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REACTION OF THE SALT $[Cp_2Nb(CO)PPhHCl]^+$, Cl^- WITH HO^-, MeO^- AND $Fe(CO)_4^{2-}$: NEW SYNTHETIC ROUTES TO METALLOPHOSPHINITES AND FUNCTIONALIZED PHOSPHIDO-BRIDGED HETEROBIMETALLIC COMPLEXES

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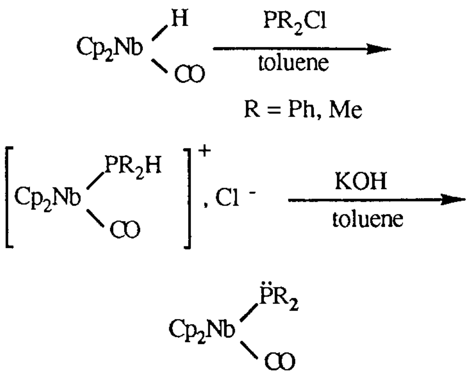
Abstract—The anions HO^- and MeO^- performed deprotonation and nucleophilic substitution at the phosphorus centre in the salt $[Cp_2Nb(CO)PPhHCl]^+$, Cl^-, affording the neutral metallophosphanes $Cp_2Nb(CO)PPhH(O)$ and $Cp_2Nb(CO)PPh(OMe)$, respectively. When the Collman reagent $Fe(CO)_4^{2-}$ was used, the same salt led to a mixture of mono- and dibridged heterobimetallic complexes $Cp_2Nb(CO)(\mu\text{-}PPhH)Fe(CO)_4$ and $Cp_2Nb(\mu\text{-}PPhH, CO)Fe(CO)_3$. Removal by photolysis of one carbonyl ligand from the monobridged compound produced the dibridged one. The treatment of binuclear complexes with KH and CH_3I achieved the substitution of the hydrogen atom at the phosphido bridge by a methyl group. All the new complexes have been characterized by ^1H and ^{31}P NMR and IR spectroscopies.

The coordination of terminal phosphido derivatives of bent metallocenes to metal carbonyl fragments can be considered now as a well known synthetic route to phosphido-bridged heterobimetallic systems.[1] The reaction below[2] represents an example relevant to this possibility where the diphosphido precursor $Cp_2Hf(PEt_2)_2$ has been prepared from Cp_2HfCl_2 and $LiPEt_2$:

$$Cp_2Hf(PEt_2)_2 + Fe_2(CO)_9 \xrightarrow[-Fe(CO)_5,CO]{\text{toluene}, \Delta} Cp_2Hf(\mu-PEt_2)_2Fe(CO)_3. \quad (1)$$

We have recently described an alternative synthetic route to terminal phosphido complexes from the reaction of group 5 or group 6 hydrido derivatives with chlorophosphines.[3-5] The reaction affords in a first step phosphonium salts which are easily deprotonated in basic medium to give metallophosphines. The example below describes the synthesis of metallophosphines derived from niobocene:[4]



(2)

With the aim of preparing new metallophosphanes, we extended this reaction potential to dichlorophosphines $PRCl_2$ and recently reported[6] the reaction between the monohydride complex $Cp_2Nb(CO)H$ and phenyldichlorophosphine leading to the "chlorophosphonium" salt **1**:

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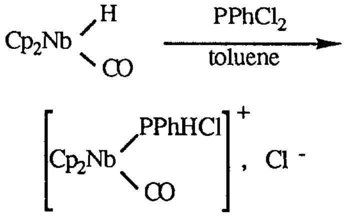

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(3)

The bifunctionality located at the phosphorus atom allows different reaction pathways depending on whether a deprotonation or a substitution reaction takes place in the first step. Consequently, we decided to undertake investigations in this area by treating the salt **1** with organic and organometallic anionic species. In this paper, we report our results on the synthesis of new classes of metallophosphanes by treating the salt **1** with HO^- and MeO^-, as well as on the formation of phosphido-bridged binuclear systems when the Collman reagent $Fe(CO)_4^{2-}$ was used.

