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COMMUNICATION

NIOBIUM AND TANTALUM PHOSPHONATO COMPLEXES BY ARBUZOV-LIKE REARRANGEMENT

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Abstract—Niobium and tantalum metallophosphines give rise to phosphonate complexes of the type [$Cp_2M(PR_2Me)(POR'R'')$] by intramolecular Arbuzov rearrangement probably involving nucleophilic attack by phosphorus as shown by ^1H and ^{31}P NMR. The reaction rate depends both on the phosphido group and the metal atom. The Lewis basicity of the phosphoryl group in [$Cp_2M(PR_2Me)(POR'R'')$] is used in reactions with $Cr(CO)_6$ to synthesize a bimetallic complex as shown by its ^1H and ^{31}P NMR and IR spectra.

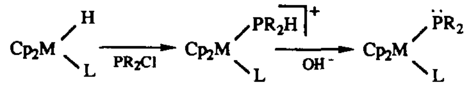
Arbuzov rearrangements are well-known reactions both in organic[1] and in organometallic[2] chemistry. With transition metal complexes most examples are encountered from cationic species bearing a metal-bound phosphito ligand: the dealkylation process giving phosphonate complexes are carried out by nucleophilic attack of halide or pseudohalide anions[2,3] (ionic mechanism); however, an intramolecular dealkylation involving a sulfur atom has been reported.[4] In the course of our work on the synthesis of metallophosphines and their use as precursors for bimetallic systems, we have observed unexpected Arbuzov-like intramolecular rearrangements and we wish to report in this communication our results.

We have recently described a new synthetic route to metallophosphines **3** as outlined in Scheme 1.

Monohydrides **1** react with chlorophosphines PR_2Cl to give phosphonium salts **2** which after deprotonation by OH^- lead to the metallophosphines **3**.[5] When L = CO and R = Me or Ph the metallophosphines **3** are effectively obtained in good yields (60%) and can be subsequently involved in the synthesis of phosphido bridged heterobimetallic complexes.[6] However the structure of reaction products is fundamentally modified when the above transformations are performed with phosphito derivatives [$L = P(OMe)_3$ or $PPh(OMe)_2$]: the phosphonate complexes **4** are isolated as sole products (M = Nb, R = Me; M = Ta, R = Ph) or accompanied by the metallophosphines **3** in variable amounts (M = Nb, R = Ph); for the latter complete transformation to **4** is obtained over 24 h.

Clearly an intramolecular Arbuzov-like rearrangement can be assumed to account for the formation of metallophosphonates **4**: the phosphorus lone pair achieves the nucleophilic attack on the methyl group of the ester giving the dealkylation reaction and the conversion of phosphorus(III) to phosphorus(V) (Scheme 2).

Steric and electronic effects strongly influence the reaction rate as evidenced by the fast rearrangement observed with the more basic and less hindered PMe_2 phosphido group. Furthermore the enhanced



1 **2** **3**

M=Nb,Ta R=Me,Ph L=CO,P(OMe)$_3$,PPh(OMe)$_2$

Scheme 1.

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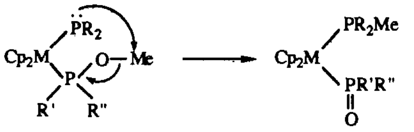

3

4 a:R'=R"=OMe
b:R'=OMe,R"=Ph

Scheme 2.

basic character of a tantalum bonded phosphido group is clearly exemplified by comparison of ^{31}P NMR data: in metallophosphines **3** ($L = CO$, $R = Ph$) ^{31}P resonances are found at -30 and -3 ppm for $M = Ta$ and Nb respectively.

Spectroscopic data establish unambiguously the structure of metallophosphonates **4**. ^{31}P NMR spectra shown conversion of phosphorus(III) phosphito to phosphorus(V) phosphonato ligand leads to a characteristic upfield shift (about 50 ppm) in accord with literature[2] data; ^{1}H NMR spectra provide further proof; the most striking example can be found with the metallophosphine **3** ($M = Nb$, $R = Ph$, $L = P(OMe)_3$): as mentioned above its rearrangement rate is sufficiently slow to permit detection of both phosphito and phosphonato species. The methoxy groups resonate at 3.20 ppm in **3** and at 3.78 ppm in the corresponding "Arbuzov product" **4**; the methyl signal of the "new" ligand PPh_2Me appears at 2.29 ppm. Table 1 summarizes the main ^{1}H NMR data for complexes **4**.

It is worth noting that the Cp non-equivalence in complexes **4b** are owing to the presence of a chiral phosphorus centre in the phosphonato group. IR detection of the P=O stretching frequency is uncertain because this is obscured by C—C and C—O modes.

In order to test the ability of the phosphoryl oxygen to bind electrophile we have examined the behaviour of **4a** ($M = Nb$) toward the unsaturated organometallic species $[Cr(CO)_5]$.[7] The reaction, performed in THF, proceeds cleanly and leads after treatment to the heterobimetallic complex $[Cp_2Nb(PMe_2Ph)P(OMe)_2OCr(CO)_5]$ in a reasonable yield (40%).

The spectroscopic data are listed in Table 2.

Thus metallophosphanes **4** show interesting possibilities to access to new bimetallic structures: work in this area is currently underway.

Table 1. ^{1}H NMR data for Arbuzov complexes of **4** [δ(ppm), J(Hz) in C_6D_6]

Complexes **4**	Cp $J[^{31}P,H]$	PR_2Me $J[^{31}P,H]$	MeO $J[^{31}P,H]$
4a ($M = Nb$			
$R = Me$	4.64 t ($J = 2.1$)(10H)	1.06 d ($J = 7.9$)(9H)	3.71 d ($J = 9.8$)(6H)
$R = Ph$	4.65 t ($J = 2.1$)(10H)	2.29 d ($J = 7.7$)(3H)	3.78 d ($J = 9.8$)(6H)
4b ($M = Nb$)			
$R = Me$	4.47 t ($J = 2.1$)(5H) 4.52 t ($J = 2$)(5H)	1.12 d ($J = 7.9$)(9H)	3.45 d ($J = 9.9$)(3H)
$R = Ph$	4.48 dd ($J = 2.3$; $J = 1.7$)(5H) 4.51 dd ($J = 2.1$; $J = 1.7$)(5H)	2.53 d ($J = 8$)(3H)	3.47 d ($J = 9.9$)(3H)
4a ($M = Ta$)			
$R = Ph$	4.54 t ($J = 2$)(10H)	2.38 d ($J = 8$)(3H)	3.81 d ($J = 9.6$)(6H)

Table 2. IR and NMR data of $[Cp_2Nb(PMe_2Ph)P(OMe)_2OCr(CO)_5$

IR (THF) $\nu_{co}(cm^{-1})$	^{31}P NMR (CD_3COCD_3)	^{1}H NMR [CD_3COCD_3 δ(ppm)J(Hz)]			
2061w	PPh_2Me 56.9	Ph 7.05–7.25	Cp 4.37	Me 1.93	MeO 3.22
1923s	$P(OMe)_2$ 171	(5H)	t ($J = 2.2$)	d ($J = 7.9$)	d ($J = 10$)
1867s			(10H)	(6H)	(6H)

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