Inorganica Chimica Acta, 14 (1975) L39

Paramagnetic Phosphido Cobalt Carbonyl Clusters

L. MARKÓ

Department of Organic Chemistry, University of Chemical Engineering, H-8200 Veszprém, Hungary

and B. MARKÓ

Hungarian Oil and Gas Research Institute, H-8200 Veszprém, Hungary

(Received June 11, 1975)

$RPCl_2$ derivatives react vigorously with $Co_2(CO)_8$ dissolved in hexane forming $CoCl_2$ and several cobalt carbonyl complexes. Monitoring the reaction by IR spectroscopy and using stepwise addition the $RPCl_2$: $Co_2(CO)_8$ ratio was adjusted to values (0.5 - 0.6) at which the hexane soluble part of the reaction products contained practically only the new cobalt carbonyl clusters $RPCo_3(CO)_9$ (R = Ph, t-Bu, Et_2N). These complexes were isolated after filtration from the deep green solutions at −78 °C and purified by recrystallisation from hexane (yields 45 - 60%). All three compounds gave satisfactory elemental analyses.

The new compounds form air-sensitive paramagnetic black crystals (average magnetic moments 1.7 BM) soluble in organic solvents. Their infrared spectrum (see Table) suggests the trigonal pyramidal structure characteristic for $ZCo_3(CO)_9$ complexes.

TABLE. ν_{CO} Stretching Frequencies of $ZCo_3(CO)_9$ Complexes (cm^{-1}, hexane solution).

	(m)	(vs)	(s)	(w)
$PhPCo_3(CO)_9$	2094	2039	2033(sh)	2009
$t\text{-}BuPCo_3(CO)_9$	2093	2036	2031	2007
$Et_2NPCo_3(CO)_9$	2091	2032	2027(sh)	2004
$PhCCo_3(CO)_9$	2101	2054	2040	2021
$SCo_3(CO)_9$	2103(w)	2050	2038	2024

As compared to diamagnetic $PhCCo_3(CO)_9$ and paramagnetic $SCo_3(CO)_9$ the ν_{CO} frequencies are shifted towards somewhat lower values in accordance with the higher basicity of the RP group compared to that of RC or S.

The electron in surplus of the noble gas configuration is probably located in an antibonding orbital of the Co_3 cluster and should cause – analogously to that observed in $SCo_3(CO)_9$[3] – a significant increase of the Co–Co distances above the normal single bond value.

References

1 G. Bor, L. Markó and B. Markó, *Chem. Ber., 95*, 333 (1962).
2 L. Markó, G. Bor, E. Klumpp, B. Markó and G. Almásy, *Chem. Ber., 96*, 955 (1963).
3 D. L. Stevenson, C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc., 93*, 6027 (1971).