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Preliminary communication

The first evidence for a stereostable centrometalled chirality in a dicyclopentadienyltantalum complex

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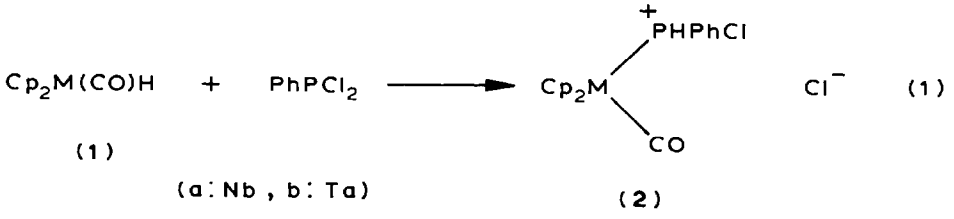
Abstract

Reaction of dichlorophenylphosphine with monohydrides $Cp_2M(CO)H$ (M = Nb or Ta) gives the salts $[Cp_2M(CO)(PPhClH)]^+ Cl^-$ in good yields. In a basic medium these salts give the neutral complexes $Cp_2M(CO)$ [P(O)(H)Ph]. In a reaction starting from the chiral hydride $Cp^*CpTa(CO)H$, ($Cp^* = C_5Me_5$), two diastereoisomers are obtained, and can be isolated as stereostable structures.

Chiral organometallic complexes are of great interest owing to their potential use in catalytic enantioselective syntheses [1]. Two structural types can be distinguished, depending on whether the molecular chirality arises from one ligand or from the asymmetric environment around the metallic atom. In the latter case, configurational stability is, of course, necessary to prevent racemization of optically active compounds. Numerous transition elements have served as chiral centers [2], but examples involving group 5 elements are rather scarce. Recently, we described chiral but stereolabile dicyclopentadienylniobium(III) complexes [3] and, we now report an example of a chiral configurationally-stable tantalum derivative.

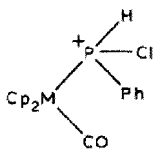
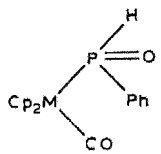
As a first step we examined the stereostability at the Ta (or Nb) center on the time scale of the ^1H NMR spectroscopy. We made the salts **2** by reaction of the monohydrides **1** with dichlorophenylphosphine (eq. 1).

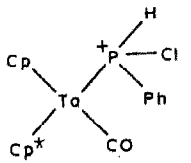
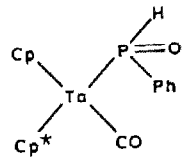


0022-328X/88/$03.50

Table 1

NMR and IR data

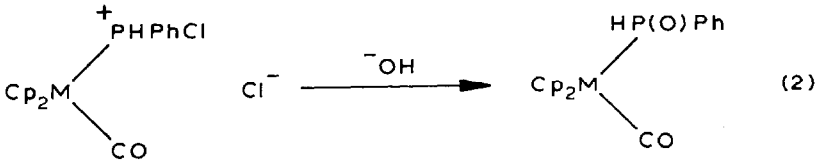
Compound		^{1}H NMR [a]			^{31}P NMR [b]	IR [c]
		P–H	Cp	Cp*		(cm^{-1})
	**2a** M = Nb	8.24 d (J(P–H) 384 Hz)	5.42 d (J(Cp–P) 2.4Hz) 5.82 d (J(Cp–P) 2.8 Hz)		126	ν(CO) 1959
	2b M = Ta	8.55 d (J(P–H) 392 Hz)	5.3 d 5.78 d (J(Cp–P) 2.4 Hz)		99.3	ν(CO) 1949
	**3a** M = Nb	8.9 d (J(P–H) 340 Hz)	4.83 d (J(Cp–P) 2 Hz) 5.13 d (J(Cp–P) 2.4 Hz)		92	ν(CO) 1922 ν(PH) 2204
	3b M = Ta	8.58 d (J(P–H) 334 Hz)	5.06 d 5.5 d (J(Cp–P) 2.3 Hz)		64.8	ν(CO) 1905 ν(PH) 2225

	$2'\alpha + 2'\beta$	8.08 d 8.25 d (J(P–H) 370 Hz)	5.51 d (J(Cp–P) 2.7 Hz) 5.1 d (J(Cp–P) 2.1 Hz)	2.12 d (J(Cp*–P) 0.5 Hz) 2.25s		ν(CO) 1910
	$3'\alpha$	8.42 d (J(P–H) 320 Hz)	5.16 d (J(Cp–P) 2.4 Hz)	1.94 s	73.3	ν(CO) 1878
	$3'\beta$	8.42 d (J(P–H) 328 Hz)	4.84 d (J(Cp–P) 1.9 Hz)	2.14 d (J(Cp*–P) 0.4 Hz)	70.6	ν(PH) 2216

[a] In CD_3COCD_3, (δ (ppm)/TMS) excepted for compound **3a** (C_6D_6). [b] In CD_3COCD_3 (δ (ppm)/H_3PO_4). [c] In KBr, excepted for **2α,2'β** (Nujol).

The formation of these salts can involve nucleophilic substitution at the phosphorus atom by the d^2 monohydrides **1** followed by an H^+ transfer to the basic heteroatom. As expected, the chiral phosphorus center induces non-equivalence of the Cp ligands, which in the ^1H NMR spectrum show two doublets ($\Delta\nu$ 40 Hz). The signal from the P-bonded hydrogen nucleus appears near 8.5 ppm (J(PH) ≃ 390 Hz), and the γ(P–H) bond in the near 2230 cm^{-1} (Table 1).

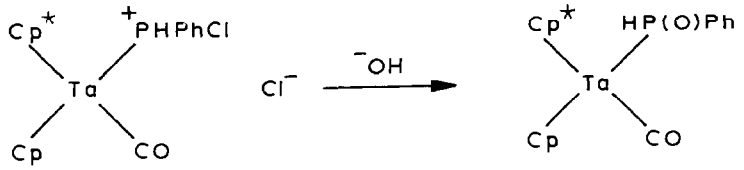
Treatment of the salts **2** with a basic reagent gives the neutral complexes **3** (eq. 2).



(2) (2) (3)

These complexes are formed by the expected deprotonation reaction accompanied by nucleophilic displacement of the chloride atom: the hydroxyl form tautomerizes to give the phosphoryl form: MP(OH)Ph ⇌ MP(O)(H)Ph. The ^1H NMR and IR spectra show clearly the presence of P–H bonds and the non-equivalence of the Cp groups.

When the chiral Cp*CpTa(CO)H (**1′** Cp* = C_5Me_5) was treated with dichlorophenylphosphine, a mixture of two distereoisomeric salts (**2′α** and **2′β**) was obtained, as indicated by the ^1H NMR spectrum (which showed two doublets for PH, two doublets for Cp, and two singlets for Cp*). The relative intensities of these signals indicated a slight diastereoselectivity (60/40).



(2′α + 2′β) (3′α + 3′β)

As expected, reaction with NaOH gives rise to a diastereoisomeric mixture of the phosphoryl complexes **3′α** and **3′β**. The main spectroscopic data of **2′** and **3′** are shown in Table 1, and are very similar to those for **2b** and **3b**. Complete separation of **3′α** and **3′β** was achieved by low temperature chromatography (with methanol as eluent). The stereostability of each form was investigated by ^1H NMR spectrometry, and no epimerization **3′α** ⇌ **3′β** was observed.

The fact that these diastereoisomeric species can be separated and isolated pure illustrates the stereostability at the tantalum chiral center. This feature could be useful in stereochemical studies and in resolving racemic complexes.

References

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