EXPERIMENTAL

All reactions were carried out under argon with use of standard Schlenk techniques. The solvents and eluents were distilled under argon from sodium and benzophenone immediately before use. Column chromatographies were prepared under argon and with silica gel (70–230 mesh). IR spectra were recorded with a Nicolet 205 spectrophotometer; ^1H and ^{31}P NMR spectra were recorded on a Bruker WM 400 spectrometer; chemical shifts are given in ppm relative to Me_4Si (^1H) or (external) H_3PO_4 (^{31}P). Elemental (C, H, P) analyses were performed by the "Service Central d'Analyse du CNRS" (Gif sur Yvette). $Cp_2Nb(CO)H$[7] and $Na_2Fe(CO)_4 \cdot 1.5$ dioxane[8] were prepared according to literature procedures. Commercial dichlorophosphine $PPhCl_2$ (STREM) was used as-received.

Preparation of $[Cp_2Nb(CO)PPhHCl]^+$, Cl^- (**1**)

To a toluene solution (20 cm^3) of $Cp_2Nb(CO)H$ (0.5 g, 2 mmol) was added $PPhCl_2$ (0.2 g, 2 mmol). A beige precipitate was formed instantaneously. After 30 min stirring it was filtered, washed with pentane and dried *in vacuo* (yield 0.68 g, 80%). This complex is extremely air sensitive. NMR (δ, ppm): ^1H (D_2O) 5.31 (d, $J = 2.4$ Hz; Cp), 5.59 (d, $J = 2.8$ Hz; Cp), 7.50–7.70 (m, Ph), 8.19 (d, $J = 381$ Hz, PH); ^{31}P (D_2O) 126.0. IR (CH_2Cl_2): $\nu(CO)$ 1964 cm^{-1}. Found: C, 47.3; H, 4.0. Calc. for $C_{17}H_{16}O_1PCl_2Nb$ (**1**): C, 47.3; H, 3.7.

Preparation of $Cp_2Nb(CO)PPhH(O)$ (**2**)

To 0.3 g (0.7 mmol) of dried **1** was added 10 cm^3 of an aqueous solution of KOH (prepared with 1.15 g in 20 cm^3 of water). After 30 min stirring, the complex was extracted with 15 cm^3 of CH_2Cl_2. The organic layer was isolated and evaporated *in vacuo*. The clear orange solid was washed with pentane and dried *in vacuo* giving 0.24 g of **2** (yield 90%). Complex **2** is air sensitive. NMR (δ, ppm): ^1H (C_6D_6) 4.83 (d, $J = 2$ Hz; Cp), 5.13 (d, $J = 2.4$ Hz; Cp), 7.80–8.10 (m, Ph), 8.84 (d, $J = 335$ Hz, PH); ^{31}P (C_6D_6) 92.0. IR (CH_2Cl_2): $\nu(CO)$ 1936 cm^{-1}. Found: C, 52.7; H, 4.4. Calc. for $C_{17}H_{16}O_2PNb$ (**1**): C, 54.3; H, 4.3%.

Preparation of $Cp_2Nb(CO)PPh(OMe)$ (**3**)

To a THF (20 cm^3) suspension of 0.3 g (0.7 mmol) of **1** was added 0.08 g (1.4 mmol) of sodium methylate powder. After 1 h of stirring the solvent was removed *in vacuo* and the solid residue was extracted with 2×10 cm^3 of toluene. After evaporation and drying, the red–maroon complex **3** was obtained in 80% yield (0.24 g). Compound **3** is extremely air sensitive. NMR (δ, ppm): ^1H (C_6D_6) 3.53 (OMe, d, $J_{PH} = 12.6$ Hz), 4.37 (Cp, s), 4.73 (Cp, d, $J_{PH} = 2$ Hz), 6.90–7.70 (Ph, m); ^{31}P (C_6D_6) 227. IR (THF): $\nu(CO)$ 1915 cm^{-1}. Found: C, 49.5; H, 4.5. Calc. for $C_{18}H_{18}O_2PNb$ (**3**): C, 55.4; H, 4.7%.

Preparation of $Cp_2Nb(CO)(\mu\text{-}PPhH)Fe(CO)_4$ (**4**) *and* $Cp_2Nb(\mu\text{-}PPhH)(\mu\text{-}CO)Fe(CO)_3$ (**5**)

