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Preliminary communication

The chemistry of the Group V metal carbonyls

I. The preparation of some seven coordinate derivatives of niobium, tantalum and vanadium

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Although the hexacarbonyl metallate ions of the Group V metals have been known[1] for nearly ten years, the chemistry of these species, particularly those of niobium and tantalum, has received scant attention. In this communication we report some of our studies on these systems, in particular the isolation of the new seven coordinate complexes $Ph_3SnM(CO)_6$, $Ph_3SnM(CO)_5PPh_3$ (M = V, Nb, and Ta), $Ph_3PAuM(CO)_5PPh_3$ (M = V and Ta), and $Ph_3PAuTa(CO)_6$. In addition we report a new improved synthesis of the known[2] $[V(CO)_5PPh_3]^-$ anion and the first characterization of the corresponding anions of niobium and tantalum.

The triphenylphosphine substituted pentacarbonyl metallates were prepared from the hexacarbonyl metallates by the following procedure. A slurry of the hexacarbonylate salt and triphenylphosphine (1/2 molar ratio) in benzene was vigorously stirred with an excess of 4*N* HCl under strictly anerobic conditions. The benzene phase became deep red. It was quickly separated and treated with an excess of a 1% sodium amalgam. The resulting crude sodium salt was converted, by metathesis, to either the tetraethylammonium salt, in the case of vanadium, or the tetraphenylarsonium salts for niobium and tantalum. The golden yellow $[Et_4N][V(CO)_5PPh_3]$ was obtained in 30% yield and was identical to the material obtained by the previously published procedure[2]. The orange-red niobium and tantalum complexes were produced in much lower yields (ca. 1%) but at present this method represents the only synthesis of these species.

Since triphenylphosphine does not substitute the hexacarbonylate salts directly it is felt that the reactions may go via the unstable, as yet uncharacterized, hydrido intermediates $[HM(CO)_6]$ and $[HM(CO)_5PPh_3]$ (M = V, Nb and Ta).

In general the complexes derived from the $[M(CO)_5PPh_3]^-$ ions are more thermally and oxidatively stable than the ones obtained from the unsubstituted ions. We have prepared the new seven coordinate species $Ph_3SnM(CO)_5PPh_3$ (M = V, Nb, and Ta)

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TABLE 1

THE INFRARED SPECTRA IN THE CARBONYL REGION

Complex	Solvent	C–O Stretching frequencies (cm^{-1})
$[Ph_3PAuV(CO)_6]$[a]	C_6H_{12}	2042vs, 1988m, 1958m, 1922s, 1888m(sh), 1870m
$[Ph_3PAuTa(CO)_6]$	C_6H_{12}	2055vs, 1985m, 1955m, 1920s, 1900m(broad sh)
$[Ph_3SnV(CO)_6]$	C_6H_{12}	2067vs, 2012m, 1987s, 1958vs, 1932vs
$[Ph_3SnTa(CO)_6]$	C_6H_{12}	2075vs, 2005m(sh), 1985s, 1960s(sh), 1945vs
$[Ph_3PAuV(CO)_5PPh_3]$	CH_2Cl_2	1995s, 1922s, 1875vs, 1810s
$[Ph_3PAuTa(CO)_5PPh_3]$	CH_2Cl_2	2010s, 1920s, 1880vs, 1815s
$[Ph_3SnV(CO)_5PPh_3]$	CH_2Cl_2	2030s, 1970m, 1920vs(sh), 1902vs, 1878s
$[Ph_3SnNb(CO)_5PPh_3]$	CH_2Cl_2	2050s, 1977m, 1929vs, 1885s
$[Ph_3SnTa(CO)_5PPh_3]$	CH_2Cl_2	2045s, 1970m, 1925vs, 1887s
$[Et_4N][V(CO)_5PPh_3]$[a]	Nujol mull	1959m, 1845m(sh), 1810vs, 1766s
$[Ph_4As][Nb(CO)_5PPh_3]$	Nujol mull	1968m, 1862m, 1803vs, 1780s
$[Ph_4As][Ta(CO)_5PPh_3]$	Nujol mull	1968m, 1860m, 1800vs, 1782s

[a] These compounds have been reported previously [1,2].
[b] All compounds have satisfactory analytical data.

by two routes. The first, the reaction of Ph_3SnCl with salts of the $[M(CO)_6]^-$ ions gives rather unstable intermediates, $Ph_3SnM(CO)_6$, subsequent reaction of which with triphenylphosphine results in facile replacement of carbon monoxide at 0°. Alternatively, they could easily be prepared by the direct reaction of Ph_3SnCl with salts of the $[M(CO)_5PPh_3]^-$ ions. The infrared spectra (Table 1) of the complexes produced by both methods are identical confirming that the products are the same for the two pathways. The yellow $Ph_3SnV(CO)_6$, and the orange $Ph_3SnTa(CO)_6$ are thermally unstable and decompose slowly, in an inert atmosphere at -10°, over several weeks. The solids and solutions are extremely air sensitive. The orange $Ph_3SnV(CO)_5PPh_3$ the red-orange $Ph_3SnNb(CO)_5PPh_3$, and the deep red $Ph_3SnTa(CO)_5PPh_3$ are significantly more stable and do not decompose over several months at room temperature under an inert atmosphere. The phosphine substituted complexes are stable in THF while the unsubstituted derivatives are heterolytically cleaved to generate the hexacarbonylate salts.

The reaction of Ph_3PAuCl and salts of the $[Ta(CO)_6]^-$ ions react quantitatively in THF solution, at 0°, to give $Ph_3PAuTa(CO)_6$. This complex was obtained as moderately air-stable crystals. The complex decomposes completely when dissolved in THF at room temperature over a period of 24 h. A small amount (ca. 4%) of dark-red $Ph_3PAuTa(CO)_5PPh_3$ was the only identifiable product. This complex was subsequently prepared directly from $[Ph_4As][Ta(CO)_5PPh_3]$ and Ph_3PAuCl. The gold–tantalum hexacarbonyl species, unlike the tin–tantalum hexacorbonyl one does not undergo rapid heterolytic cleavage in THF solution. Surprisingly, a rapid cleavage of $Ph_3PAuTa(CO)_6$ by triphenylphosphine occurs in this solvent to give the $[Ta(CO)_6]^-$ ion rather than the expected substitution product. For spectral comparison with the gold–tantalum compounds, we have synthesized the known[3] $Ph_3PAuV(CO)_6$ and the new seven coordinate complex $Ph_3PAuV(CO)_5PPh_3$.

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