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SHORT PAPER

Synthesis of triphenyl-phosphine, -arsine and -stibine derivatives of phenylmethinyltricobalt enneacarbonyls and their catalytic properties

Yun-pu Wang, Zi-qiang Lei,* Han-yu Feng and Yong-hong Liu
Department of Chemistry, Northwest Normal University, Lanzhou (730070), People's Republic of China

Mono-substituted triphenyl-phosphine, -arsine and -stibine derivatives of phenylmethinyltricobalt enneacarbonyls $PhCCo_3(CO)_8L$ (where $L = PPh_3$, $AsPh_3$ and $SbPh_3$) were synthesized. The $Co(2p_{3/2})$ binding energy (E_b) was lowered from 781.3 eV in $PhCCo_3(CO)_9$, to 780.0 eV in $PhCCo_3(CO)_8PPh_3$, to 780.3 eV in $PhCCo_3(CO)_8AsPh_3$ and to 780.5 eV in $PhCCO_3(CO)_8SbPh_3$. Hydroformylation selectivity to total aldehyde and alcohol of the substituted clusters $PhCCo_3(CO)_8L$ was about 100%, but that of the parent cluster $PhCCo_3(CO)_9$ was 93.8%. Hydroformylation products of styrene and di-isobutene were the completely normal aldehyde when using $PhCCo_3(CO)_8AsPh_3$ as catalyst.

Keywords: Arsine- and stibine-substituted metal clusters, cobalt complex, hydroformylation, binding energy

INTRODUCTION

The chemical activity of metal clusters has much to do with their metal–ligand bonds. In order to obtain useful catalysts, it is very important to adjust or change stabilities and catalytic properties of metal clusters by selecting various ligands with which the metal clusters may be coordinated. Phosphine-coordinated metal clusters are well documented,[1–5] but there has been less study of arsine- and stibine-substituted metal clusters. In this paper, mono-substituted tricobalt clusters $PhCCO_3(CO)_8L$ [where $L = PPh_3$ (**1**), $AsPh_3$ (**2**) and $SbPh_3$ (**3**)] were employed as catalysts in olefin hydroformylation. The clusters make it possible for us to use carbon monoxide and show promise of future commercial success.

* Author to whom correspondence should be addressed.

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Table 1 Binding energies (E_b) of $Co(2p_{3/2})$ in clusters **1–3** and $PhCCo_3(CO)_9$

Cluster	Binding Energy of $Co(2p_{3/2})$, E_b (eV)	ΔE_b of $Co(2p_{3/2})$ (eV)
$PhCCo_3(CO)_9$	781.3	
1	780.0	−1.3
2	780.3	−1.0
3	780.5	−0.8

EXPERIMENTAL

Synthesis of $PhCCo_3(CO)_8SbPh_3$ (3)

Under an argon atmosphere, 1.5 mmol $SbPh_3$ and 1.0 mmol $PhCCo_3(CO)_9$ were placed in a 250 cm^3 three-necked flask, to which 70 cm^3 of dry ether was then added. The mixture was refluxed with stirring for 4 h and then cooled to room temperature. The solvent was removed under vacuum from the combined filtrates to give a dark-brown viscous oil, which was then purified by chromatography on a silica-gel column using petroleum ether as the eluant. The analytical sample was obtained by recrystallization from an n-pentane solution at −10 °C, with a yield of 0.3 g (36%) of black $PhCCo_3(CO)_8SbPh_3$. The atomic ratio of Co to Sb was 2.8:1 (required Co/Sb = 3.0:1.0), using ICP (ARL Model 3250). Carbon and hydrogen were analysed using a Carlo Erba 1106 analyser (Found C = 47.7%, H = 2.4%; calculated C = 47.0%, H = 2.4%).

Hydroformylation procedure

Hydroformylation was carried out in a 20 cm^3 bomb. The hydroformylation products were analysed by GLC using a model 2305E gas chromatograph with hydrogen as carrier gas; a 3 m × 3 mm squalance column was used for hydrocarbons and

Table 2 IR spectra of clusters **1–3** and $PhCCo_3(CO)_9$

Cluster	ν(C≡O (cm^{-1})					
$PhCCo_3(CO)_9$	2101 (m)	2056 (s)	2040 (vs)	2021 (s)		
1	2074 (m)	2033 (s)	2006 (vs)	1992 (s)	1983 (s)	1960 (m)
2	2080 (m)	2039 (s)	2014 (vs)	2003 (s)	1975 (s)	1963 (m)
3	2079 (m)	2047 (s)	2014 (vs)	2003 (s)	1979 (s)	1960 (m)

Table 3 The catalytic activity of different clusters[a]

Cluster	Conversion (mol%)	Yield of aldehyde and alcohol (mol %)	Selectivity (% aldehyde and alcohol)	Specific activity conversion (mol Co s)$^{-1}$	n/i[d]
$PhCCo_3(CO)_9$[b]	100.0	93.8	93.8	6.0	1.0
1[c]	92.9	92.9	100.0	3.2	0.2
2[c]	97.0	97.0	100.0	3.6	0.5
3[c]	64.2	64.2	100.0	2.5	0.9

[a] Reaction conditions: Catalyst, 0.1 g; $H_2/CO = 1$, 40 kg cm^{-2}; 1-heptene, 1 cm^3; toluene, 5 cm^3; 130 °C. Duration: [b] 6 h; [c] 20 h. [d] Mol ratio of normal/iso-aldehyde.