To a THF suspension (30 cm^3) of $[Cp_2Nb(CO)PPhHCl]^+$, Cl^- (**1**; 0.5 g, 1.16 mmol) was added $Na_2Fe(CO)_4 \cdot 1.5$ dioxane (0.4 g, 1.16 mmol). The mixture was stirred for 1 h at room temperature. The solvent was removed *in vacuo* and the crude product was washed with 3×15 cm^3 of pentane. The reaction products were dissolved in 10 cm^3 of toluene and chromatographed. Elution with toluene led to **4**. Recrystallization from CH_3COCH_3 gave an orange powder of **4** in 40% yield (0.24 g). Then **5** was obtained by using THF as eluent. Recrystallization from CH_3COCH_3 gave a red powder of **5** in 30% yield (0.17 g). Complex **5** can be prepared by UV irradiation in an HANAU TQ 150 lamp of a THF solution (60 cm^3) of **4** (0.3 g, 0.57 mmol). Freeze–thaw circles removed the CO generated from the photoreaction during irradiation. The reaction was monitored by IR spectroscopy. Total irradiation time was about 10 min and complex **5** was obtained quantitatively (0.28 g). Complexes **4** and **5** are air sensitive. Found: C, 47.6; H, 3.3; P, 5.6. Calc. for $C_{21}H_{15}O_5PNbFe$ (**4**): C, 47.8; H, 3.1;

P, 5.9%. Found: C, 47.9; H, 3.5; P, 5.8. Calc. for $C_{20}H_{15}O_4PNbFe$ (**5**): C, 48.0; H, 3.2; P, 6.2%.

Preparation of $Cp_2Nb(CO)(\mu\text{-}PPhMe)Fe(CO)_4$ (**4′**)

To a THF solution (20 cm³) of $Cp_2Nb(CO)(\mu\text{-}PPhH)Fe(CO)_4$ (**4**; 0.25 g, 0.47 mmol) was added an excess of KH (0.02 g, 0.5 mmol). The resulting mixture became black–red and was stirred for 30 min. Then CH_3I (0.07 g, 0.5 mmol) was added and the mixture instantaneously turned orange. The solvent was removed *in vacuo* and the solid residue was washed with pentane (2 × 10 cm³) and dried *in vacuo* giving an orange powder of **4′** quantitatively (0.25 g). Complex **4′** is air sensitive.

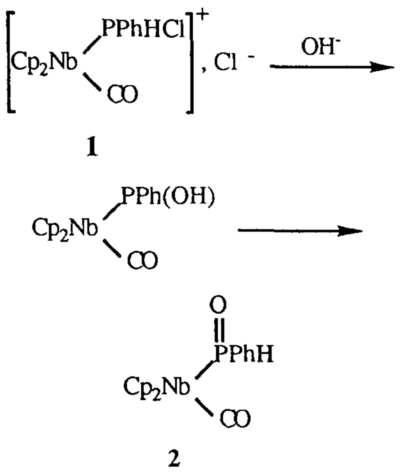
Preparation of $Cp_2Nb(\mu\text{-}PPhMe)(\mu\text{-}CO)Fe(CO)_3$ (**5′**)

This complex was prepared by a procedure similar to that for **4′**. The air-sensitive complex **5′** is obtained quantitatively as a red solid.

RESULTS AND DISCUSSION

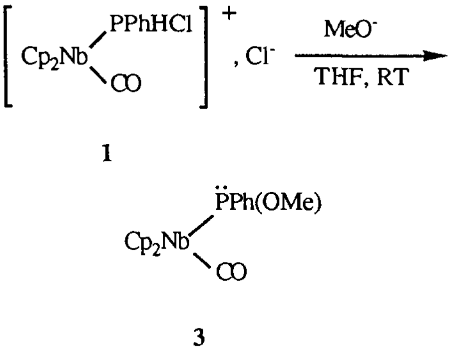
Reaction with OH^- *and* OMe^-

As reported previously,[6] treatment of salt **1** with OH^- affords the neutral phosphonyl derivative **2**:



(4)

The formation of **2** involves a deprotonation reaction coupled with a nucleophilic substitution (or vice versa) followed by tautomerization of the hydroxyl form. ¹H NMR spectra clearly show the presence of a P—H bond ($^1J_{PH} \approx 380$ Hz) and the expected non-equivalence of the cyclopentadienyl ligands due to the chiral phosphorus centre. By a similar two-step transformation the salt **1** led to the metallophosphinite **3** by using MeO^- instead of HO^-:

