As ₃ Co(CO) ₂ (PBu ₃) ^f (As ₃ CoPC ₁₄ H ₂₇ O ₂)	10.3 (10.88)		2020.8vs, 1979.8s ^g
As ₃ Co(CO)(PBu ₃) ₂ ^h (As ₃ CoP ₂ C ₂₅ H ₅₄ O)	7.4 (7.85)		1950.6 ^g
As ₂ Co ₂ (CO) ₅ [P(OPh) ₃] ⁱ			2072vs, 2028vs, 2021vs, 2007w(sh) 1993w
AsCo ₃ (CO) ₈ [P(OPh) ₃] ^j			2088s, 2049vs, 2043vs, 2032s, 2010m, 1857m, 1843m

^a In n-hexane. ^b cf. (CO)₅CrAsCo₃(CO)₉ [5]. ^c cf. (CO)₅MoAsCo₃(CO)₉ [5]. ^d cf. (CO)₅WAsCo₃(CO)₉ [5]. ^e cf. As analogue. ^f cf. ref. 16. Mass spec. (*m/e*): M^+ 542 (16); ($M^+ - \text{CO}$) 514 (11); ($M^+ - 2 \text{ CO}$) 486 (39); ($M^+ - (2 \text{ CO} + \text{Bu})$) 429 (35); ($M^+ - (2 \text{ CO} + 2 \text{ Bu})$) 372 (30); (As_3CoP^+) 315 (39); (As_3)⁺ 225 (100). ^g cf. (π -allyl)Co(CO)₂PR₃ derivatives [17]. ^h cf. ref. 16. Mass spec. (*m/e*): M^+ 716 (3); ($M^+ - \text{CO}$) 688 (6); ($M^+ - (\text{CO} + \text{PBu}_3)$) 486 (100); (As_3CoP^+) 315 (18); (As_3Co^+) 384 (10). ⁱ cf. P(OEt)₃ analogue [8]. ^j cf. MeCCo₃(CO)₈(PPh₃) and PhCCo₃(CO)₈(PBu₃) [19].

silica gel column (80–90 cm × 20 mm). With n-hexane as eluent, two coloured fractions were obtained, and identified by their IR $\nu(\text{C—O})$ spectra as As₂Co₂-(CO)₆ (orange, IR [14], 1–2%) and (CO)₅WAsCo₃(CO)₉ (dark red, IR [5], 2–3%). Use of n-hexane/benzene (7/3) as eluent gave a dark green fraction identified as As₃Co₉(CO)₂₄ (IR [11], 5–10%).

Reaction of As₃Co(CO)₃ with PBu₃

To a solution of 37 mg (0.1 mmol) of As₃Co(CO)₃ in 30 ml n-heptane was added 60 μ l (0.25 mmol) of PBu₃. The mixture was refluxed and the progress of the reaction monitored by IR spectroscopy. After 70–80 min the intensity of the 2032 cm^{-1} band of As₃Co(CO)₃ had diminished to ~20% its initial value, and the mixture was cooled to room temperature and a 5 ml portion was chromatographed on a preparative 20 × 20 cm TLC plate (Kieselgel G, E. Merck, Darmstadt, GFR) using benzene/n-hexane (3/7) as eluent. The first, light yellow, fraction contained the unreacted As₃Co(CO)₃, while the second and third, dark yellow, fractions were identified as the mono- and disubstitution products. The individual fractions were removed from the plate and eluted with Et₂O in a small column. Since no crystals could be obtained by cooling, the solvent was drawn off and the dark yellow oily residues shown by analyses to be As₃Co(CO)₂(PBu₃) and As₃Co(CO)(PBu₃)₂ (Table 1). The yields were 35–40

and 8–10%, respectively.

$\text{P}_3\text{Co}(\text{CO})_3$ was similarly treated and the mono- and disubstitution products were identified from their IR spectra in n-hexane.

Reaction of $\text{AsCo}_3(\text{CO})_9$ with $\text{P}(\text{n-alkyl})_3$ compounds

A solution of $\text{AsCo}_3(\text{CO})_9$ was prepared from 0.17 g (0.5 mmol) of $\text{Co}_2(\text{CO})_8$ and 0.15 g (0.33 mmol) of AsI_3 in 20 ml of n-hexane [11]. The solution was filtered, and an IR spectrum recorded to show that it contained only $\text{AsCo}_3(\text{CO})_9$ (>95%). Then 0.24 mmol tris(n-alkyl)phosphine was added and the solution was stirred under an atmosphere of CO for 15 min. (After a gluey material which separated was soluble only in CH_2Cl_2 ; its solution in this solvent showed several $\nu(\text{C—O})$ bands, and it remains to be characterized.) The IR spectrum of the hexane solution showed that the bands of $\text{AsCo}_3(\text{CO})_9$ had almost disappeared, so 3/4 of the solvent was evaporated off and the residual solution chromatographed on preparative 20×20 cm TLC plates (Kieselgel G, E. Merck, Darmstadt, GFR) in 1 ml portions. The first ($R_F \approx 0.8$), reddish-brown, fraction was identified as $\text{As}_2\text{Co}_2(\text{CO})_5\text{PR}_3$ from its IR spectrum. The second fraction was light yellow ($R_F \approx 0.2$) showed two IR bands, and analysed approximately for $\text{As}_4\text{Co}_2(\text{CO})_2(\text{PR}_3)_4$ (c.f. Results section). A broad band near the base line seemed to contain most of the reaction products. It yielded an oily substance, rich in $\nu(\text{C—O})$ bands (indicating that it was a mixture), and insoluble in n-hexane.

Reaction of $\text{AsCo}_3(\text{CO})_9$ with $\text{P}(\text{OPh})_3$

A solution of $\text{AsCo}_3(\text{CO})_9$ was prepared from 0.34 g (1 mmol) of $\text{Co}_2(\text{CO})_8$ and 0.30 g (0.66 mmol) of AsI_3 in 40 ml of n-hexane [11]. This solution was filtered, and its IR $\nu(\text{C—O})$ spectrum checked. 125 μl (0.48 mmol) triphenylphosphite was added and the solution was stirred for 3 h at room temperature under CO. (A fairly large quantity of a dark gluey material separated, and has still to be characterized.) After this period 3/4 of the solvent was evaporated off and the residual solution was chromatographed on 20×20 cm preparative TLC plates (Kieselgel G, E. Merck, Darmstadt, GFR) with n-hexane/ CH_2Cl_2 (10/1.5) eluent. A red ($R_F \approx 0.6$) fraction was identified as $\text{As}_2\text{Co}_2(\text{CO})_5[\text{P}(\text{OPh})_3]$ from its IR spectrum (Table 1). Another deep red, fraction was obtained at $R_F \approx 0.35$, and was identified as $\text{AsCo}_3(\text{CO})_8[\text{P}(\text{OPh})_3]$ (Table 1); it showed a $\nu(\text{C—O})$ band pattern similar to that of the analogous bridged $\text{RCo}_3(\text{CO})_8(\text{PR}_3)$ compounds. Yields were ~ 1 and $\sim 0.5\%$, respectively.

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