A mixed Co- and Os-containing n,π-bicluster complex based on β-phenylpropionitrile

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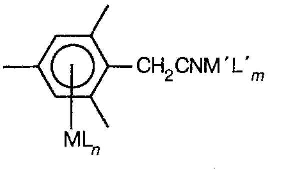
The $PhCH_2CH_2CNOs_3(CO)_{11}$ complex was prepared by the reaction of $Os_3(CO)_{12}$ with β-cyanoethylbenzene, while the reaction with $(CO)_3CrPhCH_2CH_2CN$ gave a heterometallic derivative, $(CO)_3CrPhCH_2CH_2CNOs_3(CO)_{11}$. A bicluster complex, $Co_4(CO)_9PhCH_2CH_2CNOs_3(CO)_{11}$, was synthesized for the first time by the reaction of $PhCH_2CH_2CNOs_3(CO)_{11}$ with $Co_2(CO)_8$; $Co_4(CO)_9PhCH_2CH_2CN$ was also obtained.

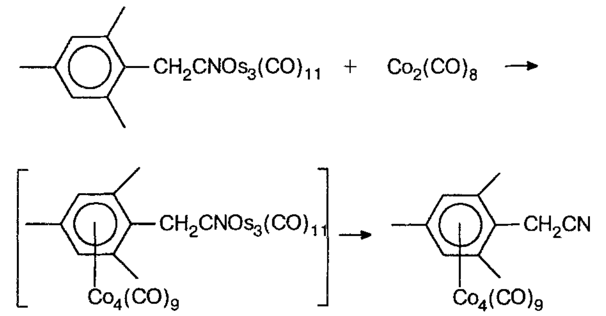
Key words: β-phenylpropionitrile; cobalt clusters, osmium clusters, synthesis; IR spectroscopy.

Previously we prepared a number of n,π-binuclear and polynuclear complexes of transition metals based on mesitylacetonitrile.[1,2] In particular, type **A** complexes, which contain a $Co_4(CO)_9$ fragment as the π-bonded ML_n group and a $W(CO)_5$ or $Mn_2(CO)_9$ fragment as the n-bonded $M'L'_m$ group, were synthesized (see Ref. 1).



A

However, in an attempt to prepare a similar complex with the $Os_3(CO)_{11}$ cluster fragment coordinated at the nitrogen atom of the nitrile group, the previously inaccessible* nitrile-containing π-arene cobalt derivative **B** was isolated.[2]



A' **B**

One may suggest that the close spatial arrangement of the two cluster fragments prevents their simultaneous presence in molecule **A'**. Therefore, at the second stage of our investigation we decided to use β-phenylpropionitrile as the common ligand in which the nitrile function is separated from the benzene ring by two methylene groups. The other reason for the formation of complex **B** could be the low thermal stability of the CN—Os bond in the $CNOs_3(CO)_{11}$ group. This hypothesis needed to be experimentally verified. Finally, it could not be ruled out that upon the action of carbonyl on the intermediate complex **A**, the CN—Os bond cleaves owing to the displacement of the nitrile group by the carbonyl ligand.

In the present work we undertook an attempt to verify these suggestions and to carry out the synthesis of a mixed Co- and Os-containing n,π-bicluster complex based on β-phenylpropionitrile.

Results and Discussion

The reaction of β-phenylpropionitrile with $Os_3(CO)_{12}$ in the presence of trimethylamine oxide afforded a nitrile n-complex of osmium (**1**).

$$PhCH_2CH_2CN + Os_3(CO)_{12} \xrightarrow{Me_3NO} \underset{\mathbf{1}}{PhCH_2CH_2CNOs_3(CO)_{11}}$$

The thermal stability of the resulting complex was confirmed in a control run: the complex did not change upon prolonged (24 h) boiling in hexane (the same was also shown for its mesitylacetonitrile analog).

It should be noted that the interaction of the CN group with $Os_3(CO)_{12}$ occurs so smoothly that it can also be readily carried out for the known complex,

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* The direct reaction[1] of mesitylacetonitrile with cobalt carbonyl affords the n-complex, $MesCH_2CNCo_4(CO)_{11}$.

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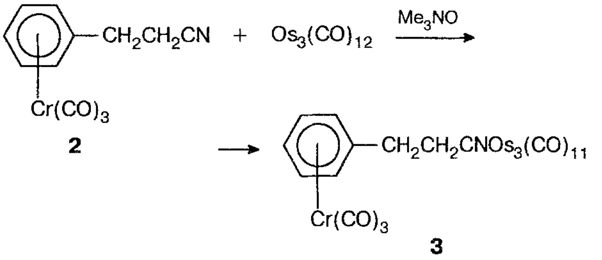
Table 1. Characteristics of the compounds synthesized

Compound	Yield (%)	Decomp.p. /°C	Found/Calculated (%)					Molecular formula
			C	H	Os	Cr	Co	
$PhCH_2CH_2CNOs_3(CO)_{11}$ (**1**)	74	118—121	23.66 23.70	0.89 0.90	56.28 56.50	—	—	$C_{20}H_9NO_{11}Os_3$
$(CO)_3CrPhCH_2CH_2CNOs_3(CO)_{11}$ (**3**)	28	128—132	24.79 24.11	0.95 0.79	—	4.91 4.54	—	$C_{23}H_9CrNO_{14}Os_3$
$(CO)_9Co_4PhCH_2CH_2CNOs_3(CO)_{11}$ (**4**)	14	105—109	22.88 23.26	0.90 0.60	—	—	15.30 15.74	$C_{29}H_9Co_4NO_{20}Os_3$