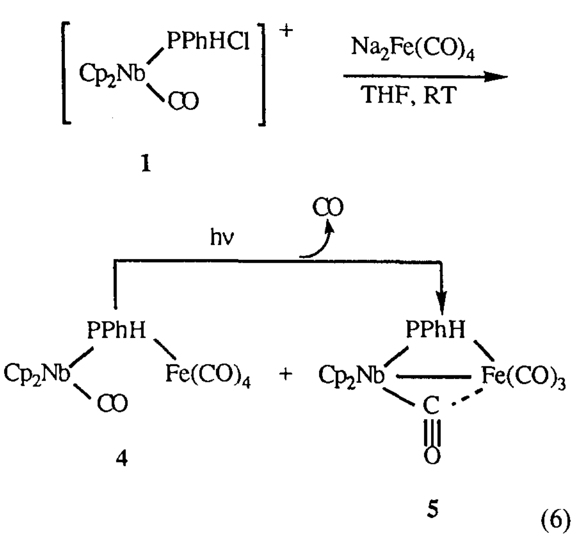


(5)

Two distinct resonances were again observed for the Cp groups at room temperature, but coalescence occurred at higher temperature: for complex **3** the coalescence temperature was found at +60°C corresponding to a ΔG value for the inversion barrier at the phosphorus centre of $+66 \pm 2$ kJ mol⁻¹. This value is higher than the one found in the related metallophosphine $Cp_2Nb(CO)P^iPrPh$ estimated to be $+48 \pm 2$ kJ mol⁻¹.[3] This enhanced stereostability could be due to the electron withdrawing character of the OMe group in accordance with the observations of Baechler and Mislow.[9]

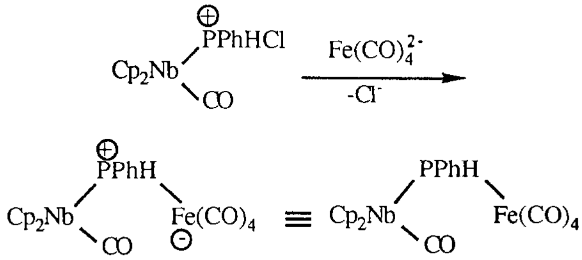
Reaction with $Fe(CO)_4^{2-}$

Treatment of the salt **1** with $Fe(CO)_4^{2-}$ in THF at room temperature gave rise to a mixture of bimetallic complexes **4** and **5**, which were easily separated by chromatography under anaerobic conditions. Complex **5** can be quantitatively produced by UV irradiation of compound **4**:



(6)

In contrast with the anions HO^- and MeO^-, for which the reaction sequence (deprotonation–substitution or vice versa) cannot be established, the iron reagent $Fe(CO)_4^{2-}$ thus achieves only the displacement of the chloride ion (Scheme 1).



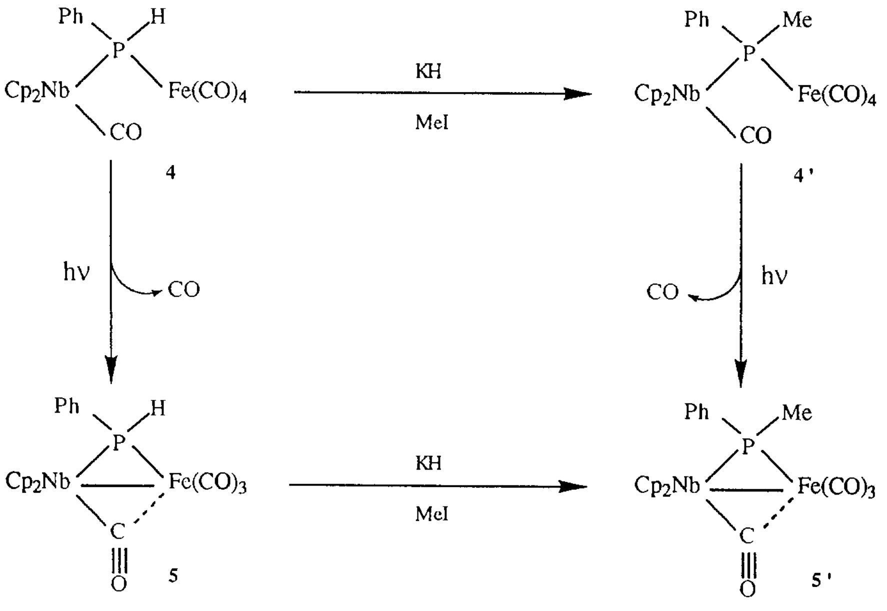
Scheme 1.

This trend agrees with the relatively poor basicity of the dianion associated with a noticeable nucleophilic power. The binuclear complexes **4** and **5** possess a functionalized phosphido bridge due to the presence of the P—H bond. Analogous phosphido-bridged μ-PPhH systems have already been reported and their reactivity studied.[10] In our case, the treatment of **4** and **5** with KH and CH_3I quickly led to the complexes **4′** and **5′**, respectively. Transformation of **4′** into **5′** was readily achieved by photochemical irradiation (Scheme 2).