Table 4 Data of catalytic reaction of cluster **2**[a]

Olefin	Conversion (mol %)	Yield of aldehyde and alcohol (mol %)	Selectivity (%)	n/i
1-Heptene	97.0	97.0	100.0	0.5
2-Octene	89.2	89.2	100.0	1.3
Cyclohexene	71.5	71.5	100.0	
Di-isobutene	41.6	41.6	100.0	n only
Styrene	86.7	86.7	100.0	n only

[a] Reaction conditions the same as Table 3, footnote a, except for the olefin. Duration 20 h.

Table 5 The catalytic activity of different clusters[a]

Cluster[b]	Conversion (mol %)	Yield of aldehyde and alcohol (mol %)	Selectivity (%)	n/i
1	89.7	89.7	100.0	0.5
2	84.3	84.3	100.0	1.6
3	50.3	50.3	100.0	1.3

[a] Reaction conditions the same as Table 3. Duration 20 h. [b] Used as catalyst after exposure to air at room temperature for half a year.

a 5 m × 3 mm polyethylene glycol adipate column for alcohols and aldehydes.

$PhCCo_3(CO)_8PPh_3$ (**1**), $PhCCo_3(CO)_8AsPh_3$ (**2**) and $PhCCo_3(CO)_9$ were prepared according to published methods.[3,6] IR spectra were recorded in KBr disks using a PE model 983 instrument.

RESULTS AND DISCUSSION

XPS and IR spectra were obtained using a PHI-550 ESC/SA and a Perkin–Elmer model 983 instrument respectively. The results are listed in Tables 1 and 2. The Co($2p_{3/2}$) binding energies (E_b) of the substituted clusters **1–3** were lowered compared with that of the parent cluster $PhCCo_3(CO)_9$. E_b is 780.0 eV in **1**, 780.3 eV in **2**, 780.5 eV in **3** and 781.3 eV in $PhCCo_3(CO)_9$. These changes of Co($2p_{3/2}$) binding energy reveal that electron-donating substituents such as triphenyl-phosphine and -arsine increase the charge on the cobalt atoms,[7–9] which strengthens cobalt–cobalt (Co–Co) and cobalt–carbon (Co–C) bonds in the clusters and which increases back-donation from cobalt atoms to the 2*p* orbitals of the coordinated carbonyls of the cluster, hence weakening carbon–oxygen (C–O) bonds in the carbonyl. This consequently reduces the catalytic

activity of the cluster and makes the carbonyl stretching frequencies in the IR spectra of the cluster shift to lower values.

Differential thermal analysis showed that the cluster **1** decomposed at 139 °C, **2** at 152 °C and **3** at 130 °C.

The catalytic properties of clusters **1–3** are shown in Tables 3, 4 and 5.

Specific activity

The hydroformylation of 1-heptene catalysed by clusters **1**, **2** and **3** and $PhCCo_3(CO)_9$ was investigated and the results show (Table 2) that the specific activity was reduced when one of the carbonyls of the parent cluster $PhCCo_3(CO)_9$ was replaced by triphenylphosphine (or triphenylarsine, or triphenylstibine). This result relates to the stability of the cluster, which is associated with the binding energy of $Co(2p_{3/2})$.

Selectivity and effect of the olefin structure

Table 3 shows that the aldehyde and alcohol selectivity of 1-heptene was raised to 100% by using substituted clusters **1**, **2** and **3** as catalyst compared with 93.8% for $PhCCo_3(CO)_9$. The results of hydroformylation of 1-heptene, 2-octene, cyclohexene, di-isobutene and styrene are given in Table 4, which shows that the conversion of olefins decreased in the following order: 1-heptene > 2-octene > styrene > cyclohexene > di-isobutene. It is useful that the hydroformylation products of styrene and di-isobutene were about 100% of the normal aldehydes when these olefins reacted with a mixed gas (CO/H_2) using $PhCCo_3(CO)_8AsPh_3$ as a catalyst.

CONCLUSION

Phosphine-, arsine- and stibine-substituted cobalt metal clusters were synthesized and these clusters provide a promising catalyst system for olefin hydroformylation.

The catalytic properties were as follows:

(1) The selectivity was about 100% (catalysts **1–3**).
(2) The conversion of olefins decreased in this order: 1-heptene > 2-octene > styrene > cyclohexene > di-isobutene (for catalyst **2**).
(3) The hydroformylation products of styrene and di-isobutene were about 100% normal aldehyde (for catalyst 2).

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