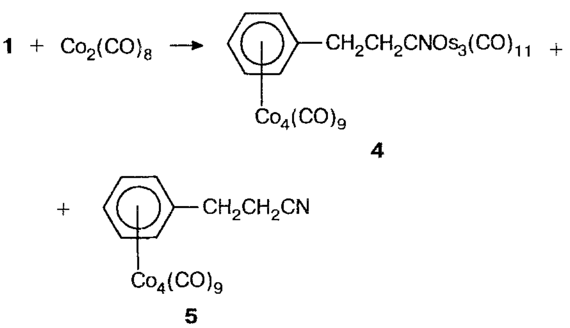
Note. For complex **1** m.p. (decomp.) is given, the other compounds decompose without melting.

$(CO)_3CrPhCH_2CH_2CN$ (**2**), containing the π-bonded tricarbonylchromium fragment.[3]



This reaction gave compound **3** which turned out to be more stable than the mesitylacetonitrile analog[2] and was isolated in the analytically pure state.

Nitrile complex **1** was used for preparing the bicluster complex $Co_4(CO)_9PhCH_2CH_2CNOs(CO)_{11}$ (**4**) containing Co and Os. Actually, the target product forms when compound **1** is boiled with $Co_2(CO)_8$ in hexane, but, along with it, the η^6-arene nitrile-containing cobalt cluster (**5**) can be detected (its analog was the only product in the case of mesitylacetonitrile).[2]



When the duration of the reaction is increased, the yield of compound **4** decreases, while that of compound **5** increases. This may indicate that prolonged boiling of complex **1** (or **4**) in the presence of $Co_2(CO)_8$, results in the cleavage of the CN—Os bond. To confirm this, we carried out a control reaction with $MeCNOs_3(CO)_{11}$. In fact, boiling this compound with $Co_2(CO)_8$ in hexane results in its complete decomposition to give $Os_3(CO)_{12}$ in 38 % yield.

$$MeCNOs_3(CO)_{11} + Co_2(CO)_8 \xrightarrow[\Delta]{C_6H_{14}} Os_3(CO)_{12}$$

Thus, it has been shown that the nitrile ligand is displaced from the complex by carbon monoxide. There is a good probability that a similar process leads to the decomposition of complex **4** and its mesitylacetonitrile analog. At the same time, the fact that in the case of β-phenylpropionitrile the mixed product **4** can still be isolated, attests that steric factors play some role.

The structures of the compounds obtained (**1**, **3**, and **4**) were confirmed by the data of elemental analysis (Table 1) and the IR spectra in the metal-carbonyl region (Table 2). Complex **2** proved not to be stable enough for satisfactory elemental analysis to be carried out, and was identified on the basis of its IR spectrum and the similarity of its R_f on Silufol with the R_f of the mesitylacetonitrile analog. Unfortunately, attempts to grow a crystal of complex **4** for an X-ray structural investigation were unsuccessful.

It is significant that the IR spectrum of the heterometallic complex **3** is a superposition of the spectra of complexes **1** and **2**, while the spectrum of complex **4**

Table 2. The IR spectra of compounds **1**—**5** (in heptane)

Compound	$\nu(C{\equiv}O)/cm^{-1}$
1	1102 w, 2050 s, 2038 s, 2019 m, 1999 s, 1982 m
2	1980 s, 1916 m, 1908 m
3	2065 s, 2050 m, 2036 m, 2030 s, 2017 m, 2000 s, 1978 m, 1915 w, 1906 w
4*	2072 m, 2060 s, 2052 s, 2028 s, 2009 m, 1981 w, 1850 w, 1814 w
5	2074 s, 2066 w, 2029 s, 2011 s, 1998 m, 1828 m

* In CH_2Cl_2.

is a superposition of those of **1** and **5**, which implies that there is no mutual influence of the metalcarbonyl groups. It is of interest that the splitting of the *E*-band in the spectrum of the tricarbonylchromium fragment typical of the starting compound **2** is retained for the bimetallic complex **3**.

Experimental

Complexes **1** and **3** were prepared by analogy with mesitylacetonitrile derivatives,[2] complex **2** was synthesized by the previously described procedure.[3] The IR spectra were recorded on a Specord 75 IR spectrophotometer in heptane.

The reaction of complex 1 with $Co_2(CO)_8$. A mixture of 0.1 g (0.1 mmol) of complex **1** and 0.1 g (0.3 mmol) of $Co_2(CO)_8$ in 70 mL of hexane was boiled for 6 h under argon and chromatographed on a column with silica gel; the elution was carried out with petroleum ether—methylene chloride mixtures, the polarity of the eluent was gradually increased. In addition to a great amount of cobalt carbonyl, 5 mg (8 %) of complex **5** was isolated from the first green band, and 21 mg (14 %) of complex **4** was obtained from the second green band. When the duration of the reaction was increased to 16 h, the yield of compound **5** increased to 10 mg (16 %), and that of **4** decreased to 1 mg.

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