Determination of structures can be established on the basis of their spectroscopic data (Table 1). The IR spectra of complexes **4** and **4′** show a set of four carbonyl stretching bands (one due to the niobium bonded CO), while compounds **5** and **5′** exhibit the typical pattern for the $Fe(CO)_3$ fragment. Moreover, for complexes **5** and **5′** one ν(CO) vibration appears at 1755 and 1745 cm^{-1}, respectively, typical for bridging carbonyl groups.

The dramatic downfield shifts (about 200 ppm) observed in the dibridged complexes **5** and **5′** with respect to the parent monobridged compounds **4** and **4′** agree with a large decrease of the Nb—P—Fe angle, together with the occurrence of an Nb—Fe bond.[11–13]

The NMR data (Table 1) are also significant: the ^1H NMR spectra of complexes **4** and **5** unequivocally establish the presence of P—H bonds with doublet resonances. The $^1J_{PH}$ coupling constant value in "open" complex **4** is *ca* 50 Hz smaller than the one in dibridged molecule **5**. The same values are observed in the corresponding ^{31}P NMR spectra. The presence of the asymmetric phosphorus centre in compounds **4**, **4′**, **5** and **5′** results in the non-equivalence of the Cp groups, which resonate as separated doublets. The larger $\Delta\delta_{Cp}$ recorded for complexes **5** and **5′** can be ascribed to a stronger rigidity of these molecules due to the bridging carbonyl ligand. It is finally noteworthy that the Cp resonances in **5** and **5′** are shifted upfield with respect to the corresponding ones in **4** and **4′**. The above analysis of spectroscopic data for all new



Scheme 2.

bimetallic complexes shows that their structures are closely related to monobridged $Cp_2Nb(CO)(\mu\text{-}PR_2)Fe(CO)_4$ and dibridged $Cp_2Nb(\mu\text{-}PR_2)(\mu\text{-}CO)Fe(CO)_3$ (R = Ph, Me) compounds, respectively, for which syntheses, spectroscopic studies and molecular structure have been reported recently.[4]

Table 1. ^1H and ^{31}P NMR and IR [$\nu(CO)$] data for complexes **4**, **4′**, **5** and **5′**

Complex	Cp	$^1H(CD_3COCD_3)$ H (PH)	Ph and/or Me	^{31}P (CD_3COCD_3)	IR (cm^{-1}, THF)
4	5.33 (d) $^3J_{PH} = 2.5$ Hz 5.50 (d) $^3J_{PH} = 1\ 5$Hz	4.63 (d) $^1J_{PH} = 293$ Hz	7.1–7.8 (m)	−21.8 (d) $^1J_{PH} = 293$ Hz	2025 w, 1945 s, 1919 s,[a] 1901 s
4′	5.32 (d) $^3J_{PH} = 2.5$ Hz 5.36 (d) $^3J_{PH} = 2.2$ Hz		1.97 (d) $^2J_{PH} = 6.3$ Hz 7.1–7.8 (m)	6.1 (s)	2023 w, 1941 s, 1916 s,[a] 1899 s
5	4.91 (d) $^3J_{PH} = 2.5$ Hz 5.31 (d) $^3J_{PH} = 1.4$ Hz	5.94 (d) $^1J_{PH} = 358$ Hz	7.2–8.1 (m)	167.3 (d) $^1J_{PH} = 358$ Hz	1978 s, 1919 m, 1899 s, 1755 m[a]
5′	4.94 (d) $^3J_{PH} = 2.0$ Hz 5.19 (d) $^3J_{PH} = 1.7$ Hz		2.41 (d) $^2J_{PH} = 10.0$ Hz 7.3–7.9 (m)	211.9 (s)	1972 s, 1914 m, 1897 s, 1745 m[a]

[a] $\nu(CO)$ of Nb—CO.

CONCLUSION

The dibridged complexes provide new examples of binuclear structures probably involving donor–acceptor type metal–metal bonds: a d^2 18-electron niobium centre allows an electron-deficient iron fragment to reach a saturated configuration. This feature is promising for extension to another metallic acceptor and to afford a wide range of bimetallic structures. Our work is currently focussed on this field and on the synthetic potential of the PH functionality.

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